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# DEPARTMENT OF THE AIR FORCE

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# Environmental Statement

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DISPOSITION OF ORANGE HERBICIDE BY INCINERATION

NOVEMBER 1974

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**Air Force**
**Environmental Planning Division**
**(HQ USAF/CEVP)**

Room 5B269
1260 Air Force Pentagon
Washington, DC 20330-1260

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# FINAL ENVIRONMENTAL STATEMENT
# ON
# DISPOSITION OF ORANGE HERBICIDE BY INCINERATION

## Summary Sheet

This final environmental statement was prepared by the Department of the Air Force. For additional information about this proposed action, contact Dr. Billy E. Welch, Special Assistant for Environmental Quality, SAF/ILE, Washington, D.C. 20330, 202-697-9297.

1. The proposal described is an administrative action.

2. Description:

The Air Force plans to incinerate Orange herbicide in a remote area of the Pacific Ocean. Incineration will be of only that quantity of the approximately 2.3 million gallons of Orange herbicide which is not registered by the Environmental Protection Agency. The 2.3 million gallons include approximately 1.4 million gallons stored on Johnston Island, and 0.86 million gallons stored at the Naval Construction Battalion Center, Gulfport, Mississippi. Empty drums which once contained the herbicide will be recycled into the manufacture of steel.

The proposed action of incineration on a specially designed vessel in the open tropical sea near Johnston Island would take place during three 7 to 9 day periods. Since publication of the revised draft environmental statement, the EPA has reversed their previous position that the Marine Protection, Research and Sanctuaries Act does not apply to incineration at sea aboard an "incineration vessel". The EPA position is now that ocean incineration requires an ocean dumping permit. The Air Force plans to seek a permit for ocean incineration of Orange herbicide. If, however, the EPA Administrator decides not to issue a permit, the Air Force will pursue the principal alternative of incineration in an incineration facility that would be constructed on Johnston Island.

3. Environmental impact and adverse environmental effects of the proposed action:

The proposed incineration will convert the Orange herbicide to its combustion products of carbon dioxide, hydrogen chloride, and water which will be released without scrubbing into the atmosphere. Also, a relatively small amount of elemental carbon and carbon monoxide will be generated in the incineration process and discharged into the atmosphere. Evidence is presented to demonstrate the incineration process can reduce the levels of Orange herbicide to below the detectable limits in the combustion gases. Based on achievable efficiencies ranging from 99.9 to 99.999 percent, environmentally insignificant amounts of unburned and pyrolyzates of herbicide and its impurity 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) may be released into the atmosphere.

There will be no adverse effect on the environment caused by the incineration of Orange herbicide in a remote area of the Pacific.

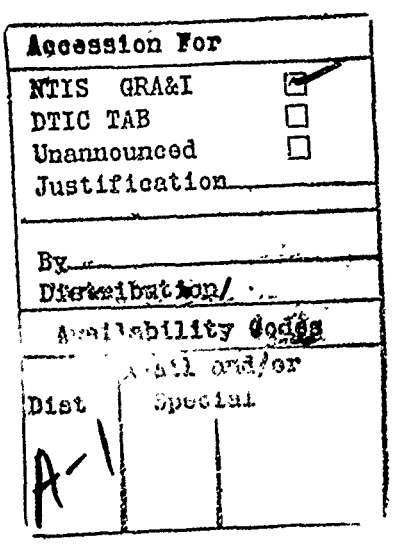
4. Alternative methods of disposition:

a. Principal alternative of incineration on Johnston Island.
b. Incineration in one of the 50 States.
c. Use of herbicide.
d. Return to manufacturer.
e. Deep well disposal.
f. Burial in underground nuclear test cavities.
g. Sludge burial.
h. Microbial reduction.
i. Fractionation.
j. Chlorinolysis.
k. Soil biodegradation.
l. No disposal action.

5. Federal and State Agencies and other sources from which written comments have been received:

Atomic Energy Commission
Department of Agriculture
Department of Commerce
Department of Defense (Health and Environment)
Department of Health, Education and Welfare
Department of Interior
Department of Transportation
Environmental Protection Agency
State of Hawaii
State of Mississippi
American Eagle Foundation
Center for Law and Social Policy (representing Friends of the Earth and the National Audubon Society)
The Marquardt Company

6. The draft environmental statement was made available to the Council on Environmental Quality and the public in January 1972. The revised draft environmental statement and final environmental statement were made available in April 1974 and November 1974, respectively.


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## ABBREVIATIONS

| | |
|---|---|
| AAAS | American Association for the Advancement of Science |
| ACGIH | American Conference of Governmental Industrial Hygienists |
| BOD | biochemical oxygen demand |
| BTU | British Thermal Unit |
| $^{14}C$ | radioactive carbon |
| cbm | cubic meters |
| CJTF | Commander, Joint Task Force |
| cm | centimeter |
| CONUS | Continental United States |
| 2,4-D | 2,4-dichlorophenoxyacetic acid |
| DASA | Defense Atomic Support Agency |
| DMA-2,4-D | dimethylamine salt of 2,4-D |
| DNA | Defense Nuclear Agency |
| DoD | Department of Defense |
| EHL(K) | USAF Environmental Health Laboratory, Kelly AFB TX |
| EHL(M) | USAF Environmental Health Laboratory, McClellan AFB CA |
| EPA | Environmental Protection Agency |
| ESSA | Environmental Sciences Service Agency |
| GB | nerve agent |
| HAC | Herbicide Assessment Commission of the AAAS |
| HATV | High Altitude Test Vehicle |
| HEW | Department of Health, Education and Welfare |
| H & N | Holmes and Narver, Inc. |
| IMCO | Inter-Governmental Maritime Consultative Organization |
| JCS | Joint Chiefs of Staff |

| | |
|---|---|
| JP-4 | jet engine fuel |
| kg | kilogram |
| km | kilometer |
| KW | kilowatt |
| l | liter |
| lb/A | pounds per acre |
| lb ai/A | pounds of active ingredient per acre |
| $LD_{50}$ | Dose which will kill 50% of a species of test animals in a stated period. |
| LORAN | Long Range Air to Navigation |
| m | meter |
| MG | million gallons |
| mg | milligram |
| mg/kg | milligrams per kilogram |
| mg/l | milligrams per liter |
| mm | millimeters |
| MUSTARD | a blister agent |
| NBE (nbe) | normal butyl ester |
| NCBC | Naval Construction Battalion Center |
| NNTRP | National Nuclear Test Readiness Program |
| PCB | Polychlorinated biphenyl |
| PERT | Program Evaluation and Review Technique |
| PGBE | propylene glycol butyl ester |
| ppb | parts per billion (weight to weight ratio) |
| $ppb_{v/v}$ ($ppb_v$) | parts per billion (volume to volume ratio) |
| ppm | parts per million (weight to weight ratio) |
| $ppm_{v/v}$ ($ppm_v$) | parts per million (volume to volume ratio) |
| pps | Pounds per second |

| | |
|---|---|
| pKa | Acid dissociation constant |
| ppt | parts per trillion (weight to weight ratio) |
| $ppt_{v/v}$ ($ppt_v$) | parts per trillion (volume to volume ratio) |
| RDES | revised draft environmental statement |
| RMA | Rocky Mountain Arsenal |
| SMAMA | Sacramento Air Material Area (Sacramento Air Logistics Center) |
| SUE® | "Sudden Expansion" Burner, Registered Trade Mark, The Marquardt® Company |
| 2,4,5-T | 2,4,5-trichlorophenoxyacetic acid |
| TACAN | Tactical Air Navigation |
| TCDD | 2,3,7,8-tetrachlorodibenzo-*p*-dioxin |
| THOR | a medium-range ballistic missile |
| USDA | U.S. Department of Agriculture |
| VX | a nerve agent |
| µg | micrograms |
| µg/l | micrograms per liter |
| ~ | approximately |
| > | greater than |

## EXECUTIVE SUMMARY

In April 1970 the Secretaries of Agriculture, HEW, and Interior jointly announced the suspension of certain uses of 2,4,5-T. As a result of this announcement the Department of Defense suspended the use of Orange herbicide since this herbicide consists of approximately 50 percent 2,4,5-T and 50 percent 2,4-D. This suspension left the Air Force with 1.5 million gallons of Orange herbicide in Vietnam and 0.8 million gallons in Gulfport, Mississippi. In September 1971, the Department of Defense directed that the Orange herbicide in Vietnam be returned to the United States and that the entire 2.3 million gallons be disposed in an ecologically safe and efficient manner. The 1.5 million gallons were moved from Vietnam to Johnston Island for storage in April 1972.

The initial method proposed for disposal was incineration at a commercial facility in the United States. The details of this proposed course of action were documented in a draft environmental statement which was filed with the Council on Environmental Quality and the public in January 1972. The draft statement discussed the studies that were being accomplished but not completed when the statement was filed. Based on the fact that studies were still in progress and the interest evidenced in comments received on the draft statement, the Air Force decided to conduct additional studies on incineration as well as additional investigation of alternative disposal methods. (See Appendix L for comments.)

As a result, numerous studies were conducted to determine the feasibility of soil biodegradation, fractionation, chlorinolysis, and incineration. Also, the Air Force submitted an application to the Environmental Protection Agency (EPA) for registration of that portion of the herbicide which was expected to meet EPA criteria. Return of the herbicide to the original manufacturers was investigated. In addition, the possibility of deep well disposal, burial in underground nuclear cavities, and sludge burial were investigated. It was concluded that the best disposal technique is incineration in a remote area. The revised draft environmental statement was published to update the work accomplished between January 1972 and April 1974.

Thermal decomposition research using differential thermal analysis was conducted to determine the temperatures required for complete combustion of Orange herbicide and its impurity 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Dynamic laboratory studies were next completed to further substantiate the feasibility of incineration and to refine monitoring techniques for subsequent tests. A test program was conducted in a commercial incinerator to document the feasibility of destroying undiluted Orange herbicide by means of combustion. Particular emphasis was placed on the ability to destroy the low quantity of TCDD (low milligram per kilogram concentration, mg/kg) present in the herbicide. Extensive sampling, utilizing time-weighted and concentration techniques, was conducted to evaluate the unscrubbed combustion gases, the scrubbing liquid used to cool and scrub the combustion gases, scrubbed effluent gases, and any solid residues deposited in the system. Program objectives were outlined to determine, among other things, engineering data relative to controlling and monitoring the incineration process, the composition of the combustion products, the toxicity of discharged scrubber water to several aquatic organisms, and the

toxicity of scrubbed effluent gases to tomato plants. These series of tests demonstrated that incineration of Orange herbicide can be accomplished in an environmentally acceptable manner. In addition to the above tests, information on combustion of chlorinated hydrocarbons aboard incinerator ships indicates destruction efficiencies of at least 99.9 percent.

The average concentration of TCDD in the herbicide is about 2 mg/kg and the total amount of TCDD in the entire Orange stock is approximately 50 pounds. The commercial incinerator test program indicates that if any TCDD were present in the exhaust stream, it was analytically nondetectable. Orange destruction efficiencies of 99.9 percent or better appear feasible for a large scale incineration project. This will result in a total discharge of 0.05 pounds or less of TCDD via the exhaust streams over the duration of the project.

The data accumulated, together with theoretical considerations and applied thermochemistry, clearly indicate that the production of incomplete combustion products can be minimized to insignificant levels. Incineration will convert the Orange herbicide to its combustion products of carbon dioxide, hydrogen chloride, and water which will be released to the atmosphere. In addition, a relatively small amount of elemental carbon and carbon monoxide will be generated in the incineration process and discharged to the atmosphere. With proper concern for the environment in which such incineration will take place, incineration is an environmentally safe method of disposal of Orange herbicide.

The Air Force proposes incineration upon the open tropical sea west of Johnston Island on a specially designed vessel of that quantity of Orange herbicide not registered by the EPA. Since publication of the revised draft environmental statement, the EPA has reversed their previous position that the Marine Protection, Research and Sanctuaries Act of 1972 does not apply to incineration at sea aboard an "incineration vessel". The EPA position is now that incineration at sea requires an ocean dumping permit. Therefore, the Air Force plans to apply for a permit for disposal of Orange herbicide via incineration at sea. The incineration would occur during three 7 to 9 day periods. The effects of combustion gas discharges upon the environment was accomplished by utilizing "worst case" analyses techniques. A dispersion zone model was used to estimate mass concentrations of unburned Orange and hydrogen chloride in the air and water environment in the vicinity of the discharge, and a meteorological model was applied to predict the atmospheric concentration of unburned Orange and hydrogen chloride at sea level downwind of the discharge location. Predicted results from these models revealed that there will be no significant environmental impact upon either the air or ocean environment.

If, however, the EPA Administrator decides not to issue a permit for incineration at sea, the Air Force will pursue the principal alternative of incineration in facility that would be constructed on Johnston Island. Incineration on Johnston Island would require a higher efficiency owing to the ecology of the Atoll and would, for the analysis presented in the text, require approximately 200 days. A complete ecological survey was conducted of Johnston Island by the Smithsonian Institution in order to document the areas of concern. Incineration on-board a specially designed ocean vessel and incineration in a facility of Johnston Island both meet the criteria of remoteness. Incineration can be successfully conducted using either method; however, the predicted environmental effects are minimized by incineration in a remote area of the Pacific on the open tropical ocean.

# PART I INTRODUCTION


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A. THE PROBLEM AND PROPOSED ACTION: The Air Force is charged with the responsibility for the ecologically safe, efficient and, if possible, low cost disposal of approximately 2.3 million gallons of Orange herbicide. Proposed action is to incinerate the herbicide in a remote area of the Pacific Ocean either on a specially designed vessel or on Johnston Island. Combustion gases from both options are discharged into the atmosphere in an environmentally safe manner and without any significant effect upon the beneficial uses of the area.

1. DESCRIPTION OF ORANGE: This herbicide consists of approximately 50% by volume of the normal butyl ester of 2,4-dichlorophenoxyacetic (2,4-D) acid and 50% by volume normal butyl ester of 2,4,5-trichlorophenoxyacetic (2,4,5-T) acid. A small quantity, known as Orange II, contained the isooctyl ester of 2,4,5-T in place of the normal butyl ester. Unfortunately, as a result of a malfunction in the production process, certain lots of the herbicide contain a contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). In experimental animals this compound was shown to be teratogenic, i.e., it caused the production of malformed fetuses and living offspring in animals. For this reason the military and certain other uses of 2,4,5-T ceased in 1970.

2. LOCATION OF ORANGE: The herbicide is stored in 55 gallon steel drums at two locations. At the Naval Construction Battalion Center (NCBC), Gulfport, Mississippi, there are approximately 860,000 gallons and on Johnston Island, Central Pacific Ocean, there are approximately 1,400,000 gallons.

B. HISTORICAL DOCUMENTATION OF EVENTS

1. In 1962, the herbicide formulation, Orange, was developed for military use as a defoliant. This herbicide formulation is a mixture of n-butyl esters of 2,4-D and 2,4,5-T.

2. South Vietnamese newspapers reported an increased occurrence of birth defects during June and July 1969. This action elicited far-reaching reactions from governmental agencies, segments of the scientific community, lay groups concerned with environmental problems, and from the communications media. Government-sponsored panels of experts, special commissions established by scientific organizations, hearings before subcommittees of the U.S. Congress, and conferences attended by representatives from industry, government, and universities examined available data and heard expert opinions. These groups were not able to provide a generally acceptable answer to the central question of whether 2,4,5-T as currently produced and used, constituted a risk for human pregnancy (HAC, 1972).

3. On October 29, 1969, it was announced that a series of coordinated actions were being taken by several governmental agencies to restrict the use of the herbicide 2,4,5-T. This was precipitated by release a few days earlier of the findings of a study by Bionetics Research Laboratories, Litton Industries, Inc., in which it was found that mice and rats treated during early pregnancy with large doses of 2,4,5-T gave birth to defective offspring.

4. Additional animal experiments performed early in 1970 confirmed that pregnant mice did deliver some malformed offspring. The question then was one of whether, or to what extent, such animal data could be extrapolated to man. On April 14, 1970, the Secretary of Health, Education and Welfare (HEW), advised the Secretary of Agriculture that: "In spite of these uncertainties, the Surgeon General feels that a prudent course of action must be based on the decision that exposure to this herbicide may present an imminent hazard to women of childbearing age." Accordingly, on the following day, the Secretaries of Agriculture, HEW and Interior jointly announced the suspension of the registration of 2,4,5-T for: "I. All uses in lakes, ponds or on ditch banks. II. Liquid formulations for use around the home, recreation areas and similar sites" (USDA-PR 70-1, 1970). A notice for cancellation of registration was issued on May 1, 1970 for: "I. All granular 2,4,5-T formulations for use around the home, recreation areas and similar sites. II. All 2,4,5-T uses on crops intended for human consumption" (USDA-PR 70-3, 1970).

5. All registrants of 2,4,5-T were advised of these actions. Two of the registrants, Dow Chemical Co. and Hercules Inc., exercised their right under Section 4.c. of the Federal Insecticide, Fungicide and Rodenticide Act (7 USC 135 et seq) to petition for referral of the matter to an Advisory Committee. The National Academy of Sciences supplied a list from which was selected a nine-member Advisory Committee of scientists with appropriate qualifications from universities and research institutes over the country. It was the concensus of the committee that the central issue was whether use of the herbicide does in fact constitute an imminent health hazard, especially with respect to human reproduction.

6. During the intervening months since restrictions were placed on the use of 2,4,5-T, a number of additional studies have been carried out on several animal species and a few reports of human exposure during pregnancy have been further evaluated. Although the new data have not answered all of the questions that have been or could be raised, they undoubtedly provided a more substantial basis for making a scientific judgment about possible effects of this herbicide on prenatal development than previously existed. In undertaking such judgment, the committee took into account certain considerations that seemed appropriate to the issue, as follows: 1) As is frequently the case, available data are insufficient for a definitive statement of conditions under which a specified risk might occur, assuming that freedom from risk is ever attained; 2) Since most chemicals under suitable laboratory conditions could probably be demonstrated to have teratogenic effects, and certainly all could be shown to produce some toxic effects if dosages were high enough, it would not be reasonable to consider the demonstration of toxic effects under conditions of greatly elevated dosage to be sufficient grounds for prohibiting further use of a particular chemical; and 3) Benefits are to be expected from the continued use of 2,4,5-T. The necessity of making a value judgment of benefit versus risk, therefore, must be accepted, not only for this herbicide, but for numerous valuable drugs, some natural nutrients, and many other chemicals, some of which are known to be teratogenic in laboratory animals. The risk versus benefit judgment for a particular herbicide or drug can be evaded only if it can be shown that another compound is equally as efficient and involves less risk. This presupposes that the risk potential of a substitute herbicide is at least as well known as that of the original (in this case 2,4,5-T) -- a fact that may be difficult or impossible to ascertain. The substitution of a relatively unknown pesticide for an older one with known adverse effects is not a step to be taken lightly.

7. The task of making a judgment about the central question of hazard to human pregnancy is complicated by still other considerations. Although herbicides are of economic benefit to man, their use is not without possible hazard to the environment and to other aspects of human welfare. In various connections, questions have been raised about: a) damage to nontarget plants caused by spray drift or by movement in water, b) damage to subsequently planted sensitive crops owing to herbicide persistence in the soils, and c) acute or chronic toxicity to man or other animals aside from that related to pregnancy.

8. It is scientifically impossible to prove that a chemical is without hazard. Pesticide regulations now require that new agents be tested for acute and chronic toxicity, mutagenicity and carcinogenicity. These tests may involve the use of two or more species of animals taken through several generations and the examination of thousands of individuals. Since it is necessary to extrapolate from effects in test animals to man and since species are known to differ in sensitivity to chemicals, the permissible residue levels in food must always be manifold below the minimal effect level for the species tested.

9. A major producer of 2,4,5-T submitted evidence that the 2,4,5-T used in the Bionetics test contained 27 ± 8 ppm of an impurity identified as TCDD. This impurity was tested and found to produce teratogenic effects in several species of animals at widely varying dose/body weight ratios and by different routes of administration.

10. Human exposure to an environmental chemical such as 2,4,5-T depends on: a) pattern of usage, i.e., how widely and frequently it is applied and in what amounts and b) its fate in the environment, i.e., how it accumulates and degrades in relation to its application rate. The chlorophenoxy herbicides 2,4-D and 2,4,5-T have been widely used to control broad-leaved weeds for over 20 years. Because 2,4,5-T is more expensive than 2,4-D, it has been primarily used to control woody plants and a few herbaceous species against which it is more effective than 2,4-D. Also because of the cost difference, commercial formulations containing 2,4,5-T are usually mixtures of the two herbicides.

11. Most of the 2,4,5-T is applied as a spray to foliage. Lesser amounts are sprayed on the trunks and branches of dormant trees, injected into the bases of trees, poured or sprayed into frills around the trunks of trees, sprayed or painted on newly cut stumps of trees. Amino salts of 2,4,5-T dissolved in water are most often used when the herbicide is applied to foliage and esters dissolved in oil are most often used when it is applied to bark. The spray concentrations usually vary between 0.1 and 2.5% and the rates of application are usually between 0.5 and 8 pounds per acre, depending on the size and sensitivity of the plants being treated. Higher rates and concentrations were used in Vietnam for military purposes (U.S. Army, 1969).

12. In September 1971, the Secretary of Defense directed the Joint Chiefs of Staff (JCS) to dispose both Continental United States (CONUS) and Vietnam stocks of herbicide Orange. The Air Force was assigned this responsibility.

C. USES OF PHENOXY HERBICIDES

1. REASONS FOR USE: The phenoxy herbicides 2,4-D and 2,4,5-T, their salts, esters and other compounds, are well established pesticides for the control of

weeds and shrubs in agriculture. In particular, as noted by Kingman and Shaw (1967), the phenoxy herbicides are especially useful because; a) they are selective, they kill most broad leaf plants but do not kill grasses or grain crops; b) they are potent, many species of weeds are controlled by less than one pound of active ingredient per acre; c) they are easy to use; d) they are only mildly to moderately toxic to man, domestic animals, or wildlife when applied as recommended; and e) they do not accumulate in the soil and they have minimal if any harmful effects on soil organisms. Klingman and Shaw noted that ester formulations are generally more potent, pound for pound, than salt formulations. The esters are more effective than salts for killing weeds that are growing slowly; and because esters are oily, they are less likely to be washed off the foliage if rain falls soon after application.

2. EXTENT OF USE: The herbicides 2,4-D and 2,4,5-T were first employed by farmers and ranchers in the mid-1940's and remain the most common synthetic organic herbicides. The largest use of 2,4-D is for broadleaf weed control in corn and other grains; the major use of 2,4,5-T is to kill brush (Fox et al., 1970). The combined production of 2,4-D and 2,4,5-T has increased steadily from 34.6 million pounds in 1958 to 96.8 million pounds in 1968. At present, the phenoxy herbicides are the only group of herbicides used to any extent on pasture and rangeland. In 1964, the uses of 2,4,5-T were: rights-of-way - 49%; nonfarm forests - 10%; hay, pasture, and rangelands - 7%; all other farm uses - 12%; lawns and turfs - 7%; federal agencies - 6%; and other miscellaneous uses - 9% (Advisory Committee). Incomplete information indicates that about nine million pounds of 2,4,5-T esters, acids, and salts were domestically used during 1970. Weeds and brush infesting pasture and rangeland are most widely controlled by 2,4-D and 2,4,5-T, respectively. In 1966, nearly 8 million acres (more than 1 percent) of pasture and rangeland were treated with phenoxy herbicides (Fox et al., 1970). The herbicide 2,4,5-T is a particularly effective tool for vegetation management on forest lands (Montgomery and Norris, 1970). It is used on power-line, railroad rights-of-way; but its most important use is in connection with the establishment and release of conifers on forest lands. For these purposes, 0.5 to 4 pounds of 2,4,5-T per acre were applied as low volatile esters dissolved or emulsified in diesel oil or water.

3. REGISTRATION

a. The 15 April 1970 government edict on 2,4,5-T suspended the registration of liquid formulations for use around the home and recreational areas, and for uses on lakes, ponds, and ditch banks. This restriction did not include its use on range and pasture lands, nonagricultural lands, or in weed and brush control programs on communications and highway rights-of-way. Several formulations of 2,4-D and 2,4,5-T are currently registered for domestic use. Orange herbicide is not a registered herbicide and cannot be domestically used or sold.

b. The Orange herbicide stock to be destroyed by the action proposed in this environmental statement, incineration at sea, or by the principal alternative of incineration on Johnston Island represents a resource of considerable monetary value. The safe and appropriate utilization of all or part of this resource would be a beneficial action, see Part V.C. The Air Force has been and is continuing to pursue the possibility of EPA registration of portions of the Orange herbicide stock. The Air Force is seeking registration of the maximum possible quantity found acceptable by the EPA. Depending upon the level of TCDD allowed, approximately 1.5 million gallons could conceivably be registered.

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A. INTRODUCTION: This part of the Environmental Statement is primarily to describe the proposed incineration of Orange herbicide from the standpoint of facility and operational requirements and effluent stream characteristics. The proposed action of incineration at sea and the principal alternative of incineration on Johnston Island are described. Since publication of the revised draft environmental statement, the EPA has taken the position that the Marine Protection, Research and Sanctuaries Act of 1972 does not apply to incineration at sea. Therefore, the Air Force plans to apply for a permit for disposal of Orange herbicide via incineration at sea. The factors applicable to the selection of a disposal site and the situation regarding disposal of empty herbicide drums is also discussed. In view of the importance and interest in the properties of the herbicide, a section titled "Characteristics of the Herbicide" has been included as the final section of this part.

B. INCINERATION SITE CRITERIA: This Environmental Statement is for the disposal of Orange herbicide via incineration in a remote area. The proposed action will take place aboard a specially designed incinerator vessel in an isolated location of the Pacific Ocean. The principal alternative would be incineration on the west side of Johnston Island. Either location meets the remoteness requirement. Either location will involve an industrial operation of considerable magnitude in which the undiluted herbicide will be handled and will be the fuel feed into the incinerator(s). Since Johnston Island and the surrounding area will be involved in the proposed action or the principal alternative, considerable information on this locale is presented in Appendix H. General considerations that were used for site selection are summarized and presented below.

1. PHYSICAL FACTORS

a. The site should be as remote as possible from both residential and industrial population centers and from land currently in agronomic production. Vegetation should be sparse, of little agronomic value, and of species resistant to the phenoxyacetic acid herbicides contained in Orange or to the pyrolytic products of these herbicides. The site should be selected so that women of childbearing age have the lowest possible probability of contact with the Orange.

b. The topography or surface features of the surrounding area should be relatively flat and with a symmetrical, uniform surface.

c. A prevailing wind of as nearly constant direction and velocity as possible would be highly desirable. Insofar as possible, the incinerator(s) should be sited downwind of any inhabited areas such as housing, work shop and storage areas, recreational areas, etc.

d. The site should be located to provide accessibility of water, rail, or truck transportation but cause negligible interference with any existing patterns of transportation. Further discussion of transportation is contained in Appendix I.

2. BIOLOGICAL FACTORS

a. The site should be so located to minimize any unacceptable adverse impact or municipal water supplies, shellfish beds, wildlife, fisheries (including spawning and breeding areas), or recreational areas.

b. The site should be located such that the disposal operations will cause no unacceptable adverse effects to known nursery or productive fishing areas. The currents should be such that any suspended or dissolved matter would not be carried to known nursery or productive fishing areas or populated or protected shoreline areas.

3. MANAGEMENT FACTORS: The site should be so located and configured such that it will be conducive to single manager control of the entire disposal operation and peripheral activities, and that adequate control can be exercised over the general population in the area to allow immediate response in the event of an accident, incident, or act of God. Adequate communications must be available that will further enhance management at all levels.

4. SOCIO-POLITICAL FACTORS: The site selected or the transport of the Orange should not require the exercise of the right of eminent domain or result in a trespass or encroachment to private citizens within the U.S. or its possessions or to any other nation's interests. If possible, the site should be completely under the control of the Federal Government to minimize the local political controversial effects on state or other government units. The site location should not result in international controversy, be in conflict with international law, or impair the economic activity of any commercial enterprise.

C. METHOD OF INCINERATION

1. INTRODUCTION: Incineration of Orange has been investigated and it has been concluded that high temperature incineration is capable of destroying the Orange herbicide and its TCDD content in an environmentally safe manner. Appendix D, "Incineration of Orange Herbicide," describes the theoretical aspects of Orange incineration, reviews five separate studies directed toward the evaluation of Orange incineration, and concludes that incineration is an acceptable disposal method. These studies were performed by: 1) the USAF Environmental Health Laboratory, Kelly AFB, TX; 2) the U.S. Department of Agriculture and Mississippi State University, State College, MS; 3) the Combustion Power Company, Menlo Park, CA; 4) the Marquardt Co., Van Nuys, CA; and 5) a joint effort between The Marquardt Co. and the USAF Environmental Health Laboratories (EHLs) at Kelly and McClellan AFB. As shown in Appendix D the first four studies conducted on Orange (1 through 4 above) were of small scale as regards quantity of Orange incinerated and sampling and analyses conducted. To further evaluate the high temperature combustion of Orange and to obtain incinerator operation parameters which may be appropriate to a commercial incinerator system, it was apparent that a large scale completely monitored Orange test burn using an incinerator with an acid gas scrubbing system was required. As an initial choice, a large scale test burn of Orange incineration was programmed at the Rollins Environmental Services facility in New Jersey. This project never passed the planning state and was concluded because of technical, environmental and regulatory problems. With this setback and after careful consideration of alternative incineration options, the Marquardt Company SUE® incinerator was selected for a test burn. Factors in this decision included: 1) The SUE® is a flame incinerator which could utilize Orange herbicide as the fuel and air to supply the required oxygen; and 2) The modular concept of the SUE® is very advantageous because it eliminates scale-up considerations (capacity is increased by increasing the number of modules), and permits ease of shipment, installation, maintenance and dismantling. The purpose of the test burn was to obtain data on Orange incineration and not to determine specifically if the SUE® system was acceptable for the disposal of the entire Orange stock. It is the Air Force opinion that selection of the SUE® was a sound choice for a test burn and that while pure data extrapolations are not possible, the requirements for an overall incineration system for the destruction of Orange can now be specified with a high degree of certainty. The report on the study with a SUE® incinerator, prepared by the Marquardt Co. and both the USAF EHLs, is titled "Report on the Destruction of Orange Herbicide by Incineration," and is presented as Appendix E. In view of these studies and the disposal site criteria, this environmental statement proposes the action of destruction of Orange herbicide via incineration on a ship at sea. In addition, this Environmental Statement proposes the principal alternative of incineration on Johnston Island. It is noted that this proposal is for "incineration as a method of destruction of Orange" and in no way is it intended to imply or state that the product of any given contractor, firm, company, etc., must be used.

2. INCINERATION AT SEA

a. Introduction: As stated, the Air Force proposes the destruction of Orange herbicide via incineration on a ship at sea; however, its implementation is dependent on the EPA issuing a permit in accordance with the Marine Protection, Research and Sanctuaries Act of 1972. The above mentioned studies and other information from Ocean Combustion Service B.V., Rotterdam, The Netherlands, indicate that shipboard incineration would be capable of destroying Orange herbicide and its TCDD content in an environmentally safe manner. Since September 1972, a ship, the "Vulcanus" has been equipped to carry certain hazardous liquid chemcial cargoes from northern European ports and approved by participating countries to incinerate the waste cargo in prescribed areas of the North Sea. Additionally, U.S. companies have suggested shipboard incineration and have indicated a willingness to investigate it. The following information describes the "Vulcanus" from material supplied by the Ocean Combustion Service B.V.

b. The Vessel

(1) The ship is a double hulled and double bottom tanker with an overall length of 331.4 feet, a beam of 47.2 feet and a draft of 22.9 feet. Her construction complies with the latest Inter-Governmental Maritime Consultative Organization (IMCO) regulations of bulk carriage of dangerous chemicals at sea. Because of her size, the vessel is able to operate world-wide, and she is able to operate in very rough weather. The ship has a crew of ten to operate the ship and a crew of six solely to operate and continuously man the incineration process. Two diesel engines drive the single propeller to give service cruising speeds of 10-13 knots.

(2) The vessel's cargo tank capacity of 3,503 cubic meters (cbm) (925,493 gallons) is divided into 15 cargo tanks ranging in volume from 115 cbm to 574 cbm. None of these tanks are in contact with the vessel's hull and/or bottom. The engine room is separated from the cargo tanks by double bulkheads, the pump room and generator room being situated in between.

c. Incineration System

(1) Physical Features: The two combustion chambers are installed right aft of the upper deck. Each of the bricklined incinerators has a maximum outer diameter of 5.50 meters (m), and inside diameter of 4.80 m, and a total height, including the stack, of 10.45 m. The volume of each combustion chamber is calculated to be 87.9 cbm. Each chamber has three burners with rotating cup fuel injection systems which provide vortex turbulence and distribution of fuel feed throughout the whole chamber. This incinerator is considered a conventional incinerator as discussed in Part V.B.

(2) Operation: Incineration will be conducted in a designated area 50-60 miles clear of normal shipping lanes and on the open tropical sea down wind of Johnston Island. Gas or diesel oil will be used to bring the chambers to the required combustion temperature, normally 1400°C (2552°F); the maximum operating temperature is reported as 1650°C. Only when the required temperature is reached will the feed pumps allow waste to enter the combustion chambers. Waste feed flow and air will be carefully controlled to insure complete combustion. Once the required temperature is obtained, the chambers will be fed solely by the undiluted Orange. The Orange can be pumped to each of two chambers at a rate of 10-12 tons per hour for a total daily pump rate of

about 576 tons. Therefore, about 22-26 days of continuous incineration would be required to burn the entire Orange stock (2.3 million gallons). The vessel's capacity of about 925,000 gallons of Orange will require three voyages; 925,000 gallons of Orange would be burned during each of the first two voyages, and the remaining 380,000 gallons of Orange plus any solvents used in drum cleaning would be burned during the third voyage.

(3) Effluent Discharges: Data presented in Appendices D and E indicate that incineration of herbicide Orange can be accomplished in an environmentally acceptable manner. A comparison of the incineration characteristics of the "Vulcanus" versus those known to be acceptable based on the data presented in Appendices D and E indicated that Orange herbicide can be successfully incinerated on board the "Vulcanus." (Acceptable parameters: measured combustion temperatures 2400 - 2800°F; dwell time equal to or greater than 0.14 seconds; a fuel to air mass ratio of approximately 0.1; and excess air greater than 30%. Vulcanus data: 2550°F; 0.6 seconds; 0.1 to 0.12; and 35% respectively.) Information from Ocean Combustion Services has been used to predict the inorganic constituents of the exhaust stack discharges. A total throughput of 576 tons per day (24 tons/hour) of Orange with an average of 30 percent (by weight) chlorine content will give a discharge of approximately 178 tons/day of hydrogen chloride, some 1,000 tons/day of carbon dioxide, about 50 tons/day of carbon monoxide, and about 3.0 tons/day of carbon particles. Although very low quantities of unchlorinated hydrocarbon pyrolyzates (µg/l range) were detected in the combustion areas of Orange in a commercial incinerator (Appendix E), information from Ocean Combustion Service indicated 99.9 percent of a chlorinated hydrocarbon feed is destroyed. At this high efficiency, approximately 0.576 ton/day (48 pounds/hour) of Orange feed constituents and their pyrolyzates are not completely incinerated and are thus discharged hourly into the atmosphere. Ocean Combustion Services reported that negligible amounts of combustion chamber coke deposits have ever accumulated in the ship's incinerators. This has been attributed to their waste injection system, very high vortex turbulence in the chambers, and 1400°C temperatures on the chamber's firewalls. From such experience, no consequent combustor chamber coke deposit is expected.

(4) Monitoring

(a) Operational Monitoring: A special monitoring panel continuously displays the following: temperature near the center of each incinerator chamber, temperature in the centerline and about two meters from each incinerator stack exit, date and time, on/off mode of each feed pump and each burner, and grid location of the vessel. This panel is photographed at preset desired intervals by an automatic camera. This panel and camera can be sealed by regulatory authorities to prevent tampering and provide accurate documentation of the incinerator operation and location. Additionally, a navigation plotter automatically charts the vessel's course on a map and is made available to authorities along with certified copies of the ship's log. These operational and navigational documentations have been used to establish the ship's successful incineration of waste cargoes in a designated area. For this project, automatic photographs of the panel and manual observation records

of the incineration parameters will be accomplished. However, the navigational log book rather than the automatic plotter will be acceptable due to the vast expanse affordable in the Pacific Ocean as compared to the North Sea. Based upon the successful past history of incinerating some 60,000 tons of chlorinated hydrocarbons and upon the basis of documentation of operational parameters as outlined above, success of this option is predicted. Additional documentation can be provided by a regulatory representative who can accompany the vessel. As no significant impact is envisioned (See Part III), combustion gas analyses is not necessary as an operational requirement.

(b) Ecological Monitoring: Ecological monitoring is neither required nor feasible for the following reasons: 1) the ship will complete the project within a month and always be moving and operating over a large area of the open tropical sea; and 2) as described in Part III, the predicted impact will be very minimal and transient for this incineration option.

(5) Additional Environmental Considerations: The ship does not have on board facilities for handling, emptying, or cleaning the drums nor does it have pumping capability for on-loading the Orange herbicide. This means that facilities for transferring of the herbicide, emptying and cleaning of drums, and pumping the herbicide aboard the ship will be necessary. Additionally, ultimate disposal of the empty drums will also be required. Duplication of these required facilities at Johnston Island and Gulfport MS depends on either of two methods to be selected for transporting the Gulfport herbicide to Johnston Island: 1) provide facilities at Gulfport for transferring Orange to the ship's cargo tanks, or 2) transport the Gulfport herbicide in existing drums to Johnston Island for loading onto the incinerator ship. The selection of either of these alternatives will depend on considerations of economic, environmental, and operational aspects of the drum disposal method selected.

3. PRINCIPAL ALTERNATIVE - INCINERATION ON JOHNSTON ISLAND.

a. Introduction: The system described below is conceptual and based upon prior studies which developed the operational parameters required for successful incineration of undiluted Orange herbicide (see Appendices D and E).

b. Proposed Incinerator on Johnston Island

(1) Incineration System

(a) The proposed incineration system on Johnston Island would incinerate the Orange herbicide at a rate of 1.4 pounds per second (pps) for 24 hours per day and discharge the combustion gases directly into the atmosphere on the west end of the island. At this rate, 11,300 gallons or 206 drums of herbicide could be incinerated per day for ~200 burn days to incinerate the entire stock of 2.3 million gallons. The details and design of the hardware for the entire system have not been addressed. However, incinerator systems both with and without combustion gas scrubbers have been considered in order to demonstrate the potential impact of spent scrubber water versus unscrubbed combustion gas dispersions into the atmosphere. For a system operating within the acceptable parameters described in Appendix E (measured combustion chamber

temperatures of 2400-2800°F; dwell time equal to or greater than 0.14 seconds; fuel to air mass ratio of about 0.1; and excess air greater than 30%), it can be stated that: 1) combustion gas and scrubbed effluent gases are free to undetectable levels (~$0.20 \times 10^{-3}$ µg/l for each compound) of herbicide esters, acids, and TCDD; 2) about 10% of the carbon dioxide and greater than 99.9% of both the hydrogen chloride and carbon particulates are removed from the combustion gases via an alkaline scrubber; 3) combustion pyrolyzates are unchlorinated hydrocarbons whose total concentrations average less than 0.50 µg/l; 4) alkali scrubbing removes a small fraction of the pyrolyzates from the combustion gases, and with gaseous condensation in presence of chlorine, converts some of the pyrolyzates into chlorinated hydrolyzates; 5) total unchlorinated pyrolyzates average less than 13.0 µg/l and total chlorinated hydrolyzates average less than 3.0 µg/l in the spent scrubber water; 6) carbon particulates contain no detectable levels of any type of hydrocarbon and the mass of these particulates was less than 0.5% of the carbon in the herbicide; 7) carbon dioxide, carbon monoxide, and heat of combustion gases are not environmentally significant; and 8) dispersions of scrubbed effluent gases into the atmosphere have no effect on tomato plant bioassays and attest to the lack of phytotoxicity of the gases.

(b) Considering the quality of the combustion gases and absence of herbicide feed constituents and TCDD content, treatment of the combustion gases is not required. Discharged combustion gases from the west end of the island will have minor environmental significance but spent scrubber water discharges, if used, could have an impact on the island's aquatic environment. For completeness both here and in Part III, both alkali and sea water scrubbers are discussed, but it is emphasized that the most environmentally acceptable incineration system on Johnston Island is one which does not scrub the combustion gases.

(c) Combustion gases would be discharged without scrubbing via a high stack on the west end of the island. These gases would be free to undetectable levels of herbicide feed constituents and TCDD but would discharge some 18.5 tons of hydrogen chloride during each burn day. Additionally, the stack gas would also discharge about 0.3 tons of particulate carbon per day and contain microgram per liter concentrations of unchlorinated hydrocarbon pyrolyzates. This option is attractive because it eliminates environmental problems associated with the discharge of spent scrubber water and the economic and logistic problems associated with the procurement and handling of neutralization chemicals and/or acidic scrubber water.

(2) Discussion of Scrubbers Considered

(a) Alkaline Scrubber

1. Hydroxide as a Neutralizer: An average volume of 250,000 gallons of fresh scrubber water containing about 81,000 pounds of sodium hydroxide (NaOH) would be required to scrub/neutralize the 37,000 pounds of hydrogen chloride produced per burn day in the combustion gas. The excess amount of sodium hydroxide required in the scrubber water is attributed to combustion gas carbon dioxide reactions with the alkali and scrubber system efficiency. If the NaOH were supplied in 55 gallon drums of 50 percent by weight NaOH, then 1-1/4 drums of this NaOH stock solution would be required per drum

of herbicide incinerated for a total of 50,000 drums of NaOH. This NaOH requirement may be reduced by 25% if the alkali were recycled and the scrubber design optimized to discharge spent scrubber water at pH 8.5. Daily discharge of spent scrubber water would be about 200,000 gallons because about 50,000 gallons of fresh scrubber water feed are volatilized and discharged with the stack gas as water vapor, see Appendix E.

2. Coral Carbonate as a Neutralizer: Coral is the primary constituent of the geological mass of Johnston Island. As primarily calcium carbonate ($CaCO_3$) it represents a source of alkalinity which may be suitable as a neutralizer for scrubber water which contains acid gas, hydrogen chloride. On the basis of hydrogen chloride neutralization only, about 43 pounds of $CaCO_3$ would be required for each 100 pounds of Orange burned. The daily incineration of 206 drums of Orange would require approximately 26 tons of $CaCO_3$. For consideration of the incineration of 2.3 million gallons (200 days), the neutralization of HCl would require approximately 5,000 tons of $CaCO_3$. This figure would undoubtedly be higher when system efficiencies and absorption of carbon dioxide are considered. Since $CaCO_3$ does not dissolve in sea water, the scrubber neutralizing system would require two units consisting of a sea water scrubber and a crushed coral contact unit for exposure of the scrubbing water to the coral. The availability of coral and a small scale test of coral usage would be required prior to selection of this method of combustion gas treatment.

3. Spent Alkali Scrubber Water Character: For an incineration system operating at the acceptable parameters, the spent scrubber waters are free to undetectable levels (~45 nanograms/l for each compound) of herbicide esters, acids, and TCDD and contain less than 16.0 µg/l of total hydrocarbon pyrolyzates and hydrolyzates. However, the spent scrubber water is 160-170°F and contains significant concentrations of suspended solids, 80-100 mg/l; free available chlorine, 250 mg/l; and chlorides, 20,000 mg/l (see Appendix E). The free available chlorine, 417 pounds in 200,000 gallons of spent scrubber water per day, and the heat content are primary problems in disposing of the scrubber water. Bioassays on the spent scrubber water required conditioning of the water for heat and chlorine removal, after which, the toxicity of the spent scrubber water was essentially the same as that of the fresh scrubber water and synthetically prepared spent scrubber water.

4. Spent Alkali Scrubber Water Treatment and Discharge: Spent scrubber water would need processing through cooling towers or spray ponds to reduce heat and free available chlorine content. The scrubber water would then have to be transferred via force main to the existing sewage outfall pumping station on the southside of the island for discharge with the sanitary sewage. Mixing sanitary sewage with spent scrubber water would further reduce the heat and free available chlorine content to levels acceptable for discharge. The outfall discharge point would be near the north-south axis of the island and approximately 500 feet from the shore.

5. Scrubbed Effluent Gas Character/Discharge: Scrubbed effluent gases would be free to undetectable levels of herbicide feed ester, acids, and TCDD. Expected hydrocarbons would be unchlorinated pyrolyzates whose total concentration is less than 0.30 µg/l. Inorganic quality of scrubbed ef-

fluent gases would be excellent: particulates, <0.1 grains per standard cubic foot, consisting of scrubber water salts and negligible amounts of carbon particles; carbon dioxide, 12-13% by volume; carbon monoxide, <1.0% by volume; water vapor, <50% by volume; nitrogen oxides, <100 ppm; and essentially free of hydrogen chloride. The scrubbed effluent gases would be discharged via stack on the incinerator site on the west end of the island.

(b) Sea Water Scrubber

1. Treatment: A scrubber system, utilizing sea water as the scrubbing liquid without an alkali agent, could be used for removal of carbon particulates and hydrogen chloride from the combustion gas. Water absorption devices are used to collect hydrogen chlorides gas in the manufacture of hydrochloric acid. Such devices are also used as gas emission control systems.

2. Scrubber Water Character: The heat, hydrogen chloride, suspended carbon particles, and hydrocarbon pyrolyzates and hydrolyzate mass loadings in the spent sea water scrubber would be similar to those obtained with alkali scrubbers. In this system, however, the absorption and reactions of hydrogen chloride would make the scrubber water very acidic. For example, if 500,000 gallons of sea water were 100 percent efficient in absorbing 18.5 tons of hydrogen chloride during each day's burn, the resulting spent scrubber water would be about a 1.0 percent HCl solution and have a pH of <1. Incineration of the 2.3 million gallon herbicide stock would result in the release via a sea water scrubber outfall of about 3,700 tons of hydrogen chloride into the receiving water environment.

3. Scrubber Water Discharge: The acidic nature of the scrubber water would preclude its discharge with sanitary sewage due to material incompatibility with existing sewage pipeline. A separate discharge line and outfall would be required to insure that the reef is not affected by this acidic discharge. The outfall would be located either on the southside of the island beyond the location of the present sewage discharge or to the southwest of the island.

4. Scrubbed Effluent Gas Character/Discharge: The scrubbed effluent gas quality will be essentially the same as that described for the alkaline scrubber except that the hydrogen chloride concentration may be greater. Assuming a 90 percent efficiency of scrubbing, some 370 tons of hydrogen chloride would be discharged in the exhaust gases. The discharge would be from a stack located at the incineration site on the west end of the island.

c. Summary: Incineration systems can be used on Johnston Island to provide 99.999 percent efficient incineration of undiluted Orange herbicide. Discharge effluent streams will be free of herbicide feed constituents and TCDD to undetectable levels, see Appendices D and E. An incinerator system has been described which would incinerate the 2.3 million gallons of herbicide in about 200 burn days and discharge the combustion gases from an exhaust stack on the west end of the island. Scrubbing of the combustion gases was discussed for completeness only and to demonstrate the quality and quantity of expected spent scrubber waters.

D. FAILSAFE: As with any process involving mechanical equipment, incineration operations are subject to malfunction and therefore require adequate safeguards to protect the environment and provide safety of personnel. The necessary safeguards for each of the incineration options are discussed below.

1. INCINERATION AT SEA

a. Procedures and construction of facilities to transfer the Orange to the ship will be accomplished in a manner to preclude and contain any spillage/leakage into the soil or waters. Procedures will include action to be taken during any unforeseen event resulting in the spillage of Orange.

b. The ship has been constructed according to IMCO regulations and will meet current U.S. Coast Guard requirements regarding loading and carriage of hazardous liquid cargoes. Her double hull and double bottom provide added containment protection from collision or other marine hazards. Crew quarters are not located above cargo space, and the incinerator is located on the stern at a safe distance from the crew quarters. Fuel oil for the ship's engines is isolated by double bulkhead from the waste cargo tanks.

c. The vessel is designed so that liquid waste cargoes can only be on-loaded via pumps on shore. Once loaded, shipboard pumps are only capable of discharging the liquid wastes directly into the combustion chambers. However, international regulations require that in the event the safety of the vessel and crew may be threatened, there must be some means of discharging the cargo directly into the sea. This could be effected through gravity release valves which remain officially sealed in normal circumstances.

d. Incinerator system monitoring and control of operational parameters have the following failsafe items:

(1) Electric waste pumps will not operate to feed herbicide to an incinerator's burners if that incinerator's combustion chamber temperature falls below 1400°C. If such a situation occurs, the incinerator malfunction is corrected and the combustion chamber temperature is returned to above 1400°C with fuel oil before any herbicide is reintroduced.

(2) An incinerator's burner is automatically shut down if any of the following conditions fall below preset levels: the air feed pressure to a burner, the herbicide feed rate to a burner, and the flame intensity of the burner.

(3) Operational controls and monitoring panels are manned at all times by an engineer whose sole ship responsibility is operating and maintaining the incinerator system at the desired combustion parameters.

2. PRINCIPAL ALTERNATIVE - INCINERATION ON JOHNSTON ISLAND

a. The incinerator complex will be constructed so that all transfer operations, such as transfer of Orange from the drums to storage or feed tanks, will be accomplished in a curbed or diked area to insure containment of spills. Procedures will be instituted so that spillage will be minimized during maintenance operations and so that operations will cease if any leaks develop in transfer systems.

b. The incinerator will be instrumented so that the combustion zone temperature will be constantly read-out and recorded. An automatic system will be included to notify the incinerator operator if the prescribed temperature condition is violated; upon notification, procedures will provide for immediate cut-off of fuel (Orange). The incinerator will be operated by qualified personnel continuously during an incineration of Orange herbicide. The fuel feed rate, air flow rate, and certain operating pressures will be read-out and recorded at prescribed intervals. Any deviation from acceptable values will require immediate cut-off of the fuel feed. Possible accidental modes will be investigated and procedures will be written for action to counter the situation. These procedures will provide for the immediate cut-off of fuel.

c. Real-time stack gas monitoring will be incorporated into the final design. Monitoring of combustion gas temperature and inorganic parameters (carbon monoxide, hydrocarbons, etc.) to determine concentrations and efficiency will be accomplished because of concern for the environment of Johnston Island. A system of operator notification in the event of unacceptable levels will be included.

d. The incinerator system will be run by electric power. Probable power failure modes will be identified and investigated, and procedures will be developed for system shut down and corrective action.

## E. HERBICIDE DEDRUM/TRANSFER AND DRUM DISPOSAL

### 1. INTRODUCTION

a. The proposed action, incineration at sea, will result in the accumulation of about 15,700 empty fifty-five gallon drums at NCBC and about 25,000 empty drums at Johnston Island. These drums will accumulate because the herbicide will be bulk loaded aboard the incinerator ship; the ship will be loaded once at the port of Gulfport and twice at Johnston Island. For the principal alternative, incineration at Johnston Island, the Orange stored at Gulfport will be shipped in drums to Johnston Island; therefore, about 40,000 empty drums will result from an incineration operation at Johnston Island. These empty drums will require disposal, and, in either case the ultimate drum disposal will consist of recycling the drums as "scrap steel" into steel manufacturing. Recycling as scrap steel is in accordance with the EPA preference for smelting as expressed in their comments to the revised draft environmental statement (Appendix O), and recycling is also deemed to be within the intent of the recommended EPA guidelines on disposal of pesticides and pesticide containers (39 FR85).

b. For the proposed action, incineration at sea, it is planned that the incinerator ship be bulk loaded at a rate equivalent to 1000 drums per day. Facilities are being designed at NCBC Gulfport and at Johnston Island by the Naval Ordinance Station MD to accommodate this transfer operation. To obtain data relative to this operation, the EHL(K) has conducted ecological surveys at NCBC Gulfport and Johnston Island, and conducted an Orange herbicide drum draining experiment at Gulfport. During the drum draining experiment, personnel from the EHL(M) conducted air sampling for the herbicide in the immediate work area occupied by the personnel performing the drum draining experiment. The ecological survey at NCBC revealed that the normal flora in proximity to NCBC are not generally susceptible to damage from Orange herbicide vapors. The transfer operation is presently planned for the winter months when the plant life would be least susceptible to damage from herbicide exposure. Therefore, the transfer operation can be accomplished with little or no concern for herbicide vapor control as regards phytoxicity at NCBC and the surrounding area. The air sampling conducted during the drum draining experiment revealed that the atmospheric concentrations of Orange vapors (0.6 $ppb_v$ for 2,4-D and 0.4 $ppb_v$ of 2,4,5-T) were well below the ACGIH Threshold Limit Values (TLV) of 10 mg/cbm for 2,4-D acid (1100 $ppb_v$) and 2,4,5-T acid (960 $ppb_v$). These very low results were anticipated because the vapor pressure of Orange is only $3.6 \times 10^{-4}$ mm mercury at $30^{o}C$, and therefore the atmospheric saturation concentration is calculated to be 470 $ppb_v$. This is the maximum concentration attainable by vaporization, and it is well below the above mentioned TLV. While it is realized that the surface area available for vaporization will be greater during the actual transfer operation than during the drum drainage experiment (16 drums), the concentration of Orange is expected to remain at least an order of magnitude below the TLV during the transfer operation. Therefore, the atmospheric concentration to which some unprotected project personnel will be exposured during the 16 day project will be below the acceptable value for an occupational life time exposure. The low concentration of Orange in the atmosphere exisiting in the drum draining area will be rapidly decreased by diffusion and dispersion as this air moves downwind, thus the transfer project could be accomplished with little or no concern for herbicide vapor control

as regards exposure to either project or non-project personnel. Despite the predicted ecological and personnel safety of the operation, it is the Air Force's intention to insure that all appropriate action is taken to minimize the emission of herbicide vapors and, therefore, minimize any possible impact upon personnel or the environment. Also, the controversial situation which has surrounded the use of Orange herbicide ("The Effects of Herbicides in South Vietnam, Part A," National Academy of Sciences, 1974) dictates that any herbicide exposure to personnel or herbicide loss to the environment should be minimized. The action to accomplish this at NCBC Gulfport will consists of protective clothing, mechanical ventilation, and where required the use of cartridge type respirator protective devices. Concerning the latter, Orange herbicide has a very strong, persistent phenol-like odor that is present below the TLV and which can be very disagreeable to personnel. At Johnston Island the precautions will be similar; however, ventilation will not be required because the natural ventilation will be adequate and the environmental impact of vapors from the transfer operation will not be significant. At both locations, a monitoring program will be conducted to document herbicide exposures and environmental affects should they occur. It is anticipated that this program will generate sufficient data to demonstrate the personnel and environmental safety of this operation. For the principal alternative, the NCBC Gulfport bulk transfer operation will not be required and the Johnston Island operation will be expanded. However, under the principal alternative, the dedrum rate would probably be lowered to about 200 drums per day (Part II.C.3.) as opposed to the 1,000 drums per day required under the proposed action.

c. The drum experiment at NCBC Gulfport revealed that about 1.5 pounds of herbicide remains in a well drained drum. This quantity when carried as a film on "scrap drum metal" into the furnaces associated with steel manufacturing is of negligible environmental significance. However, to eliminate any potential for adverse environmental impact during the shipment and storage period between drum drainage and placement of the scrap metal into a furnace, action will be taken to reduce the quantity of residual Orange in the drums. At NCBC, the drums will be drained and rinsed with solvent; the solvent will be allowed to drain, and the drums will be crushed for storage and subsequent disposal. At Johnston Island, the drums will be drained and then allowed to weather, i.e. be exposed to the environment, after which they will be crushed for storage and subsequent disposal. This action, solvent rinse and weathering, while of questionable necessity as regards environmental impact is being accomplished in keeping with the overall intent of minimizing the potential for adverse environmental impact from the disposal project. Details of the drum draining/cleaning procedures, transfer operation, and recycling of the drums are presented in the following paragraphs of this section.

2. HERBICIDE RESIDUAL IN DRAINED DRUMS

a. General: Data obtained during the incineration project at the Marquardt Co. (Appendix E) and the Orange herbicide drum draining experiment conducted at NCBC have indicated that about 1.0 and 1.5 pounds of herbicide, respectively, remains in a well-drained drum. Most of this residual was removed effectively from the drum by rinsing with a solvent - about 83 per cent removal after 3 rinses of JP-4 (Marquardt Study) and greater than 97 per cent removal after 4 rinses with diesel fuel (Gulfport Study). The diesel fuel appeared to be a more effective solvent for the Orange than did the JP-4. Rinse schemes involving various volumes of fresh rinse solvent and different numbers of rinses were investigated and it was found that the initial solvent rinse was responsible for practically all of the Orange which was removed by the rinsing process. It was also found during the Gulfport test that weathering, i.e. allowing the drained drums to remain exposed to the environment, could reduce the Orange residual in the drums markedly. The drums which were deheaded, drained, and weathered for 14 days prior to the rinse protocol had about 0.32 pounds of herbicide remaining and similiarly drained and weathered notched drums averaged about 0.66 pounds of herbicide remaining. It was concluded that the Orange residual in the notched drum was removed more slowly by weathering than such residual in deheaded drums. A comparison of draining efficiency between drums which were opened by being "deheaded" or "notched" revealed no significant differences and it was concluded that either method was acceptable. The notched drums actually contained slightly less herbicide than the deheaded drums as revealed by the rinse analyses. The deheaded drums were drained in an essentially vertical position and the notched drums were drained at about a 30° angle. The drum draining experiments are described below.

b. The Marquardt Company - Drum Draining: During the test burn conducted at the Marquardt Co., the 28 drums involved were drained and triple rinsed with various quantities of JP-4. Samples of each rinse were collected and analyzed for 2,4,D and 2,4,5-T esters. The quantity of Orange in each rinse was back calculated and extrapolated to determine the quantity of Orange remaining in a drained drum. The data analysis and discussion of these experiments are contained in the Marquardt Co. Final Report in (Appendix E). Less than two quarts of Orange remained in the drums after initial emptying and some of the emptied drums had been sitting in a vertical position for 20 - 25 days when the draining was started. Each drum was upended and allowed to free board drain through the bung; the draining was continued until the steady dripping stopped. The drain time ranged from 6 to 9 minutes and the air temperature during the drum draining was 60°F. The data analyses revealed that approximately one pound of herbicide remains in a drum after drainage under the above conditions. In addition, a single rinse with five gallons of JP-4 removed about 75% of the herbicide from the drum. The second and third rinse (5 gal) increased the removal efficiency to approximately 79% and 83% respectively. The rinses were accomplished by adding the required JP-4, replacing the cap, and rotating the drum on a drum rolling device for five minutes.

c. NCBC, Gulfport Drum Draining: On 10 and 11 September 1974, tests were conducted on 16 Orange herbicide drums at NCBC Gulfport MS. The purpose of these tests was to determine the quantity of Orange remaining immediately after draining for a specified time. In preparation for the tests all but

3 to 9 gallons of herbicide was removed from the drums. These drums remained in a vertical position until the draining test; however, just prior to starting the drain experiment on a given drum, that drum was rotated on a drum spinning device to coat the interior of the drum with herbicide to simulate realistic drum draining conditions. The drums were opened by a manual "notcher" device or deheaded with an electric device. The notcher device leaves a hole in the head of a drum which is similar to the hole left by an opener/spout for one quart cans of motor oil. Unlike a typical can opener which removes only the lid, the deheading device cuts off both the head and the associated "lip". Upon opening, the deheaded drums were drained in a vertical position and the notched drums at a 30° angle for from 10 - 18 minutes. The volume of herbicide dripping from the drum after 5 minutes of draining was caught and measured volumetrically until the diesel fuel rinse was accomplished. A representative portion of the diesel fuel rinse was collected and subsequently analyzed and the quantity of Orange in the drum back calculated. In addition to the immediate rinse test, some drums were stored for two weeks after drainage and then rinsed so that the effect of evaportation could be evaluated. This action was taken because inspections of the empty drum storage area (drums which contained Orange but were drained because they were leaking) at Johnston Island have revealed that this area does not have a strong odor of Orange and that the individual drums appeared relatively clean and dry. It is felt that evaporation of Orange from the drums is responsible for significally reducing the Orange content of an empty drum. At Johnston Island, the drums could be allowed to weather after a complete draining, thus providing for additional reduction of the Orange remaining in a drum. The Gulfport data although somewhat variable was sufficient so that valid conclusions could be reached on the Orange remaining in an unrinsed drum and on the efficacy of solvent rinsing. The Gulfport data is most important to actual plans for drum handling and the appropriate findings were stated in paragraph 2(a) above.

3. HERBICIDE DEDRUM AND TRANSFER TO INCINERATOR VESSEL

a. Gulfport MS: Under the proposed action, incineration at sea, the 863,000 gallons (15,700 drums) of Orange presently stored at NCBC Gulfport will be bulk loaded aboard the incinerator ship at the Port of Gulfport. A dedrum facility will be established at the NCBC and the bulk Orange will be transported via railroad tank car to the pier for loading aboard the ship. The dedrum facility will include a drum deheading and pumping station drainage racks, a solvent spray rinse station and a collection sump. Aircraft refuelers will be used to transfer the Orange from the collection sumps to railroad tank cars. The tank cars will be conveyed once per day during daylight hours to the pier where the Orange will be pumped aboard the incinerator ship. The facility will be designed and operated to dedrum and load 1,000 drums of Orange per day for a total of 16 days. The deheaded drums will be drained in a vertical position for at least 5 minutes, rinsed with high pressure solvent spray (~2 gal.), drained for 2 minutes and then crushed. The spray rinse solvent will be collected with the herbicide and loaded onto the incinerator vessel. All transfer areas including the pier area will be protected to insure that any spillage of material is contained. Strict industrial hygiene measures will be adhered to throughout the operation. As stated in the introduction, the public and scientific controversy associated with Orange necessitates the maximum possible precautions and the documentation of environmental factors during the transfer operation. Approriate safety clothing/equipment will be used in all operations. Local exhaust ventilation for the drum draining area will discharge

through activated carbon which will absorb odors and further minimize the chance of damage to nearby flora. Ambient air samplers will be utilized to document conditions throughout the operation. The normal flora of the area will be continuously observed and its condition documented, and biomonitoring with selected plans will also be accomplished. All equipment and the railroad tank cars will be flushed with solvent at the completion of the transfer operation, and the flushings will be loaded aboard the incinerator ship for incineration along with the Orange. The Naval Ordinance Station, Indian Head, MD is responsible for the engineering design and installation of the transfer system and will oversee the actual transfer operation.

b. Johnston Island: The 1.4 million gallons (25,000 drums) of orange presently stored at Johnston Island will be bulk loaded aboard the incinerator ship at Johnston Island. Two loadings to the ship will be required. The dedruming and ship loading rate will be 1,000 drums per day; approximately 13 days will be required for each load. A dedrum facility will be established at the storage area on Johnston Island. The dedrum facility will include a drum drainage rack where the drums will be opened with a notching device for herbicide drainage into a collection sump. The Orange will be pumped from the sump to the aircraft refuelers which will then transport the Orange to the pier where the Orange will be pumped onto the incinerator ship. To prevent Orange from entering the ocean, the pier transfer area will be configured to contain any spillage. The drums will be drained for at least 30 minutes. They will then be left to weather (at least 1 month) after which they will be crushed and stored for disposal. All equipment and refuelers will be flushed with solvent at the completion of the transfer operation, and the solvent will be loaded onto the ship for incineration with the Orange. Industrial hygiene measures and monitoring will be accomplished similarly to that described above for NCBC Gulfport. The Naval Ordinance Station, Indian Head MD is designing/co-ordination on the design and installation of the transfer and will oversee the transfer operation.

4. ULTIMATE DRUM DISPOSAL:

a. The drums generated by accomplishment of either the proposed action, incineration at sea, or the principal alternative of incineration at Johnston Island will be disposed of by recycle as "scrap" metal into steel manufacturing. Disposal as scrap is considered more favorable from the long term environmental standpoint than disposal of unrinsed drums in a landfill because the Orange and its components would be rapidly destroyed in the steel making process. As the scrap drum metal is reprocessed into new steel, it would be subjected to high temperatures (~2900°F) for an extended period of time (~6 hours). This exposure is much more severe than that which would be received if the non-combustible drums were subjected to incineration in a pesticide incinerator (2000°F, 2 sec) as defined by EPA in 39FR85. Recycle into steel not only conserves the drum metal but also raw materials for steel making are conserved. The utilization of one ton of scrap steel in the steel making process conserves about 4 tons of iron ore, coal, and limestone. Therefore the recycle of 45,000 - 50 pound drums as scrap will conserve approximately 4,500 tons of raw material. This method of ultimate disposal will also preclude the return of any Orange herbicide drums to manufacturers, formulators, or drum reconditioners for reuse.

b. It has never been the Air Force's intention that the Orange herbicide

drums be reconditioned for reuse. Beside the negative public relations aspect of reuse, the solvent requirements to affect a triple rinse as recommended by the EPA prior the reuse of containers (39FR85), concomitant complication and the expansion of the disposal project associated with such rinsing operations is not desirable. The solvent volume of 660,000 gallons for rinsing represents greater than one fourth the volume of the total Orange herbicide stock. Since this solvent would require incineration along with the herbicide the incineration phase of the project would be greatly expanded. The logistics of supply and handling of the solvent, including the drum rinse operation, would complicate the industrial management of the project. The frequency of handling and the tremendous quantity solvent involved would increase the possibilities of a fire hazard and spillage or Orange contaminated solvent. In addition, the use of a large quantity of a petroleum solvent during a period of energy conservation is not a prudent action if it can be safely avoided. In this regard, the rinsing operation at Gulfport may be altered to minimize solvent use i.e. recycle, if appropriate.

5. POTENTIAL FOR ENVIRONMENTAL IMPACT

a. Although the procedures described above will be accomplished to minimize the potential for any environmental impact as a result of the herbicide transfer and drum disposal aspects of this project, it is necessary to consider the following situations:

(1) The Orange residual remaining on the crushed drums which are put into the steel manufacturing process;

(2) The Orange residual which remains on the drums while the drums are in storage and or being transported to the steel manufacturing site;

(3) The operations at Gulfport and Johnston Island to reduce the Orange residual in drained drums.

b. For the drums at Gulfport, it is anticipated that the pressure solvent rinse will remove greater than 90 percent of the Orange which remains after draining, thus a crushed drum may contain a residual of about 0.15 pound of herbicide. The first rinse of deheaded drums at Gulfport removed greater than 92 percent of the herbicide which was removed by the subsequent rinses. The third and fourth rinses removed almost negligible amounts of herbicide; therefore, the quantity removed in four rinses can be considered as being just slightly less than the actual Orange residual in a drum. Since the Orange residual after draining is a film on the interior drum surface it is anticipated that a pressure spray will be even more effective than simple addition of solvent with gentle mixing.

c. At Johnston Island, the drums will be weathered for 30 days to allow for evaporation of a portion of the residual which remains after draining. It is anticipated that 30 days weathering at Johnston Is. and can reduce the residual in the drums to about 0.3 pound of herbicide. As indicated in paragraph 3.b. above the drums will be crushed after weathering for subsequent disposal as "scrap" for recycle in steel manufacturing.

6. ENVIRONMENTAL IMPACT

a. The environmental impact associated with the placement of crushed drums containing a film of Orange of 0.15 to 0.3 pounds into a steel making furnace is not significant. During the process the Orange would be converted to essentially hydrogen chloride, carbon dioxide, and water. The air pollution

control equipment normally associated with steel making operations would be sufficient to minimize any environmental impact of the combustion porducts.

b. The environmental impact associated with the storage and transport of crushed drums which contain a residual of 0.15 to 0.3 pounds of herbicide is not significant. Since the herbicide is a film on the inner surface of the crushed drums, any evaporation would be retarded. The herbicide is not water soluble nor is it easily translocated by water, thus it would also tend to remain in the drums even if subjected to rainfall.

c. The environmental impact associated with the solvent cleaning crushing, and storage of drums at NCBC Gulfport will not be significant. The solvent spray will rapidly reduce the Orange residual in the drum and the Orange removed will be contained within the solvent. The drums will be crushed after drainage of the solvent spray. The crushing of the drums will reduce the opportunity of any residual herbicide from entering the environment while the crushed drums await shipment to a steel manufacturing plant. It should be emphasized that the solvent spray cleaning process at Gulfport is being accomplished to minimize any environmental impact associated with the storage of drums at Gulfport and is not to be confused with the triple rinse recommended before reuse of pesticide containers. The use of "weathering" of the drums at Gulfport was considered as a means of reducing the Orange residual to an acceptable level for subsequent storage and transportation of the drums. A subjective evaluation of this method revealed that while a portion of the drums may be safely weathered, it was not environmentally prudent to weather the entire stock (15,700 drums) at NCBC; therefore the use of the solvent spray to minimize the potential for environmental impact is justified.

d. The environmental impact associated with weathering of drums on Johnston Island is not significant. The storage area is located such that the prevailing winds would carry any Orange vapor immediately off shore and away from the island. About 5,000 drums which were emptied and drained as part of the regular maintenance of the Orange storage area have in fact weathered at Johnston Island with no noticeable environmental impact.

F. CHARACTERISTICS OF THE HERBICIDE

1. PROCUREMENT SPECIFICATIONS:

a. The USAF procured Orange under Purchase Description AFPID 6840-1, dated 23 February 1968, and Amendment 1, dated 11 April 1968. The Orange Purchase Description containing the changes and additions of Amendment 1 is quoted below:

1. SCOPE

This purchase description prescribes requirements for an herbicide identified as Orange. The material is used as a systemic growth regulator to kill and defoliate vegetation.

2. APPLICABLE DOCUMENTS

PPP-D-729, Drums: Metal 55-gallon, for shipment of noncorrosive material.

MIL-H-51148, Herbicide N-Butyl 2,4,5 Trichlorophenoxyacetate.

MIL-H-51147, Herbicide N-Butyl 2,4 Dichlorophenoxyacetate.

MIL-STD-105, Sampling Procedures and Tables for Inspection of Attributes.

MIL-I-45208, Inspection System Requirements.

3. REQUIREMENTS

3.1 Materials. The herbicide shall be composed of the following two ingredient materials.

a. N-Butyl 2,4,5 Trichlorophenoxyacetate.

b. N-Butyl 2,4 Dichlorophenoxyacetate.

3.1.1 The ingredient materials shall meet the following requirements:

a. Specification MIL-H-51148, N-Butyl 2,4,5 Trichlorophenoxyacetate, except free acid will be .5% maximum by weight.*

*Changed per Amendment 1

b. Specification MIL-H-51147, N-Butyl 2,4 Dichlorophenoxyacetate except composition (purity) shall be 98.0% minimum by weight, acid equivalent shall not be less than 79.0% nor more than 8.0% and free acid shall be .5% maximum by weight.**

3.2 Finished Mixture (Orange).

3.2.1 Composition.

50% by volume N-Butyl 2,4,5 Trichlorophenoxyacetate

50% by volume N-Butyl 2,4 Dichlorophenoxyacetate

3.2.1.1 Tolerance. Tolerance range for amount of each composition ingredient contained in the final mix will be ±1.5% including the precision allowance for the analytical method used.

a. Range for N-Butyl 2,4,5 Trichlorophenoxyacetate is 48.5 to 51.5% by volume

b. Range for N-Butyl 2,4 Dichlorophenoxyacetate is 48.5 to 51.5% by volume.

3.2.2 Free Acid. A maximum of 0.5% by weight.

3.2.3 Total Acid Equivalent (as 2,4-D Acid).

90.0% minimum by weight.
94.0% maximum by weight.

3.2.4 Specific Gravity.

1.275 to 1.295 at $20^{\circ}/20^{\circ}C$.

3.2.5 Color. A Clear reddish brown color.

3.2.6 Weight per Gallon - 10.70 ± 0.08 lbs at $20^{\circ}C$ (55 gallons will weigh 584.10 to 592.90 lbs on a $20^{\circ}C$ basis).*

4. QUALITY ASSURANCE PROVISIONS

4.1 Test Methods.

*Changed per Amendment 1
**Added per Amendment 1

4.1.1 Composition. Determined by infrared spectrophotometer - Beckman IR-4 or equivalent. An official standard will be used to calibrate the spectrophotometer made up a known 50/50% by volume mixture of the 2,4-D and 2,4,5-T normal butyl esters. This standard for calibration and quality analysis work may be obtained from the government. Request for standards should be forwarded to:

Defense Supply Agency
Defense General Supply Center
Directorate of Procurement and Production
Richmond, Virginia 23219

The infrared analysis method is attached to this purchase description.

4.1.2 Free Acid. A sample is dissolved in 91% isopropyl alcohol and titrated potentiometrically with standard alkali solution to a pH of 4.5.

a. Apparatus.

(1) pH meter equipped with glass - calomel electrodes.

(2) Stirrer.

b. Reagents.

(1) Alcohol, isopropyl, 91% neutral. Use commercial 91% isorpopyl alcohol or mix 920 ml of 99% isopropyl alcohol and 80 ml of distilled water.

(2) Sodium hydroxide solution, 0.1 N accurately standardized against potassium acid phthalate.

(3) Buffer solutions for checking pH meter, pH 7.

c. Procedure.

(1) With a graduate or automatic pipet measure 100 ml of 91% isopropyl alcohol into a 250 ml beaker. Weigh 10 grams of sample into the alcohol. Turn on the stirrer and mix the solution.

(2) Insert the electrodes of the pH meter and measure the pH of the solution. Titrate with 0.1 N NaOH solution to pH 4.5 and record the volume of titrant. If the initial pH is about pH 4.5, conclude that the herbicide is free of acid.

d. Calculation.

Calculate the percent free acid using the formula -

$$A = \frac{FxV \times N}{W}$$

A = percent free acid

F = molecular weight of acid x $\frac{100}{1000}$

V = milliliters of 0.1 N sodium hydroxide

N = normality of sodium hydroxide used

W = weight of sample in grams

4.1.3 Total Acid Equivalent.

a. Ingredient Specifications MIL-H-51148 and MIL-H-51147. The saponification back titration method or the biphenyl reagent with chloride titration method will be used to determine total acid equivalent.

b. The final Orange mix. Determine total acid equivalent using the biphenyl reagent - chloride titration methods.

4.1.4 Specific Gravity. Determine by hydrometer or other method accurate to three significant figures.

4.1.5 Color. Visual observation of a 10 ml sample in a 16 mm x 125 mm glass test tube.

4.1.6 Weight per Gallon. Specific gravity calculation or other appropriate weight measurement.

4.2 Responsibility for Inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the government. The government reserves the right to perform any of the inspections set forth in the purchase description where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.3 Contractor Inspection System Requirements. Specification MIL-I-45208 applies.

4.4 Sampling for Test. Sampling shall be conducted in accordance with MIL-STD-105.

4.5 Acceptance.* Acceptance of the final Orange mixture will be based on test results for conformance to requirements of paragraph 3.2. Test results for conformance to requirements of paragraph 3.1 will be reported.

5. PREPARATION FOR DELIVERY

Packing and marking requirements shall be specified by the procuring agency.

6. NOTES

6.1 This AFPID replaces AFPID 6840-1 dated 7 Nov 1967.

6.2 The ingredient material requirements contained herein (para 3.1.1) are based on Specification MIL-H-51147A (MU) and MIL-H-51148A (MU) dated 7 Nov 1966.

b. The USAF procured Orange II under a separate Purchase Description which was unnumbered, undated and is quoted below:

1. Orange II shall be composed of:

a. 50 percent by volume N-Butyl 2,4 Dichlorophenoxyacetate conforming to MIL-H-51147A (MU) dated 7 Nov 1966 except acid purity shall be 99.0 percent minimum by weight and acid equivalent shall not be less than 79.9 percent nor more than 80.0 percent by weight, and free acid maximum 0.5 percent.

b. 50 percent by volume of Isooctyl 2,4,5 Trichlorophenoxyacetate conforming to MIL-H-60724 (MU) dated 1 May 1967, except free acid maximum 0.5 percent.

2. The final herbicide mixture shall meet the following requirements:

a. Specific gravity - 1.220 to 1.242 at 20°C.

*Added per Amendment 1

b. Free acid maximum - 0.5 percent by weight.

c. Weight per gallon - 10.6 to 10.34 per gallon at 20°C.

2. CHEMICAL AND PHYSICAL PROPERTIES: All available reference data on the general properties of Orange herbicide are summarized and presented in Table II-1 and 2. General properties of TCDD are presented in Table II-3; the statistical analyses for the TCDD content in the Orange herbicide stocks is discussed in paragraph 3. below. The following references were used in preparation of these tables: USAF EHL(K) a, 1973; U.S. Army, 1969; USAF RPL, 1972 (Dept. Agr.); USDA, 1972; USAF EHL(K) b, 1973.

3. STATISTICAL ANALYSES OF TCDD CONCENTRATIONS IN ORANGE HERBICIDE STOCKS

a. Sampling from Johnston Island and Gulfport: Two different types of sampling procedures were used to supply samples to the Analytical Laboratory (Dow Chemical Co.). The Orange herbicide at Johnston Island could not be separated into identifiable processing lots. Therefore, two hundred separate samples were collected to represent the entire population of Orange at Johnston Island. It is assumed that these 200 samples were a random, representative sample of the population at Johnston Island. In contrast, the samples taken at Gulfport could be grouped to represent concentrations of TCDD in stocks supplied by certain manufacturers. Generally, six samples were taken to represent each manufacturer's stocks. There were seven major stocks at Gulfport. Specific gravity was assumed to be 1.285.

b. Results of Johnston Island Analyses: At the time that the 200 samples were collected the inventory of Orange stock at Johnston Island was 26,689 fifty-five gallon drums. The arithmetic mean TCDD concentration was found to be 1.909 mg/kg; therefore, the total TCDD in the Orange stock at Johnston Island is estimated to be 13.63 kg. Figure II-1 below demonstrates that the TCDD concentrations in the 200 samples from Johnston Island did not follow a normal distribution. Of the 200 samples, 153 or 76.5% contained TCDD concentrations of 1.0 mg/kg or less. Of the 200 samples, 195 or 97.5% had TCDD concentrations of 10.0 mg/kg or less. Only 5 samples (2.5%) had TCDD concentrations larger than 10.0 mg/kg. These larger values were 13, 17, 22, 33 and 47 mg/kg. None of these values were discarded as "outliers" in computing the arithmetic mean TCDD concentration of 1.909 mg/kg.

c. Results of Gulfport Analyses: Table II-4 is a compilation of the results of the TCDD analyses of the seven major manufacturer's Orange stock at Gulfport. The number of drums was obtained from the inventory at the time of the sampling. The calculations for weighted values were based on the following formula:

$$\text{average statistic} = \frac{\text{sum of each statistic times its weight}}{\text{sum of weighting values}}$$

At Gulfport, the total milligrams of TCDD were 7,265,975.8. The total kilograms of Orange were 4,100,225.7 kg. The average concentration of TCDD was therefore 1.772 mg/kg of Orange.

d. TCDD Content of Total Orange Herbicide Stocks: At the time of sample collection, the total Air Force inventory of Orange herbicide at Gulfport and Johnston Island was 42,015 fifty-five gallon drums or 2.3 million gallons. The weighted average concentration of TCDD is 1.859 mg/kg. Therefore, the total amount of TCDD in the entire Air Force inventory is estimated to be 20.1 kg.

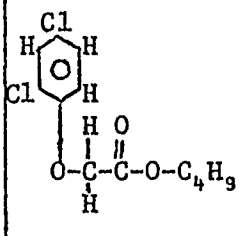
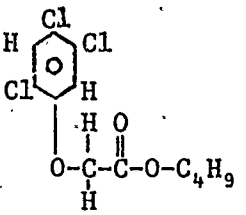
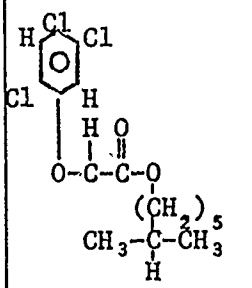
TABLE II-1. GENERAL CHEMICAL/PHYSICAL PROPERTIES OF ORANGE HERBICIDE

| Property | Orange | Orange II |
|---|---|---|
| BTU Content per Pound[1] | 10,017 ($\delta$=80) | |
| Physical State | Liquids at room temperature. | |
| Color | Clear, reddish brown to straw color. | |
| Appearance | Dark, rust-colored liquid of oily consistency. | |
| Solubility | Soluble in diesel fuel and organic solvents. Insoluble in water. | |
| Freezing Point ($^{o}$C) | 7 to 8 | 9 |
| Flash Point | 146$^{o}$C (295$^{o}$F) | Unknown |
| Specific Gravity @ 25$^{o}$C | 1.275 to 1.295 | 1.220 - 1.242 |
| Weight (lb/gal)[2] | | |
| Total ester | (@20$^{o}$C) 10.7 ($\pm$0.08) | 10.2 ($\pm$0.09) |
| Acid equivalent | 8.6 | 7.6 |
| Vapor Pressure (30°C) | ~3.6 x $10^{-4}$mm Hg †† | |
| Viscosity, centipoises @:[2] | | |
| -17.7$^{o}$C | 5,000 | unknown |
| - 6.6$^{o}$C | 940 | unknown |
| 0.0$^{o}$C | 390 | unknown |
| 10.0$^{o}$C | 134 | unknown |
| 23.8$^{o}$C | 43 | 67 |
| 37.7$^{o}$C | 24 | 27 |
| Viscosity, centipoises @:[3] | | |
| 20$^{o}$C | 46 | - |
| 30$^{o}$C | 24 | - |
| 35$^{o}$C | 18 | - |
| 40$^{o}$C | 14 | - |
| 45$^{o}$C | 11 | - |
| Theoretical % Weight[4] | | |
| Carbon | 49.11* | 52.12† |
| Chlorine | 29.87* | 27.27† |
| Oxygen | 16.37* | 15.20† |
| Hydrogen | 4.65** | 5.41** |
| Free Acid (by weight) | 0.5% maximum | 0.5% maximum |
| Total Acid Equivalent (% by weight as 2,4-D) | 90.0% minimum 94.0% maximum | 79.9% minimum 80.0% maximum |
| Corrosiveness | Noncorrosive on most metals. Deleterious to some paints, natural rubber, and neoprene. Teflon, viton, polyethylene and butyl rubber are resistant. | |

*Sample contained 14 ppm TCDD.
†Sample contained 3.7 ppm TCDD.
††Calculated and confirmed by EHL(M).
**Calculated by EHL(K), Kelly AFB TX as (100-$\Sigma$C,Cl,O weight percents).

1. USAF EHL(K) a, 1973.
2. U.S. Army, 1969.
3. USAF RPL, 1972 (Dept. Agr.).
4. USDA, 1972.

Table II-2. GENERAL CHEMICAL/PHYSICAL PROPERTIES OF INGREDIENT ESTERS OF ORANGE HERBICIDE

| Property | Normal Butyl 2,4-dichloro-phenoxyacetate NB 2,4-D | Normal Butyl 2,4,5-trichloro-phenoxyacetate NB 2,4,5-T | Iso-octyl 2,4,5-trichloro-phenoxyacetate IO 2,4,5-T |
|---|---|---|---|
| Purity (ester by weight) | 98.0% minimum | 95% minimum | 95% minimum |
| Appearance | Clear, reddish brown liquids | | |
| Acid Equivalent (by weight) | 79.0% minimum to 80.0% maximum | 78-82% | 66-69.5% |
| Free Acid (by weight) | 0.5% maximum | 0.5% maximum | 0.5% maximum |
| Specific Gravity($20^o/20^o$) | | 1.316 to 1.340 | 1.200 to 1.220 |
| Freezing Point ($^oC$) | | 29(1,2,3)* | -21 to -23 |
| Molecular Weight | 277.15 | 311.60 | 367.71 |
| Molecular Elements | $C_{12}H_{14}Cl_2O_3$ | $C_{12}H_{13}Cl_3O_3$ | $C_{16}H_{21}Cl_3O_3$ |
| Structural Formula |  |  |  |
| Theoretical % Weight | | | |
| Carbon | 57.99(4)* | 46.23(4)† | 52.24(4) |
| Chlorine | 25.60(4) | 34.14(4)† | 28.94(4) |
| Oxygen | 17.33(4) | 15.41(4)† | 13.06(4) |
| Carbon | 52.01** | 46.26** | 52.26** |
| Chlorine | 25.58** | 34.13** | 28.93** |
| Oxygen | 17.32** | 15.40** | 13.05** |
| Hydrogen | 5.09** | 4.21** | 5.76** |
| Heat of Formation(3) (cal/mole) | -152,000*** | -159,000*** | |

*Considered by EHL(K) to have been an error in the reference.

†Same value for ester containing 0.1 ppm of 2,3,7,8-tetrachlorodibenzo-p-dioxin ("Dioxin" or TCDD).

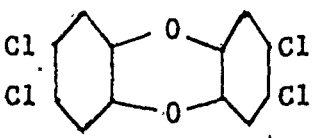
**Calculated by EHL(K), Kelly AFB TX 78241.

***"...estimated by taking the heats of formation of similar compounds and adding/subtracting the heats of formation of similar/dissimilar groups."

3. USAF RPL, 1972.

4. U.S. Dept. Agr., 1972.

TABLE II-3. GENERAL CHEMICAL/PHYSICAL PROPERTIES OF TCDD

| Property | Data |
|---|---|
| Content in Orange or Orange II | Range 0-47 mg/kg. Estimated mean of 1.9 mg/kg with a 95% upper and lower confidence limit of 2.6 and 1.2 mg/kg, respectively.(5) |
| Molecular Weight | 321.97 |
| Structural Formula |  |
| Theoretical % Weight | |
| Carbon | 44.77* 45.41(4) |
| Chlorine | 44.04* 44.61(4) |
| Oxygen | 9.94* 9.95(4) |
| Hydrogen | 1.25* |

*Calculated by EHL(K), Kelly AFB TX

4. U.S. Dept Agr, 1972.
5. USAF EHL(K) b, 1973.

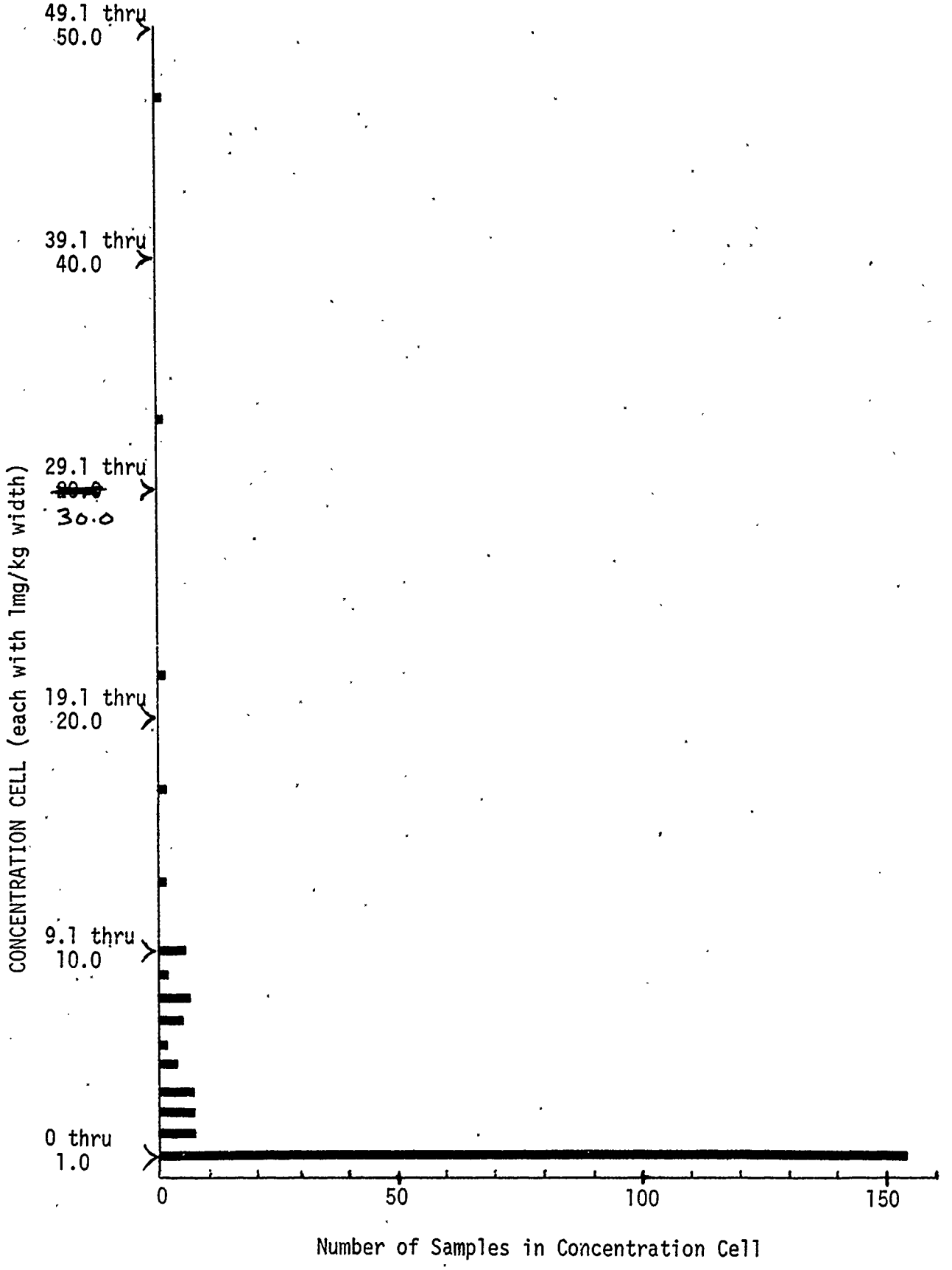



FIGURE II-1. HISTOGRAM REPRESENTATION OF TCDD CONCENTRATIONS MEASURED IN 200 ORANGE HERBICIDE SAMPLES FROM JOHNSTON ISLAND.

TABLE II-4

TCDD ANALYSES OF MAJOR MANUFACTURER STOCKS - GULFPORT

| Number of Drums | Number of Gallons | Kg Orange | Mg/Kg Conc. of TCDD | Mg of TCDD | Cumulative Total Mg of TCDD |
|---|---|---|---|---|---|
| 2,652 | 145,860 | 709,500.1 | <0.05 | 35,475.0 | 35,475 |
| 6,981 | 383,955 | 1,867,654.7 | 0.12 | 224,118.6 | 259,593.6 |
| 934 | 51,370 | 249,876.7 | 0.17 | 42,479.0 | 302,072.6 |
| 1,560 | 85,800 | 417,353.0 | 0.32 | 133,556.9 | 435.625.5 |
| 2,185 | 120,175 | 584,561.7 | 7.62 | 4,454,360.2 | 4,889,985.7 |
| 984 | 54,120 | 263,253.4 | 8.62 | 2,269,244.3 | 7,159,230.0 |
| 30 | 1,650 | 8,026.0 | 13.3 | 106,745.8 | 7,265,975.8 |
| 15,326 | 842,930.0* | 4,100,225.7 | | | 7,265,975.8 |

* Represents 98% of the 860,000 gallons of total Gulfport Stock.

4. TOXICOLOGICAL AND ECOLOGICAL CHARACTERISTICS OF CHLOROPHENOXY HERBICIDES PERTINENT TO POTENTIAL BIOLOGICAL EFFECTS OF N-BUTYL ESTERS OF 2,4-D AND 2,4,5-T: There have been many scientific studies to determine the behavior of chlorophenoxy herbicides in plant and animal systems under varied environmental conditions. The following paragraphs are not meant to list all those studies. Rather, the purpose is to logically describe the known and probable behavior of Orange herbicide components in biological systems by utilizing the most current and relative information obtainable from the literature and from studies at EHL(K). It is important to note at the outset that in biological systems and aquatic systems the N-butyl esters (NBE) of 2,4-D and 2,4,5-T can hydrolyze. Thus, the behavior of the pure acids and their salts are also pertinent and will be discussed in the following paragraphs along with characteristics of ester forms. The differences in toxic effects produced by the various salts, amines and esters of 2,4-D and 2,4,5-T can often be explained on a pharmacokinetic basis in which the concentrations at the receptor sites in the organism depends on the absorption and distribution rates in relation to the rates of metabolism and excretion. The rate of absorption into plants or animals will be dependent upon various interrelated factors such as route of entry and rate of membrane transport. Specific membrane transport rate will depend upon the characteristics of the membrane in relation to the size, shape, polarity and lipid solubility of the particular herbicide molecule being considered in each cited study.

a. Behavior in Terrestrial Animals

(1) Metabolism and Excretion Kinetics: Most of the data derived from acute toxicity studies indicate that neither 2,4-D nor 2,4,5-T are particularly toxic. (Gleason et al., 1969; Bjorklund and Erne, 1966). In the rat, the single dose, $LD_{50}$ ranges from about 250-270 mg/kg depending on the forms of the chemical administered (Christensen, 1971). Several workers have suggested that part of the reason for this lack of toxicity is that the excretion of the herbicides is very rapid in most mammals (Clark et al., 1964; Khanna and Fang, 1966). Most studies indicate that animals possessing highly developed renal function will rapidly eliminate 2,4-D and 2,4,5-T by active tubular secretion. Cattle and rabbits, which normally actively metabolize compounds mostly by acetylation, excrete 2,4-D and 2,4,5-T in the urine mostly unchanged. Erne, (1966) found that in the rat, rabbit, calf and chicken, 2,4-D and 2,4,5-T had a biological half-life varying from three to twelve hours and that urinary excretion was the most common route of elimination. Data exist to indicate that only very small amounts of 2,4-D are metabolized by the rabbit (Clark et al., 1964; Khanna and Fang, 1966). Berndt and Koschier (1973) studied the in vitro uptake of 2,4-D and 2,4,5-T by the renal cortical tissue of rabbits and rats. Renal cortical slices from both species accumulate 2,4-D and 2,4,5-T with greater uptake occuring in rabbit tissue. Nitrogen and various metabolic inhibitors reduced the uptake thus indicating that both of these organic acid herbicides are transported by the renal organic anion mechanism. Berndt and Koschier (1973) concluded that renal tubular transport by the organic anion mechanism may account for the relatively rapid disappearance of these compounds and this may account for their low toxicity.

(2) Absorption and Distribution: The most common route of accidental absorption of chlorophenoxy herbicide in terrestrial animals is via ingestion. This is especially true in herbivores. However, absorption of toxic doses via inhalation and cutaneous routes is possible, if uncommon. The literature indicates that gastric absorption of 2,4-D and 2,4,5-T and their amines and alkali salts occur readily as would be predicted from classical Henderson-Hasselbalch relationships. However, the gastro-intestinal absorption of 2,4-D in the form of an ester may be incomplete. Erne (1966) administered 2,4-D ester orally and found no detectable esters in the plasma. However, detection of low levels of 2,4-D in the plasma indicated that some hydrolysis of the ester had occurred. Erne (1966) in studies with rats, calves, chickens, and pigs found that the highest tissue levels of 2,4-D and 2,4,5-T were found in liver, kidney, lung and spleen, the levels sometimes exceeding the plasma level. In blood cells, 10-20% of the plasma level was found. Penetration of 2,4-D into adipose tissue and into the central nervous system was restricted, whereas a ready placental transfer was demonstrated in swine. The distribution pattern did not show any significant species or--in rats--sex differences. Klingman et al.(1966) measured ppb amounts of 2,4-D in the milk from cows grazing on pasture probably sprayed with esters of 2,4-D. However, these levels dropped to undetectable amounts (< 1 ppb) on the third day after the pasture had been sprayed.

(3) Acute Toxicity: One of the essential prerequisites in the selection of a herbicide for defoliation programs is selective toxicity. Orange herbicide is characterized by a low order of toxicity to man and terrestrial animals. When properly applied, chlorophenoxy herbicides have presented very minimal hazards to animal life in target areas. The acute oral toxicity of Orange herbicide is summarized below. The data are expressed as $LD_{50}$s in units of mg of chemical per kg of body weight. This is the single oral dose which was lethal for 50% of the test species. Orange herbicide $LD_{50}$: rat 566, sheep 250 and cattle 250. The oral toxicities of 2,4-D and 2,4,5-T are quite similar to those of Orange herbicide (e.g., the acute oral $LD_{50}$ of 2,4-D and 2,4,5-T in the rat are 620 and 480 mg/kg, respectively). Tables II-5 and II-6 summarize the results of several acute toxicity studies with various salt, ester and amine forms of 2,4-D and 2,4,5-T.

(4) Chronic Toxicity: Because of the active secretion of chlorophenoxy herbicides, rather large amounts must be administered over a long period of time to produce symptoms of toxicity. Enormous amounts of Orange herbicide were applied to test plots at Eglin AFB without visible toxic effects or development of herbicide residues in the native animals in the test plots (Young, 1973). In one study, (Palmer and Radeleff, 1964) sheep were given 2 gm of the acid daily and sacrificed on the day following the final dose. Residues in the tissues were less than 1 ppm in all tissues and usually less than 0.05 ppm, which was the sensitivity of the analytical method. Mitchell and co-workers (1946) pastured sheep and cattle on treated foliage without harmful effects to the animals. They also fed a lactating cow 5.5 gm of 2,4-D daily for 106 days without producing poisoning. Palmer (1963) found that cattle were not harmed by 112 daily doses (administered 5 days each week) of 5 mg/kg of alkanolamine salt and that 44 daily doses of 200 mg/kg or 20 doses of 250 mg/kg were

TABLE II-5

ACUTE TOXICITY OF 2,4-D DERIVATIVES TO TERRESTRIAL ANIMALS

| DERIVATIVE | ANIMAL | DOSE | EFFECT | REFERENCE |
|---|---|---|---|---|
| Alkanolamine | Chick | 380-765 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Isopropyl ester | Rat | 700 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Isopropyl ester | Chicks | 1420 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Isopropyl ester | Guinea pig | 550 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Butyl ester | Rat | 620 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Butyl ester | Guinea pig | 848 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Butyl ester | Chicks | 2000 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| PGBE | Rat | 570 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Acid | Dog | 100 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Acid | Chick | 541 mg/kg | $LD_{50}$ | Rowe, et al. (1954) |
| Triethanolamine | Swine | 50 mg/kg | No effect | Bjorklund & Erne (1966) |
| Triethanolamine | Swine | 500 mg/kg | Lethal | Bjorklund & Erne (1966) |
| Butyl ester | Swine | 100 mg/kg | No effect | Bjorklund & Erne (1966) |
| Triethanolamine | Chicken | 300 mg/kg | No effect | Bjorklund & Erne (1966) |
| Butyl ester | Rat | 620 mg/kg | $LD_{50}$ | Edson et al. (1964) |
| Isopropyl ester | Rat | 700 mg/kg | $LD_{50}$ | Hayes, (1963) |
| Unspecified amine | Mallard duck | 2000 mg/kg | $LD_{50}$ | Tucker & Crabtree (1970) |
| Acid | Pheasant | 472 mg/kg | $LD_{50}$ | Tucker & Crabtree (1970) |
| Acid | Mule deer | 400-800 mg/kg | $LD_{50}$ | Tucker & Crabtree (1970) |

TABLE II-6

ACUTE TOXICITY OF 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS

| DERIVATIVE | ANIMAL | DOSE | EFFECT | REFERENCE |
|---|---|---|---|---|
| Acid | Rat | 500 mg/kg | $LD_{50}$ | Rowe & Hymas (1954) |
| Isopropyl ester | Mice | 551 mg/kg | $LD_{50}$ | Rowe & Hymas (1954) |
| Butyl ester | Mice | 940 mg/kg | $LD_{50}$ | Rowe & Hymas (1954) |
| Amyl ester | Rat | 750 mg/kg | $LD_{50}$ | Rowe & Hymas (1954) |

required to produce fatal poisoning. Palmer and Radeleff (1964) reported that sheep were given 481 daily doses of 100 mg/kg doses of 2,4-D without producing poisoning. 2,4,5-T has not been investigated as thoroughly as 2,4-D, but the reaction of cattle and sheep to massive doses would indicate that absorption and excretion must follow a similar pattern. A study by Palmer and Radeleff (1964) showed that sheep required 369 doses of 100 mg/kg each to induce intoxication. The above results are summarized in Table II-7.

b. Behavior in Humans: Gehring et al., (1973) studied the effects of 2,4,5-T at a dose level of 5 mg/kg ingested directly or in a slurry of milk. Analytical grade 2,4,5-T having a purity of greater than 99% and containing less than the detectable level 0.05 ppm, of TCDD was used. Complete medical histories, physical and laboratory studies were accomplished before and repeated after the study. It was found that the clearances of 2,4,5-T and the excretion from the body were by first-order rate processes with half-lives of 23.10 and 23.06 hours, respectively. Essentially all of the ingested 2,4,5-T was absorbed into the body and was excreted unchanged in the urine. Following ingestion, 65% of the 2,4,5-T remained in the plasma where 98% was reversibly bound to the plasma proteins. "No untoward effects associated with the ingestion of 5 mg/kg 2,4,5-T were detected in any of the subjects." (Gehring et al., 1973) A metallic taste lasting 1-2 hours following ingestion was reported by most of the subjects. It was also concluded that essentially all of the ingested 2,4,5-T was absorbed and then eliminated unchanged in the urine.

c. Behavior in Aquatic Systems and Aquatic Animals

(1) Metabolism and Distribution

(a) General Comparisons: The behavior of the chlorophenoxy herbicides in non-mammalian aquatic animals is quite different than the behavior described for terrestrial mammals and birds. The herbicides have a greater toxic potential for aquatic animals. First, the route of entry is different in most instances. The aquatic animal absorbs the herbicide which is distributed throughout his total environment (absorption is mainly via gills in fish). Then, the differences in renal function must be considered. Generally, non-mammalian aquatic animals do not have highly developed kidneys. Thus, once the herbicide is in the aquatic animal's body, some metabolic changes must occur in the molecule to make it more polar if it is to be excreted. Toxicity testing is also necessarily different with aquatic animals. Usually, aquatic animals are placed in a concentration of the toxicant to gradually absorb the material at a rate depending on the animal's physiology and the behavior of the toxicant in the particular water conditions. Therefore, the actual dose to each animal is not known in most studies with aquatic animals. In contrast, toxicity studies with terrestrial animals usually allow calculation of a known dose per unit weight of each animal. Thus, toxicities are often reported as "$LD_{XX}$" (Lethal Dose) for terrestrial animals and "$LC_{XX}$" (Lethal Concentration) for aquatic animals.

(b) Metabolism in Fish: Donald P. Schultz (Fish-Pesticide Research Laboratory, Bureau of Sport Fisheries and Wildlife, 1973) studied the uptake, distribution, and dissipation of $^{14}$C-label dimethyl amine salt of 2,4-D (DMA-2,4-D). Three species of fish were exposed to 0.5, 1.0 or 2.0 mg/l concentrations of herbicide for up to 84 days exposure period. No mortalities

TABLE II-7*

CHRONIC TOXICITY OF 2,4-D AND 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS

Chronic Toxicity of 2,4-D

| DERIVATIVE | ANIMAL | DOSE | DURATION | EFFECT | REFERENCE |
|---|---|---|---|---|---|
| Triethanolamine | Swine | 50/mg/kg/day | 3 doses | None | Bjorklund & Erne (1966) |
| Triethanolamine | Swine | 50/mg/kg/day | 8-10 doses | Minor transient effects | Bjorklund & Erne (1966) |
| Butyl ester | Swine | 50/mg/kg/day | <5 doses | None | Bjorklund & Erne (1966) |
| Triethanolamine | Swine | 500 ppm in feed. | 1 month | Some locomotory disturbance, depressed growth rate, no gross pathology | Bjorklund & Erne (1966) |
| Triethanolamine | Rats | 1000 ppm in water | 10 mos. | Depressed growth rate, no gross pathology | Bjorklund & Erne (1966) |
| Triethanolamine | Chicken | 1000 ppm in water | Daily from hatching through first 2 mos. of egg production | Egg size normal, production reduced 30% | Bjorklund & Erne (1966) |
| Alkanolamine | Sheep | 100/mg/kg/day | 481 days | No effect | Palmer & Radeleff (1964) |
| Alkanolamine | Cattle | 50/mg/kg/day | 112 days | No effect | Palmer & Radeleff (1964) |
| PGBE ester | Sheep | 100/mg/kg/day | 481 days | No effect | Palmer & Radeleff (1964) |
| Ethylhexyl ester | Cattle | 250/mg/kg/day | 14 days | Ill in 3 days, survive & recover from 9 doses. 14 doses lethal. | Hunt, et al. (1970) |
| Ethylhexyl ester | Sheep | 250/mg/kg/day | 17 days | Ill in 3 days, 17 doses lethal | Hunt, et al. (1970) |

TABLE II-7 (Continued). "Chronic Toxicity"

| DERIVATIVE | ANIMAL | DOSE | DURATION | EFFECT | REFERENCE |
|---|---|---|---|---|---|
| Ethylhexyl ester | Sheep & Cattle | 100/mg/kg/day | 10 days | None to minor effects | Hunt, et al. (1970) |
| Not specified | Dog | 500 ppm in feed | 2 years | None | House et al. (1967) |
| Not specified | Rat | 1250 ppm in feed | 2 years | No effects on growth, survival hermatology or tumor incidence | House, et al. (1967) |
| Not specified | Rat | 500 ppm in feed | 2 years | No effects in reproduction studies | House, et al. (1967) |
| Alkanolamine | Chicken | 100 mg/kg/day | 10 days | No effect on weight gain | Palmer & Radeleff (1969) |
| PGBE ester | Chicken | 50 mg/kg/day | 10 days | No effect on weight gain | Palmer & Radeleff (1969) |
| PGBE ester | Cattle | 100 mg/kg/day | 10 days | No effect | Palmer & Radeleff (1969) |
| Acid | Mule deer | 80 and 240 mg/kg/day | 30 days | Minor symptoms no weight loss | Tucker and Crabtree (1970) |

Chronic Toxicity of 2,4,5-T

| FORMULATION | ORGANISM | DOSE | DURATION | EFFECT | REFERENCE |
|---|---|---|---|---|---|
| Not specified | Dog | 10 mg/kg/day | 5 days per wk. for 90 days | Minor weight loss, no other effects | Drill & Hiratzka (1953) |
| Not specified | Dog | 20 mg/kg/day | 5 days per wk. for 90 days | Lethal between 11 and 75 days | Drill & Hiratzka (1953) |
| PGBE ester | Cattle | 100 mg/kg/day | 10 days | None | Palmer & Radeleff (1969) |
| PGBE ester | Sheep | 50 mg/kg/day | 10 days | None | Palmer & Radeleff (1969) |

TABLE II-7 (Continued). "Chronic Toxicity of 2,4,5-T"

| FORMULATION | ORGANISM | DOSE | DURATION | EFFECT | REFERENCE |
|---|---|---|---|---|---|
| PGBE ester | Sheep | 100 mg/kg/day | 369 days | (dosed by capsule) Ill at 367 doses, lethal at 369 | Palmer & Radeleff (1969) |
| PGBE ester | Chicken | 100 mg/kg/day | 10 days | No effect on weight gain | Palmer & Radeleff (1969) |
| Triethylamine | Sheep | 100 mg/kg/day | 481 days | No effect | Palmer & Radeleff (1964) |
| Not specified | Mice | 21 mg/kg/day 600 ppm in diet. | 4 weeks 18 months | No mortality | Innes, et al. (1969) |

* From Oregon E.I.S. (EIS-OR, 1973)

occurred, nor were adverse biological effects observed at these exposure levels. The highest radioactive residue found in muscle tissue occurred in Bluegills exposed to 2.0 mg/l for 84 days (1.065 mg/kg). However, gas-liquid chromatography indicated that over 90% of the radioactive residues consisted of metabolites of 2,4-D. The major metabolite in the fish was found to be 2,4-D glucuronic acid conjugate. Current investigations have found at least six metabolites of 2,4-D in fish. Thus, in contrast to many of the organochlorine pesticides which undergo biomagnification through the food chain, DMA-2,4-D is metabolized in fish without accumulation of the parent compound.

(2) Behavior in Aquatic Systems

(a) Solubility Limits and Rates Vs. Hydrolysis Rates: The esters of 2,4-D or 2,4,5-T found in Orange herbicide have a very limited solubility in water. Because of this very low solubility, the actual concentrations of esters produced in a body of water by accidental contamination would likely be much less than the "expected value" calculated from the volumes involved. The USAF EHL(K) is in the process of studying the behavior of Orange herbicide in aquatic systems especially sea water. In one study using artificial sea water*, Orange herbicide was mixed into the water in an amount equal to 150 mg/l. Had all components gone right into solution, by computation, ester concentrations would have been 64 mg/l (2,4-D NBE) and 61 mg/l (2,4,5-T NBE). The actual, measured concentrations were 2 mg/l (2,4-D NBE) and 1.8 mg/l (2,4,5-T NBE) immediately after mixing. These increased to 18 and 22 mg/l of 2,4-D NBE and 2,4,5-T NBE, respectively, at 24 hours and then started a rapid decline to 7.5 and 9.5 mg/l at 48 hours after mixing. The rate of disappearance of the ester of 2,4-D was fairly rapid and was assumed to be mainly a result of hydrolysis. The half-life of the ester was 15 hours. The addition of natural biota such as bacteria, algae and fish would be expected to produce an even faster disappearance of 2,4-D NBE. Evidence that this occurs was observed in studies EHL(K) is conducting with marine animals at the National Marine Fisheries Laboratory in Port Aransas, Texas. In one of these studies, shrimp were exposed in five different concentrations of 2,4-D NBE and natural sea water. The average half-life of the ester in the five concentrations was 5 hours. This was 1/3 of the half-life observed in the situation where no biological systems existed.

(b) Circulation of Water in Relation to Availability of Herbicide for Absorption: Some of the toxicity studies completed so far indicate the complexity of trying to predict the ecological results of a planned or accidental contamination of a body of water with phenoxy herbicides. At EHL(K), Orange herbicide was mixed in a fish tank at a concentration that would theoretically produce a 200 $ppm_{v/v}$ concentration if such a high concentration were possible. Most of the herbicide rapidly sank to the bottom of the tank after mixing. Fathead minnows placed in the tank showed no ill effects during two weeks of exposure. Yet in a toxicity study under the same conditions but with continuous agitation of the water by aeration, all of the fish died in a "20 ppm concentration" of Orange herbicide water in 24 hours. Subsequent studies revealed that some circulation of the

*Instant Ocean Aquarium Systems, Inc., East Lake, Ohio

water was essential if a dose-related response was to be established in toxicity studies with the N-butyl esters of 2,4-D and 2,4,5-T. Thus, the actual effect seen in nature might well depend on a factor such as the degree of mixing in the affected body of water.

(c) Importance of Hydrolysis: It is important that when the esters of 2,4-D and 2,4,5-T hydrolyze, their toxicity to aquatic animals is decreased by almost a factor of 10 (paragraph (3)(b) below). In the static situation described in the paragraph above (no aeration), the rate of hydrolysis was probably faster than the rate that the ester went into solution so that lethal concentrations were never attained. Toxicity studies with freshwater and saltwater animals at EHL(K) have been the so-called "Static Bioassay" in which no attempt is made to maintain a constant concentration of the herbicide ester in each test chamber. "Concentrations" are theoretical and based on volumes of herbicide and water mixed together rather than from analysis of water to quantitate the herbicide. Most studies reported from literature are of the same type. The toxicity tests at EHL(K) revealed that in both freshwater and saltwater, most of the test organisms had responded at twelve hours of exposure. There was rarely any increase in mortality past 24 hours.

(d) Other Factors Affecting Actual Concentration: Many other factors can influence the concentration of N-butyl esters of 2,4-D and 2,4,5-T in a body of water. In studies where large amounts of Orange herbicide were placed in water, the globules of the herbicide appeared to become coated with an opaque material that may have inhibited the ester from going into solution. Cope (1970) treated ponds with 0.5 ppm to 10 ppm propylene glycol butyl ether ester (PGBE) of 2,4-D. He was able to measure residues of herbicide absorbed or adsorbed in vegetation and bottom sediment for 6 weeks after treatment in the 10 ppm treated pond. Crosby (1966) reported that 2,4-D decomposes rapidly in the presence of water and ultraviolet light.

(3) Toxicity

(a) Factors Affecting Toxicity: The toxicity of the chlorophenoxy herbicides to aquatic animals varies considerably with many factors such as water chemistry variables, temperature, and the particular salt, ester or amine form of the herbicide considered. Species susceptibility varies greatly. For example, the 96-hour $TL_{50}$* for fathead minnows exposed to DMA-2,4-D was found to be 335 mg/l. Yet, for bluegills and channel catfish the $TL_{50}$ values were 177 and 193 respectively. A temperature increase from 17°C to 20°C increased the relative toxicity to the catfish from a $TL_{50}$ of 193 mg/l to 125 mg/l (Schultz, 1973).

(b) Toxicity Comparisons by EHL(K): The USAF EHL(K) (1974), performed static toxicity studies with Orange herbicide. Also, toxicity studies were performed using each individual N-butyl ester of 2,4-D and 2,4,5-T. Freshwater bioassays using the fathead minnow (Pimephales promelas) resulted in a 48 hr $LC_{50}$ of 3.4 ppm for Orange herbicide containing 14 ppm TCDD. The 48 hr $LC_{50}$s for esters of 2,4-D and 2,4,5-T were 2.8 ppm and 5 ppm respectively. The 48 hr $LC_{50}$ for 2,4-D in the minnows was 270 ppm. The 2,4,5-T 48 hr $LC_{50}$ concentration was 333 ppm. Note that the toxicity of ester formulations were considerably more toxic than the respective acid. Also, EHL(K) found the N-butyl ester of 2,4-D to be more toxic that the N-butyl ester of 2,4,5-T.

*See page 47 for explanation of TD and LC

In salt water studies by EHL(K), the 48 hr $LC_{50}$ values in the shrimp (Penaeus sp.) were 5.6 ppm for 2,4-D NBE and 33 ppm for 2,4,5-T NBE. Oysters (Crassostrea virginica) were exposed to "potential concentrations" of 2,4-D NBE ranging from 0.5 ppm to 85 ppm. The only acute effect observed was the death of one of the oyster (10%) in the highest concentration at 48 hours.

(c) Other Animals and Other Effects: Many other aquatic animals besides fish can be affected by phenoxy herbicides. Saunders (1971) studied the effects of the propylene glycol butyl ether ester (PGBE) of 2,4-D on six freshwater crustaceans. He found the following 48 hr $TL_{50}$ values: Daphnia magna = 0.10 ppm, seed shrimp = 0.32 ppm, scud = 2.6 ppm, sowbug = 2.2 ppm, glass shrimp = 2.7 ppm, and crayfish had an unknown value larger than 100 ppm. Cope (1970) studied the chronic effects of PGBE ester of 2,4-D on the bluegills. Survivors of ponds treated with high concentrations (10 and 5 ppm) had a 2 week delay in spawning. For pathologic lesions, high-treatment fish had earlier and more severe effects than did low-treatment fish. The pathology involved the liver, vascular system and brain. Remarkably, growth of the fish was faster in the ponds receiving the high-treatment than in the lower-treatment ponds. Tables II-8 and II-9 were extracted from a U.S. Forest Service Environmental Impact Statement (EIS-OR, 1973). The tables indicate the effects of herbicides on other aquatic species and point out some toxic effects that can be measured other than death of the organisms.

d. Behavior in Plants

(1) Distribution and Metabolism: Orange herbicide is a systematic herbicide that affects plants by a hormonal type of action usually described as "auxin-like" or "auxin-type". Auxins are any of a group of substances which promote plant growth by cell elongation, bring about root formation, or cause bud inhibition or other effects. 2,4-D and 2,4,5-T are compounds of this type. When applied to leaves of a plant, chlorophenoxy herbicides are absorbed through the cuticle into the plant system. The N-butyl ester forms of 2,4-D and 2,4,5-T found in Orange herbicide are usually more effective than more polar forms because of better absorption into the plant. This is also demonstrated in Yamaguchi's work (1965) in which he found that 2,4-D moves into plant leaves better from acidic solutions than from alkaline solutions. Approximately ten times as much 2,4-D was abosorbed from a medium having pH 3 than one with pH 11. 2,4-D has a $pK_a$ of 2.8 and would be highly disassociated at pH 11. Once the herbicide is in the plant it is translocated to areas where food is being stored as in rapidly growing new roots and shoots. The chlorophenoxy herbicides can be stored in certain cells of the plant. Also, metabolism occurs through degradation of the acetic acid side chain, hydroxylation of the aromatic ring, or conjugation.

*$TL_{50}$ and $LC_{50}$ (Tolerance Limit and Lethal Concentration) are concentration values statistically derived from the establishment of a dose-related response of experimental organisms to a toxicant. The LC is based on a measured response of death only. The TL is based on a count of unaffected organisms. The subscript number for both indicates the percent response expected for the calculated concentration. Therefore, in most cases, the $TL_{50} = LC_{50}$ or the concentration in which 50% death is expected. Note that a more toxic chemical has a smaller $LC_{50}$.

TABLE II-8

ACUTE EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

| DERIVATIVE | ANIMAL | CONCENTRATION | EFFECT | REFERENCE |
|---|---|---|---|---|
| Isooctyl esters (From 3 manufacturers) | Bluegill | 10-31 ppm | 48 TLm | Hughes & Davis (1963) |
| PGBE ester | Bluegill | 17 ppm | 48 TLm | Hughes & Davis (1963) |
| Butoxyethanol ester | Bluegill | 1.4 ppm | 48 TLm | Hughes & Davis (1963) |
| PGBE ester | Shrimp | 1 ppm (48 hrs) | 20% mortality or paralysis | Butler (1965) |
| PGBE ester | Fish (salt water) | 0.32 ppm | 48 hr TLm | Butler (1965) |
| Alkanolamine Salt | Bluegill | 435-840 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Dimethylamine Salt | Bluegill | 166-458 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Isooctyl ester | Bluegill | 8.8-59.7 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Dimethylamine Salt | Fathead Minnow | 10 ppm | 96 hr $LC_{50}$ | Lawrence (1966) |
| Acetamide | Fathead Minnow | 5 ppm | 96 hr $LC_{50}$ | Lawrence (1966) |
| Oil soluble amine salt | Bluegill, Fathead Minnow | 2 ppm | 4 mo. $LC_{10}$ | Lawrence (1966) |
| PGBE Ester* | Bluegill, Fathead Minnow | 2 ppm | 4 mo. $LC_{10}$ | Lawrence (1966) |
| Butoxyethyl ester | Bluegill & Fathead | 2 ppm | 72 hr $LC_{50}$ | Lawrence (1966) |
| Butyl and isopropyl esters, mixed | Bluegill | 1.5 - 1.7 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| N,N-Dimethyl coco-amine salt | Bluegill | 1.5 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Ethyl ester | Bluegill | 1.4 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Butyl Ester | Bluegill | 1.3 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Isopropyl ester | Bluegill | 1.1 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |

*Propylene Glycol Butyl Ether

TABLE II-9

NON-LETHAL EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

| DERIVATIVE | ANIMAL | DOSE | EFFECT | REFERENCE |
|---|---|---|---|---|
| Butoxyethanol ester | Oyster | 3.75 ppm (96 hrs) | 50% decrease in shell growth | Butler (1965) |
| Butoxyethanol ester | Shrimp | 1 ppm (48 hrs) | No effect | Butler (1965) |
| Butoxyethanol ester | Fish (salt water) | 5 ppm | 48 hr. TLm | Butler (1965) |
| Butoxyethanol ester | Phyto-plankton | 1 ppm | 16% decrease in $CO_2$ fixation | Butler (1965) |
| Dimethylamine | Oyster | 2 ppm (96 hrs) | No effect on shell growth | Butler (1965) |
| Dimethylamine | Shrimp | 2 ppm (48 hrs) | 10% mortality or paralysis | Butler (1965) |
| Dimethylamine | Fish (salt water) | 15 ppm (48 hrs) | No effect | Butler (1965) |
| Dimethylamine | Phyto-plankton | 1 ppm (4 hrs) | No effect on $CO_2$ fixation | Butler (1965) |
| Ethylhexyl ester | Oyster | 5 ppm (96 hrs) | 38% decrease in shell growth | Butler (1965) |
| Ethylhexyl ester | Shrimp | 2 ppm (48 hrs) | 10% mortality or paralysis | Butler (1965) |
| Ethylhexyl ester | Fish (salt water) | 10 ppm (48 hrs) | No effect | Butler (1965) |
| Ethylhexyl ester | Phyto-plankton | 1 ppm (4 hrs) | 49% decrease in $CO_2$ fixation | Butler (1965) |
| PGBE 1/ ester | Oyster | 1 ppm (96 hrs) | 39% decrease in shell growth | Butler (1965) |
| PGBE 1/ ester | Shrimp | 1 ppm (48 hrs) | No Effect | Butler (1965) |
| PGBE 1/ ester | Fish (salt water) | 4.5 ppm | 48 hr TLm | Butler (1965) |

1/ PGBE is propylene glycol butyl ether.

(2) Toxicity: Once in the plant, herbicides act by interfering with the photosynthetic, respiratory, and other plant processes causing the plant to lose its leaves and ultimately die. Plant susceptibility to sub-lethal exposures of 2,4-D is markedly influenced by the growth condition of the plant and by environmental factors. Since most of the injury is expressed by growth response, the plant must be growing in order to show injury. In addition, plants in shaded areas respond more slowly than those exposed to direct sunlight. Because of these various factors which affect plant response to the 2,4-D type herbicide, differences in lists showing plant susceptibility should be expected. Orange herbicide is effective on a wide variety of woody and broadleaf plant species. Other lower plant forms can also be affected by auxin-type herbicides. Even unicellular algae exhibit toxic effects or die when exposed to 2,4-D or 2,4,5-T (Walsh, 1972). However, much higher doses of the herbicides are required than for plants with a more complex structure.

(3) Herbicides as Air Pollutants: Although herbicides have long been accepted as environmental pollutants which affect sensitive vegetation, the air pollution aspects of volatile herbicides have not been widely explored. However, there is growing evidence that some 2,4-D compounds may be present in the ambient atmosphere in some parts of the United States at levels sufficient to cause adverse growth effects on sensitive vegetation. During 1962 through 1964, Vernetti and Freed measured 2,4-D concentrations in air samples taken in an agricultural area of eastern Oregon. Concurrently, they surveyed for auxin-like plant damage in the areas where the air samples were taken. In the spring of 1962, measured concentrations of the isopropyl ester of 2,4-D in the air ranged from 0.015 ppm to 0.64 ppm. This was during the time of year when the huge wheat fields of the area were being treated for weeds by aerial application of the isopropyl ester. Plant damage to tomato crops appeared to coincide with periods of highest measured concentrations of the isopropyl ester. Other plants, especially locust trees, also showed growth regulator symptoms. Legislation in the state curtailed the use of the isopropyl ester and decidedly reduced the contamination and resulting plant damage. Laboratory studies by Vernetti and Freed indicated that 0.015 ppm would be the threshold concentration of isopropyl ester that tomato plants could be exposed to and still survive under the conditions of the experiment. Volatility studies by the same workers demonstrated that the isopropyl ester was three times more volatile than the butyl ester. In fact, complex analyses of the air samples ruled out butyl and other esters of 2,4-D as principal contaminants.

(4) Relative Species Sensitivity: Different researchers vary in their results of relative plant sensitivity to phenoxy herbicides. From field observations, grapevines and box elder appear to be among the most sensitive since they respond to 2,4-D air pollution when other plants showed no evidence of injury. Injury to grapevines may result from exposure to levels in the ppb range. Other workers report tomato plant damage in the ppt range. Walsh (1972) reports a 50% reduction in growth of unicellular marine algae exposed to phenoxy herbicide concentrations of 50 to 300 ppm. Other relative sensitivities are indicated in Table II-10.

TABLE II-10. Sensitivity of selected plants to 2,4-dichlorophenoxyacetic acid*

**Sensitive**

Apple
*Malus*, sp.
Birch
*Betula*, sp.
Boxelder
*Acer negundo*, L.
Dogwood
*Cornus*, sp.
Elderberry
*Sambucus*, sp.
Forsythia
*Forsythia*, sp.
Grape
*Vitis*, sp.
Hickory
*Carya*, sp.
Lambs-quarters
*Chenopodium album*, L.
Linden
*Tilia*, sp.
London plane tree
*Platanus acerifolia* (Ait.) Willd.
Maple, Norway
*Acer platanoides*, L.
Oak, black
*Quercus velutina*, Lam.
Sorrell
*Rumex*, sp.
Sumac
*Rhus*, sp.
Tobacco
*Nicotiana*, sp.
Tomato
*Lycopersicon esculentum*, Mill.
Treeofheaven
*Ailanthus altissima*, Mill.
Wisteria
*Wisteria*, sp.
Yellow wood
*Cladrastis lutea*, Koch
Zinnia
*Zinnia*, sp.

**Intermediate**

Aster, wild
*Aster*, sp.
Cedar
Cherry
*Prunus*, sp.
Cherry, choke
*Prunus virginiana*, L.
Corn
*Zea mays*, L.
Gladiolus
*Gladiolus*, sp.
Hemlock
*Tsuga*, sp.
Mulberry
*Morus*, sp.
Oak, pin
*Quercus palustris*, L.
Oak, red
*Quercus palustris*, L.
Peach
*Prunus persica*, Sieb. & Zucc.
Potato
*Solanum tuberosum*, L.
Privet
*Ligustrum*, sp.
Ragweed, giant
*Ambrosia trifida*, L.
Rhododendron
*Rhododendron*, sp.
Rose
*Rosa*, sp.
Spruce, Colorado blue
*Picea pungens*, Englm.
Sweetgum
*Liquidambar styraciflua*, L.
Yew
*Taxus*, sp.

**Resistant**

Ash
*Fraxinus*, sp.
Bean, bush
*Phaseolus vulgaris*, L.
Cabbage
*Brassica oleracea*, L.
Eggplant
*Solanum melongena*, L.
Pear
*Pyrus communis*, L.
Peony
*Paeonia*, sp.
Rhubarb
*Rheum rhaponticum*, L.
Sorghum
*Sorghum vulgare*, Pers.

* FROM AIR POLLUTION CONTROL ASSOCIATION REPORT NO. 1

5. TOXICOLOGICAL CHARACTERISTICS OF TCDD: The word teratology has rather recently become quite familiar to biologists, chemists and certain other persons working in various scientific disciplines. It was applied to 2,4,5-T when studies by Bionetics Research Laboratory, Division of Litton Industries, Bethseda MD in 1969-70 implied that 2,4,5-T was teratogenic in mice and rats (Courtney et al., 1970). Subsequently, studies revealed that a toxic contaminant was responsible for the findings originally attributed to 2,4,5-T. The sample of 2,4,5-T employed in the Bionetics study contained 27 ±8 ppm TCDD. Some studies have shown that oral administration of 2,4,5-T containing < 1 ppm TCDD produces no teratogenic effects on rats, rabbits, mice and other species.

a. Toxicity to Animals: TCDD was found to be the most toxic chlorodibenzo-*p*-dioxin studied. It was found to have $LD_{50}$s in the µg/kg range for several species of animals and was acnegenic, highly embryotoxic and positive for the chick edema factor. "The no-effect dose levels for embryotoxicity and chick edema were 0.03 to 0.1µg/kg/day respectively" (Schwetz et al., 1973).

(1) Acute Toxicity: Studies performed on TCDD by the Biochemical Research Laboratory, Dow Chemical Co., can be summarized as follows with the data presented as the $LD_{50}$ in µg/kg of body weight for several species: rats 20-40; mice, males >64, females 130; guinea pig 0.6-2.0; rabbits ≈30; dogs >30 (Rowe et al., n.d.). The signs of intoxication are characterized by a chronic illness and liver damage. Half of the deaths occur more than two weeks after treatment while some animals died after 48 hours. Excretion is primarily by way of feces and is very slow. The highest concentrations are found in the liver and fat with a smaller amount being found in the testes. The $LD_{50}$ for the rabbit is about the same whether administered intraperitoneally or applied to the skin. In the eye it does not cause corneal injury but does produce thickening of the lids. It does cause severe chloracne when applied to the ears of rabbits in µg quantities.

(2) Toxic Effects on the Fetus

(a) Hamsters: Commercial samples of 2,4,5-T were shown by Collins and Williams (1971) to be feticidal and teratogenic in the golden Syrian hamster. Dose levels of 2,4,5-T ranged from 20 to 100 mg/kg/day while TCDD content varied from 0.1 to 45 ppm. Doses of 100 mg/kg/day of 2,4,5-T approach levels causing maternal mortality.

(b) Rats: TCDD is highly embryotoxic in the rat. No effect was seen at a dose level of 0.03 µg/kg/day but at the 0.125 µg/kg/day dose level there was a significant incidence of fetuses with intestinal hemorrhage; fetal deaths and resorptions increased. Delayed skeletal maturation was seen. At 2 µg/kg/day there were few viable fetuses and the survivors had a high incidence of anomalies. At 8 µg/kg/day there was severe maternal toxicity and there were no viable fetuses. King et al. (1971) studied the effect of 2,4,5-T and 2,4-D administered by gavage and an intrauterine technique using Sprague-Dawley rats as the test species. "Purified" and "technical" grade 2,4,5-T were applied to Millipore® filters that were then placed on the amniotic sac of the embryo. "Purified" 2,4,5-T intrauterinely applied to 93 embryos on any one day of gestation from day 12 to 16 at a dose range of 50 to 120 µg per embryo resulted in no cleft palates. Substituting the

technical for purified grade and using the same technique on 118 embryos resulted in two cleft palates. Oral administration of 2,4-D and 2,4,5-T at a total dose range of 60 to 120 mg/kg to 245 rats yielded 2,231 fetuses, nine of which had cleft palates. Again, these are high dose levels.

b. Industrial Exposure: Dow Chemical Co. prepared an extensive health inventory of 126 manufacturing personnel in an effort to identify harmful effects of inhaled 2,4,5-T. The inhalation rate of the agent was estimated to be from 1.6 to 8.1 mg/day/worker, depending on work assignment, for periods of up to three years. The survey indicates that no illness was associated with 2,4,5-T intake. In plants where 2,4,5-T contained a high proportion of TCDD, Bleiberg et al. (1964) found 18% of the exposed employees suffered from moderate to severe chloracne, the intensity of which correlated significantly with the presence of hyperpigmentation, hirsutism and eye irritation. In the late 1940's a pressure overload resulted in the accidental rupture of a vessel containing the sodium salt of 2,4,5-trichlorophenol, a precursor of 2,4,5-T. During the following months, 228 persons developed chloracne, not only plant employees, but members of their families including wives and children. In workers more intensively exposed as a result of the accident, chloracne appeared about two weeks followed by moderate to severe pain in the skeletal muscles of the legs, arms, back and breath, decreased libido and intolerance to cold. Comedones appeared in areas of adult hair which is not typical of juvenile acne. There were pustules on the face, neck, abdomen, back and scrotum. Serum lipids, prothrombin time and glucuronates were all elevated. Biopsy of peripheral nerves revealed destruction of myelin sheaths and in some instances nerve fibers. Hyperpigmentation, fatigue and marked nervous irritability appeared. Over a period of several months, all of the symptoms and findings, except the scars of acne, returned to normal after removal from exposure. Cases in the families of the workers probably resulted from contaminated clothing and poor personal hygiene. The causative agent was not identified at the time. However, in the light of current knowledge, it was almost certainly a polychlorinated dibenzodioxin and possibly TCDD (Suskind, 1973).

c. Evaluation of Toxicological Testing

(1) Requirement for Establishing Dose-Related Response: Insistence on administering a "maximum tolerated dose" may be terribly misleading if this is the only dose tested, as in the Bionetics study (Innes, et al., 1969). There is no justification for abrogating the need to establish a dose-response relationship, which is fundamental to all toxicological experimentation. The route of administration is all important in tests for teratogenesis. We are told that "Parenteral administration is an appropriate test route for pesticides to which humans are exposed by inhalation, or for pesticides which are systemically absorbed, following ingestion" (USDHEW, 1969). It is safe to predict that, by appropriate choice of dose, concentration of solution and frequency of administration by subcutaneous route, any chemical agent can be shown to be a carcinogen or a teratogen in the rat and probably in other laboratory rodents (Goldberg, 1971).

(2) Bionetics Study: The Bionetics study began with the observation that 2,4,5-T was teratogenic and feticidal in two strains of mice when administered either subcutaneously or orally and in one strain of rats when administered orally (Courtney et al., 1970). Analyses of the sample of 2,4,5-T that had been tested against the animals revealed the presence of 27 ±8 ppm TCDD. Subsequent study of standard 2,4,5-T containing less than 1 ppm TCDD given to rats by gavage in doses up to 24 mg/kg daily, failed to reveal evidence of teratogenic or embryotoxic effects (Emerson et al., 1970). Under similar conditions, TCDD produced no effect at a dose of 0.03 µg/kg/day while doses of 0.125 µg/kg/day or greater manifested toxicity to the fetus and at 8.0 µg/kg/day to the mother also (Sparschu et al., 1970).

(3) Evaluating Data from Animal Models: The metabolism of a test compound is a highly relevant consideration in teratogenesis. If the metabolic pathway in the test animal differs radically from that in man, then the results of a study are unlikely to be useful for the assessment of hazards arising from trace contaminants. The findings of teratogenesis or embryotoxicity has meaning only in the appropriate animal species (Goldberg, 1971). Theodor D. Sterling (1971) of the Department of Applied Mathematics and Computer Science, Washington University, St Louis, examined the difficulty of evaluating the toxicity and teratogenicity of 2,4,5-T from existing animal data. He notes that the question has been raised as to whether the herbicide 2,4,5-T is toxic and teratogenic to an extent to preclude its use, in this country at least. Sterling states, "Although we can learn a great deal from animal experiments, toxicological and teratological information from animal experiments turns out to be much less useful, especially for making broad policy decisions, than is commonly thought."

(4) Design of Recent 2,4,5-T Toxicity Studies: To quote Sterling (1971) again, "...there are less than a dozen key reports...of study on toxicity of 2,4,5-T, dating back to the early 1950's for the most part, and on its teratogenicity, mostly done in the last two years. Whereas the toxicity studies were done at some leisure and the teratogenicity studies had some aspect of emergency about them, they are indistinguishable in their lack of adequate statistical experimental design and analysis of data."

6. EVALUATION OF ENVIRONMENTAL CONTAMINATION POSSIBILITY: The possibility that an extraordinarily toxic contaminant of a widely used herbicide may be sufficiently stable in the environment and soluble in fat or other tissues to enter food chains and ultimately the human diet is worthy of consideration. It was known, of course, that 2,4,5-T does not accumulate to any significant degree in animal tissues, but data on tissue storage of dioxin were not available. Chlorinated dibenzo-*p*-dioxins long have been recognized as by-products from the manufacture of certain chlorinated phenols. For example, 2,4,5-trichlorophenol is prepared industrially by the hydrolysis of 1,2,4,5-tetrachlorobenzene at elevated temperatures and pressures, a process which can also result in the formation of traces of heterocyclic impurities including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin if temperatures are permitted to exceed 160°C and if the reaction becomes alkaline. This dioxin is toxic, teratogenic and acnegenic and its presence appears to account satisfactorily for the alleged teratogenic effects of trichlorophenol derivatives such as the herbicide 2,4,5-T.

a. Knowledge Available From Use: No proven instance of toxicity associated with 2,4,5-T intake in man has been found in agricultural or industrial workers known to have had repeated, relatively high levels of exposure to 2,4,5-T of low dioxin content. The safety factor for the general population is estimated to be several orders of magnitude greater than that for 2,4,5-T factory workers. Data are too limited for a firm conclusion, but there is no evidence to suggest that TCDD as a contaminant in 2,4,5-T is likely to be encountered by animal or man in sufficient dosage to cause toxic reactions (Advisory Committee, 1971).

b. Application of Testing: "Since most chemicals under suitable laboratory conditions could probably be demonstrated to have teratogenic effects, and certainly all could be shown to produce some toxic effects if dosage were raised high enough, it would not be reasonable to consider the demonstration of toxic effects under conditions of greatly elevated dosage sufficient grounds for prohibiting further use of a particular chemical" (Goldberg, 1971).

c. Possibility of Pyrolytically Produced Contamination: The question of the formation of TCDD as a result of the pyrolysis or burning of wood, including brush treated with 2,4,5-T, has been a matter of some concern. Langer (1973) states, "The derivatives of 2,4-D, 2,4,5-T and Silvex as well as their sodium salts and esters have not produced dioxins in pyrolytic reactions whether carried out in the solid state, in the melt, or in solution. Even after conditions of extreme hydrolysis, followed by pyrolysis we could observe only trace amounts of dioxins." Langer (1973) further stated,"Even extreme conditions such as burning of treated wood or vegetation after the use of 2,4-D, 2,4,5-T, Silvex or their derivatives is not expected to produce detectable amounts of dioxins or dibenzofuran." However, in a memorandum dated

July 30, 1973, Baughman and Meselson (1973) reported that the pyrolysis of the sodium salt of 2,4,5-T at temperatures from 300 to 450°C for 30 minutes to 12 hours caused the formation TCDD ranging in concentrations from 0.1 to 0.3% (1,000 to 3,000 ppm).

d. Evaluation by EPA Advisory Committee: The data are indeed very limited. Nevertheless, certain conclusions can be made and these as made by the Advisory Committee on 2,4,5-T to the Administrator of the Environmental Protection Agency are, in part, as follows:

(1) The herbicide 2,4,5-T does not accumulate in any compartments of the biosphere, nor does it accumulate in any animal tissues or products used for human consumption.

(2) The risk of human exposure to 2,4,5-T in food, air and water is negligible.

(3) There is no indication that TCDD accumulates in air, water or plants, although it might accumulate and remain active for some time in soils after heavy application of a highly contaminated sample of 2,4,5-T.

(4) Less than 0.2% of TCDD in soil is known to be absorbed into plants.

(5) 2,4,5-T is rapidly excreted in animals studied using doses in the range of those likely to be encountered in the environment.

(6) Limited data indicate that TCDD is also eliminated, at least some by metabolic breakdown, with a half-life of 20 days.

(7) The solubility of TCDD in fat is limited which would preclude appreciable accumulation in body fat.

## PART III PROBABLE ENVIRONMENTAL IMPACT OF PROPOSED ACTION


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A. SUMMARY STATEMENT OF TOTAL IMPACT: The environmental impact is discussed in the following paragraphs for the proposed action of incineration at sea and the principal alternative of incineration on Johnston Island. In either case the incineration operation will destroy 99.9 to 99.999 percent of the herbicide. These efficiencies will insure that any unburned or pyrolyzates of herbicide and its TCDD content will not have any significant impact upon the environment. Since the herbicide will be essentially destroyed, the environmental impact of the following major combustion products have been considered: water, heat, carbon dioxide, carbon monoxide, carbon particulates, and hydrogen chloride. These combustion products will be discharged directly into the atmosphere toward the west of Johnston Island over the open tropical ocean. Incineration in either case can be accomplished with minimal environmental impact which will be transient and not significant. Incineration at sea has an advantage in that the beneficial uses of the environment in which the incineration takes place, i.e., tropical ocean, are limited. Under the principal alternative, incineration on Johnston Island, the beneficial usages of the atoll are more numerous and must receive considerations of potential impact - particularly the drinking water source, reef and aquatic community, and bird refuge.

B. AIR QUALITY

1. DISPERSION MODEL STUDIES: A dispersion study utilizing a meteorological model was accomplished by the USAF Environmental Health Lab, McClellan AFB. This study was for the emissions of hydrogen chloride and Orange herbicide for the proposed action of incineration at sea and the principal alternative of incineration on Johnston Island. The study is presented as Appendix K.

2. ENVIRONMENTAL IMPACT

a. General: The environmental impact on the air environment will be discussed for the proposed action and the principal alternative described in Part II. In either case, untreated combustion gases will be discharged directly into the atmosphere. The remote location of the incineration process combined with the high efficiency of incineration indicates that the discharge of the combustion gases directly into the atmosphere will not result in any irreversible detrimental environmental impact. The absence of any inhabited land masses or agricultural based economies in the locale of the proposed combustion gas discharges is also favorable. Although the impact upon the atmosphere of unscrubbed combustion gases is minimal and transient, even this impact could be reduced for the principal alternative by using combustion gas scrubbers on Johnston Island. However, the impact of the spent scrubber wastewater discharge would be significant. In the analyses that follows, there is no consideration required for TCDD. If any TCDD were present in the combustion gases, its calculated concentration would be an order of magnitude below the analytical detectable limit (typically 0.20 nanograms/l). The additional dispersion of the combustion gas into the atmosphere will further decrease such concentrations.

b. Incineration at Sea

(1) Potentials for Impact: The evaluation of the impact of the combustion gas will require consideration of the following combustion gas constituents: unburned or pyrolyzates of herbicide, hydrogen chloride, carbon monoxide, carbon particles, carbon dioxide, and heat. The latter three constituents are discharged daily in considerable quantities (~3.0 tons, 1,000 tons, and ~1650°F, respectively) are not significant as regards impact on the environment. That is, the open tropical sea and atmosphere west of Johnston Island will readily absorb these quantities of carbon particulates, carbon dioxide, and heat during three - 7 to 9 day incineration periods. However, hydrogen chloride discharged at about 178 tons per day and carbon monoxide discharged at about 50 tons per day are toxic and were environmentally assessed. As presented below, the impact of carbon monoxide discharge was minimal and negligible in comparison to the hydrogen chloride discharge.

(2) Probable Impact: Atmospheric impacts of hydrocarbons, hydrogen chloride, carbon monoxide, and carbon particulates in combustion gas discharges have been assessed by using two approaches: 1) determining the average mass concentration which would be present in the atmosphere in the immediate zone of the incineration operation by estimating a "worst case" dispersion zone, and 2) determining the maximum sea level concentrations at specified distances downwind from the incineration operation by utilizing a "worst case" meteorological model. Upon determination of such concentrations, judgments regarding the environmental impact are made.

(a) Hydrocarbons: An efficiency of 99.9 percent Orange herbicide destruction has been applied to the shipboard incineration process. Therefore, a daily discharge of 0.576 tons of unburned or pyrolyzates of Orange herbicide must be considered for probable environmental impact. To gain a perspective of the environmental impact, the analyses have also been accomplished for efficiencies of 99.0 and 95.0 percent, i.e. a discharge of 5.76 and 28.8 tons, respectively, of unburned or pyrolyzates of Orange. It is noted that all resulting concentrations described for all the "worst case" analyses in the next paragraph are below the ACGIH threshold limit value of 10 mg/cbm for either 2,4-D acid (1.1 ppm) or 2,4,5-T acid (0.96 ppm) which has been established for occupational exposures. Since the RDES was published the Air Force has received information on incineration from the Antillian Incinerating Company N.V. of Curaco and the Hague Holland. This packet of information is entitled "Information/Data/Analysis Incinerator Ships Mathias I & II" and a portion of it is included in Appendix N. The following quote is taken from page 1 of the "Extract from Dr. Klaus Grasshoff of Kiel University's report on possible effects of burning hydrocarbons at sea" (Appendix N). "By means of extensive controlled measurements, the Bayer Company of LeVenhusen, Germany, has established that if burning of chlorinated hydrocarbons is carried out at a temperature higher than 1000°C, more than 99.9 percent of the materials are completely burnt." The monitoring program conducted by the Bayer Co. is described below and this report is also included in Appendix N. Three separate mixtures of hydrocarbons containing chlorinated hydrocarbons were combusted at temperatures between 1400°C and 1500°C during a 3 to 6 hour operating time. Combustion gas sampling and analyses revealed that the combustion efficiency in all three cases was greater than 99.9 percent. Bioassays conducted on condensates of exhaust gas collected during each burn were satisfactory. The Air Force has also received information concerning incineration at sea which was generated by the French government as a result of requests for authorization by Ocean Combustion Services (Vulcanus) and Incimer (Mathias I & II) to incinerate chlorine wastes (hydrocarbons and chlorinated solvents) produced by the chemical industry. This information (as translated)appears in Appendix N. The information includes data from a test burn of chlorinated hydrocarbons on the Mathias II and Vulcanus. The incinerative efficiency is attested to in the following quote: ..."The pyrolysis is then practically complete in the case of the Vulcanus." For the Mathias II, pyrolysis was also very efficient, but the unburned compounds included light molecular weight compounds and "tars" which are insoluble in water. The presence of the light compounds was attributed to the failure to maintain the required temperature throughout the incinerator. The presence of the tars was not accounted for. The French Environmental Agency proposed that ..."very soon a number of arrangements will be made so that the incinerator ships can operate from french ports, and inside a marine zone which will be specially designated for this use, with all precautions concerning the protection of the sea life." The Environmental Agencies also comment on the importance of knowing physical/chemical characteristics, having test burn data from an incinerator and attaining the temperature for proper incineration, and the minimal environmental impact of chlorine and hydrogen chloride in the exhaust gases. The above is only a summary of the French document which is presented in its entirety in Appendix N. In addition to the above, information relative to the combustion efficiency of the Vulcanus for chlorinated hydrocarbons was presented at a public hearing in Houston TX on 4 Oct 74. The hearing was conducted by the EPA concerning a Shell Chemical Company application to utilize the Vulcanus for incineration of chlorinated hydrocarbon wastes. Mr. H. Compaan, National Research Council of the Netherlands, testified that tests aboard the Vulcanus revealed a combustion efficiency of 99.996 percent, the testimony appears in Appendix N.

1. Dispersion Zone: A "worst case" dispersion zone can be predicted by considering the wind speed, the speed and direction of the incinerator ship during incineration, and the mixing height for the material being dispersed. Forthese analyses the dispersion zone is based on a one knot wind speed, "crosswind" of the ship's course, 10 knot speed for the ship during incineration, and an effective mixing height of 50 meters above sea level. The ship's speed is realistic based on information received from the shipping company; the wind speed and effective mixing height are very conservative. For such a low wind speed, it is anticipated that the combustion gases would actually rise higher than 50 meters above sea level before thermal equilibrium is attained. The calculated daily area of this "worst case" dispersion zone is 240 by 24 nautical miles with a calculated daily volume of about $1.0 \times 10^{12}$ cubic meters. Assuming uniform mixing, the concentration of unburned pyrolyzates of Orange in the zone described would be approximately 42 part per trillion by volume ($ppt_{v/v}$) at an incinerative efficiency of 99.9 percent (420 $ppt_{v/v}$ for 99.0% and 2,100 $ppt_{v/v}$ for 95%). These concentrations represent the average mass loadings in the volume described and are not a function of distance/elevation from the source. As such, their interpretation is limited, however, average mass loadings of these calculated concentrations for a 22-26 day period would be acceptable for the environment affected. A meteorological model, next paragraph, has been utilized to determine sea level concentrations of the material downwind of the ship. The disposition of the unburned herbicide upon the ocean surface via fallout or plume/ocean interface reactions and its impact upon the ocean is discussed under Part III.C., Water Quality.

2. Meteorological Model: These analyses determine the concentration of unburned or pyrolyzates of Orange herbicide at/or near sea level downwind from the ship. Input conditions for the model were selected to insure that maximum sea level concentrations would be attained. These conditions include a wind speed of ~18 knots, a stationary ship, and a highly unstable atmosphere. The analyses revealed the maximum sea level concentration to be 0.81 $ppb_{v/v}$ (99.9% efficiency) at 0.47 kilometers (km) on a line directly downwind of the ship (8.1 $ppb_{v/v}$ for 99.0% and 40.5 $ppb_{v/v}$ for 95%). At a distance of 10 km from the discharge, the sea level concentration will be approximately 19 $ppt_{v/v}$ at an incinerative efficiency of 99.9 percent (190 $ppt_{v/v}$ for 99% and 950 $ppt_{v/v}$ for 95.0%). These unburned or pyrolyzate concentrations of Orange herbicide are not significant for the relatively small open tropical sea atmosphere which would be affected. Additionally, the ship will always be moving, and although the volume of affected atmosphere will be increased, the downwind concentrations of these hydrocarbons will be greatly reduced. See the vertical and horizontal distributions of these concentrations in Appendix K.

(b) Hydrogen Chloride: The hydrogen chloride discharge, 178 tons per day is also analyzed using the "worst case" dispersion zone and the meteorological model as described above.

1. Dispersion Zone: Assuming the same dispersion zone as above for hydrocarbons, the average mass concentration of hydrogen chloride in the zone would be ~0.11 $ppm_{v/v}$. The highly reactive nature of hydrogen chloride will result in considerable deposition of hydrogen chloride into the ocean; a "worst case" analyses, in which all of hydrogen chloride generated, is discharged into the ocean in the ship's wake is presented in Part III, C, Water Quality. The dispersion zone is quite large due primarily to the distance which the ship travels during the incineration. Limited data are available on hydrogen chloride dispersions over the ocean; however, information is available on hydrogen chloride emissions over broad, populated, land areas. For example in a study of air contaminant emissions in Niagara County, N.Y., it was found that 4,083 tons of hydrogen chloride were emitted into the atmosphere per year. Of this total 2,911 tons originated from processing plants, and 1,172 from the consumption of coal and oil for heating purposes. It is concluded that a discharge of 178 tons per day of hydrogen chloride by, an incinerator ship, for three periods of 7-9 days, will not cause any detrimental environmental impact to the atmosphere above the open tropical sea.

2. Meteorological Model: This analysis determines the hydrogen chloride concentration at/or near sea level downwind from the ship. This information is used to evaluate the impact of the ship's discharge upon other possible uses of the area in which the ship is operating. However, it is emphasized that the ship will be required to incinerate in selected areas which will insure no interference with other uses of the area---particularly those of other ships. Using the same "worst case" situation for sea level concentrations as described for the hydrocarbon meteorological model, the maximum sea level concentration will be 2.28 $ppm_{v/v}$ and it will occur 0.47 km directly downwind of the ship. At a distance of 10 km from the discharge the sea level concentration will be about 50 $ppb_{v/v}$. This analyses indicates that the sea level concentration does not exceed the American Conference of Governmental Hygienst's Threshold Limit Value (ACGIH TLV) of 5 $ppm_{v/v}$ at any point downwind of the ship's discharge. Also, the downwind ground level zone in which low $ppm_{v/v}$ concentrations exist is relatively small. The ship will be moving during the incineration operation and therefore the downwind concentrations will be even less than these presented for a stationary ship. For a wind which is crosswind at practically any angle to the ship's course, the downwind sea level hydrogen chloride concentrations will be reduced essentially to insignificance. The vertical and horizontal concentration distribution for the ship's hydrogen chloride discharge is given in Appendix K.

(c) Carbon Monoxide: In analogous fashion to the models used above, the ship's daily discharge of about 50 tons of carbon monoxide were assessed. Average mass concentrations of carbon monoxide would be about 0.04 $ppm_{v/v}$ within the "worst case" dispersion zone. Maximal "worst case" sea level conconcentrations predicted by the meteorological model would be 0.8 $ppm_{v/v}$ at 0.47 km directly downwind of the ship. This sea level concentration would decrease to about 18 $ppb_{v/v}$ at a distance of 10 km downwind. These predicted concentrations are very conservative because continued oxidation of carbon monoxide to carbon dioxide in the exhaust stack and discharge plume are neglected. The affected concentrations predicted by the meteorological model would actually be much smaller because the ship is not a stationary source. None of these predicted atmospheric carbon monoxide concentrations exceed the ACGIH TLV of 50 $ppm_{v/v}$

or ambient air quality standards: 9 ppm for eight hours only once a year or 35 ppm for one hour only once a year (National Primary and Secondary Ambient Air Quality Standard 40 CFR 50.8). Taking even the most conservative approach, the expected carbon monoxide discharges from the ship will cause no adverse impact on the environment of the open tropical sea.

(d) Particulates: The daily discharge of 3.0 tons of carbon particles is based on an assumption of 0.5 percent conversion of Orange to elemental carbon. With the same "worst case" dispersion zone as assumed above, the concentration of suspended particulates would be several orders of magnitude less than dust concentration of clean country air (0.2 mg per cubic meter). In reality, the majority of the particles would be deposited on the ocean surface in a relatively small impact zone; this aspect has been considered in Part III, C, Water Quality. These discharges of particulates would have no significant effect on the air environment.

(3) Monitoring: In view of the negligible impact predicted and the remoteness of the incineration area on the open tropical sea, ambient air monitoring is not considered necessary.

c. Principal Alternative - Incineration On Johnston Island

(1) Potentials for Impact: Consideration is given to the following combustion gas constituents: hydrocarbons, i.e., unchlorinated pyrolyzates of Orange herbicide and undetectable concentrations of herbicide feed constituents, hydrogen chloride, carbon particles, carbon monoxide, carbon dioxide, and heat. The latter two, while discharged at considerable quantities, 110 tons per day of carbon dioxide and a stack gas temperature of ~ 1700°F, are not environmentally significant; in fact, they can be readily absorbed into the atmosphere. The carbon monoxide, while a toxic gas and estimated to be discharged at a rate of 5.5 tons per day, is not considered environmentally significant. This statement is based on a comparison between the mass discharge rates of the carbon monoxide and hydrogen chloride (18.5 ton/day) and the impact analyses for hydrogen chloride which is described later. If scrubbers were used, the general character of the stack gas would be improved and essentially no hydrogen chloride or carbon particulates would be discharged into the atmosphere. However, the scrubber wastewater discharge would have potential for environmental impact and is discussed under Part III. C, Water Quality.

(2) Probable Impact: The potential atmospheric impact of pyrolyzates with undetectable herbicide feed constituents, hydrogen chloride, and carbon particulates are based on: 1) calculated average concentrations of these materials within a "worst case" dispersion zone downwind of the discharge point, and 2) predicted downwind concentration profiles provided by a meteorological model (see Appendix K). For the carbon particulates, only the dispersion zone analyses was accomplished. The dispersion zone is based on a wind speed of one knot (calm) and a very conservative width and height of 100 meters. On a daily basis, the area of the zone would be 24 nautical miles by 100 meters and its volume would be $4.44 \times 10^8$ cubic meters. While seemingly large, this zone represents a "worst case" volume for dispersion and it is felt that the gases will actually disperse through a greater volume on a daily basis. Similarly, "worst case" conditions were chosen for the meteorological model, i.e., wind speed of 13.6 knots and extremely unstable atmospheric conditions.

(a) Hydrocarbons: Considering a 99.999 percent destruction efficiency of herbicide feed, the daily mass emission of unchlorinated pyrolyzates and undetectable levels of feed constituents would be 1.2 pounds. This value is approximately three times that which was found in a test incineration program described in Appendix E. It is also noted that the 1.2 pounds of hydrocarbons is essentially all unchlorinated pyrolyzates since no herbicide feed constituents were ever detected in the combustion gases. The average daily mass concentration in the "worst case" dispersion zone is ~100 $ppt_{v/v}$. The maximum sea level concentration predicted by the meteorological model is approximately 7.0 $ppt_{v/v}$ and occurs 0.2 km downwind of discharge. When discharged from the west end of the island over the open tropical ocean, no significant environmental impact can be attributed to these predicted "worst case" atmospheric concentrations of these hydrocarbons. The mpact of the deposition of these pyrolyzates or any Orange constituents into the ocean from the stack plume is discussed under Part III. C, Water Quality.

(b) Hydrogen Chloride: The discharge of hydrogen chloride will be approximately 18.5 tons per day. The daily average mass concentration in the atmospheric dispersion zone described above will be ~25 $ppm_{v/v}$. The

maximum sea level concentration predicted by the meteorological model, for "worst case" sea level conditions, is 1.85 $ppm_{v/v}$ which occurs at 0.2 km directly downwind of the stack. At a distance of 10 km from the stack, the predicted sea level concentration decreases to 0.007 $ppm_{v/v}$. The maximum concentration predicted by the model occurs at a distance of 0.2 km from the stack and an elevation 38.3 meters; this concentration is 2.26 $ppm_{v/v}$.
These predicted hydrogen chloride concentrations in the atmosphere were accomplished to evaluate probable impacts of the hydrogen chloride discharge as regards: 1) interference with ships downwind of the stack, 2) interference with aircraft, particularly those on approach to landing at the west end of the runway, and 3) possible alterations of reef calcification processes due to downwind deposition of hydrogen chloride and resultant depressions of the pH of reef waters. The analyses indicates there is no significant detrimental environmental impact attributable to the hydrogen chloride discharge and resultant hydrogen chloride concentrations in the atmosphere west of Johnston Island. Interference with ships or aircraft, due to transient exposure to low ppm concentrations of hydrogen chloride, would not be a serious constraint on the operation. The reaction between hydrogen chloride and saturated air was considered in the Department of Air Force Draft ES "United States Air Force Space Launch Vehicles." Hydrogen chloride in a clear atmosphere of saturated air is not expected to result in the formation of droplets which may fall out. Droplets occur in fog or in natural clouds and due to the great affinity of hydrogen chloride for water an acid may be expected. The hydrogen chloride concentration of such droplets has been estimated at less than 1 percent. Although hydrochloric acid mists and solutions are very corrosive to most metals, a literature review in preparation of "Air Pollution Aspects of Hydrochloric Acid" (Stahl, 1969) did not reveal any information describing corrosion or damage to material from environmental concentrations of hydrochloric acid. However, meteorological constraints will be implemented to insure that the incineration is stopped during weather conditions which are not favorable for dispersion of the stack gas westward from the island. The effect upon the fringing reef is discussed under Part III.C., Water Quality.

(c) Particulates: The daily discharge of elemental carbon particulates (0.3 tons) is based on the conversion of 0.5 percent of Orange particulates. Based upon proposed incineration parameters, these particulates would not be expected to contain any detectable hydrocarbons. Dispersion of these particles in the "worst case" dispersion zone described above will result in a concentration slightly greater than that of clean country air (0.2 mg/cubic meter). Although a smaller zone will be affected at higher concentrations, the majority of particles are actually expected to fall out in the ocean over a relatively small impact area. This fallout effect on the ocean is discussed in Part III.C., Water Quality.

(3) Monitoring: Ambient air monitoring including sample collection for analytical chemistry analyses and biomonitoring with selected plants will be required to document the impact of the incineration process. The odor perception of humans to hydrogen chloride is very acute, being reported as low as 0.067 $ppm_{v/v}$. The low sensitivity to odor can be considered as a back-up

monitoring program to supplement the meteorology constraints on the incineration operation and the chemical/biological sampling program. The odor perception is obviously not to be used for quality control of the incineration operation. It is fortunate, however, that hydrogen chloride is the major quantitative constituent of concern in the stack gas and that it can be readily detected at concentrations below that considered safe for occupational exposure.

C. WATER QUALITY

1. PRESENT WATER QUALITY

a. Survey at Johnston Atoll: A visit was made to Johnston Atoll in October 1973 by personnel of the USAF Environmental Health Laboratory, Kelly AFB (EHL(K)) to collect water samples and marine biological samples for analyses for Orange herbicide components and TCDD.

b. Water Sample Collection: A total of 17 duplicate water samples were taken during the survey; see Fig III-1, and Table III-1. The rationale of the water sampling was to obtain a comprehensive set of samples which would include:

(1) Ocean samples near the herbicide storage area.

(2) Ocean samples from locations around the island.

(3) An indisputable ocean control sample.

(4) Samples at the intake and outlet of the distillation unit.

(5) Samples of the freshwater reservoir and distribution system.

(6) Samples of test wells in the herbicide storage area.

c. Biological/Sediment Sample Collection: The rationale for this sampling was to obtain representative samples of high food chain predators, coral feeders, coral sediments, etc. for subsequent analysis for herbicide components and TCDD. Figure III-2 illustrates the biological sampling locations. Area I, consisting of five locations off the west side of Johnston Island, was the most likely area for contamination due to the location of the Orange storage area and the nature of the ocean currents. Area II was north and east of North (Akau) Islands where four locations were selected as controls that would be free of possible contamination. Area III was a "catch-all area," including any area except I & II which was expected to have minimal herbicide contamination but which could have industrial/chemical products indicating man's influence. Table III-2 lists the biological specimens and the sampling areas from which they were collected. Duplicate sediment samples were collected in Biological Sampling Areas I and II and at the shoreline near the Orange storage area. The latter corresponds to the same location as water sample number 8, see Table III-1.

d. Sample Disposition:

(1) Water: One set of water samples was delivered to the Environmental Health Laboratory, McClellan AFB (EHL(M)) to be analyzed for 2,4-D and 2,4,5-T esters and acids and for polychlorinated biphenyls (PCB). The other set was delivered to the EPA Laboratory at Bay St Louis MS. The samples were prepared for analysis at this facility and then sent to the EPA Laboratory at Perrine FL for determination of TCDD.

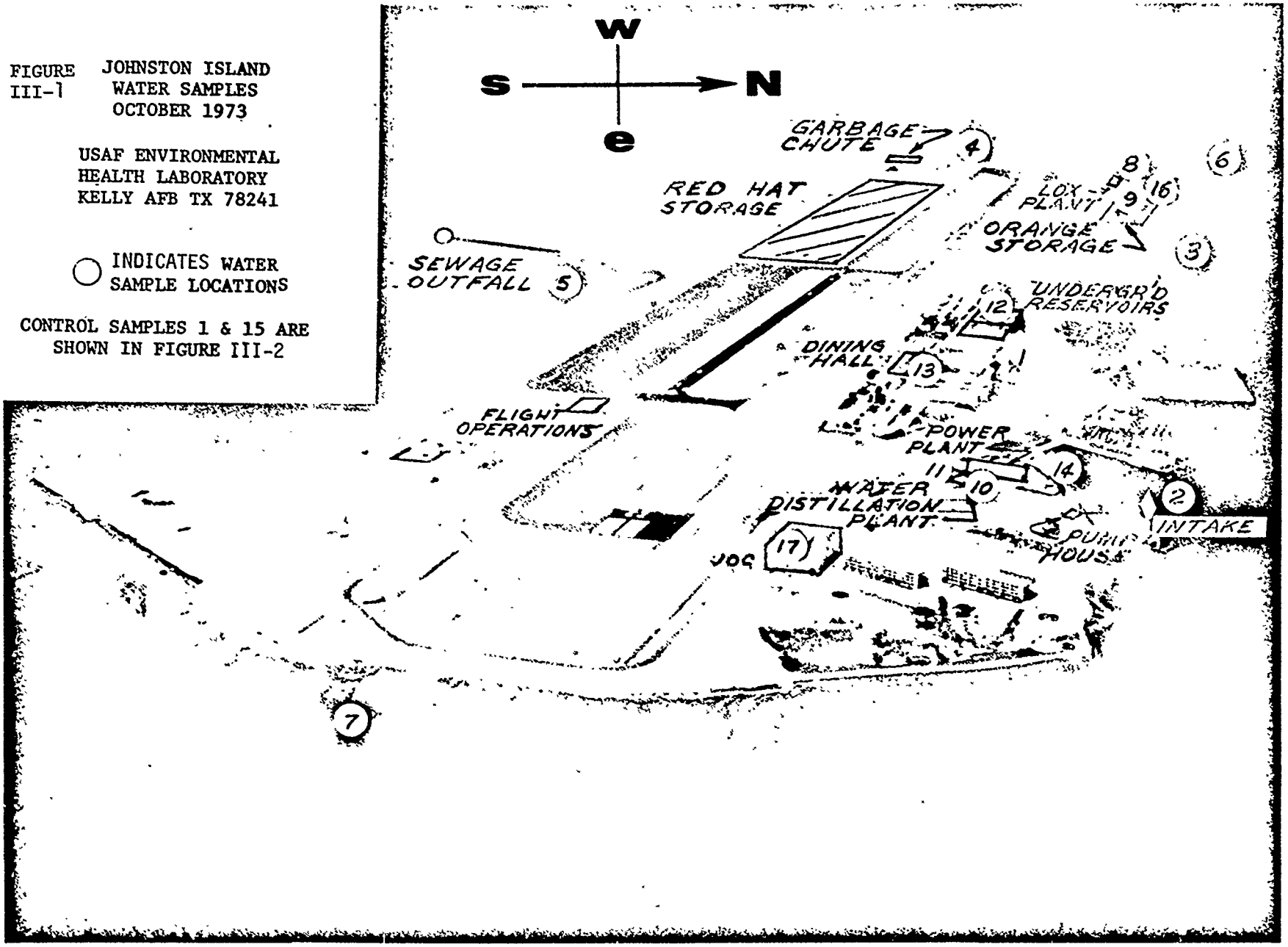
(2) Biological: One set of six frozen biological samples identified in Table III-2 was sent to Dow Chemical Co., Midland MI for TCDD analysis. A full set of frozen samples was sent with the water samples to the EPA

FIGURE III-1 JOHNSTON ISLAND WATER SAMPLES OCTOBER 1973

USAF ENVIRONMENTAL HEALTH LABORATORY KELLY AFB TX 78241

○ INDICATES WATER SAMPLE LOCATIONS

CONTROL SAMPLES 1 & 15 ARE SHOWN IN FIGURE III-2




JOHNSTON ISLAND

TABLE III-1 WATER/SEDIMENT SAMPLES

EHL(K) FIELD TRIP, JOHNSTON ISLAND, OCT 73

| General Location | Sample Ident. | Specific Location | Date | Time | Approx Sample Depth - Feet | Approx Bottom Depth - Feet |
|---|---|---|---|---|---|---|
| Ocean Samples | 1 | East of North Island - Inside Reef (Control Sample) | 1 Oct | 1530 | 20 | 40 |
| | 2 | Distillation Plant Intake* | 1 Oct | 1510 | 12 | 20 |
| | 3 | North Shore | 1 Oct | 1415 | 13 | 20 |
| | 4 | Garbage Chute - 10 yds from shore | 1 Oct | 1430 | below surface | -- |
| | 5 | Sea Turtle Area | 1 Oct | 1440 | 8 | 15 |
| | 6 | Northwest of Herbicide Area | 1 Oct | 1425 | 10 | 17 |
| | 7 | East End of Runway | 1 Oct | 1500 | 15 | 30 |
| | 8 | West of Herbicide Area - Shoreline | 1 Oct | 1720 | -- | -- |
| | 15 | ~1.2 Miles Northwest of North Island Outside Reef (Control Sample) | 3 Oct | 0900 | below surface | -- |
| Potable Water Supply System | 10 | Salt Water Reservoir | 2 Oct | 1445 | below surface | -- |
| | 11 | Distillation Unit Discharge (Sample Tap) | 2 Oct | 1500 | -- | -- |
| | 12 | Potable Water Reservoir | 2 Oct | 1545 | -- | -- |
| | 13 | Dining Hall (sink tap) | 3 Oct | 1000 | -- | -- |
| | 14 | Distillation Unit Brine | 2 Oct | 1510 | -- | -- |
| | 17 | JOC Bldg (sink tap) | 3 Oct | 1030 | -- | -- |
| Test Wells | 9 | Well Hole - Center of Herbicide Area | 2 Oct | 1000 | ~8 | -- |
| | 16 | Well Hole - West side of Herbicide Area | 3 Oct | 1115 | ~8 | -- |
| Sedi-ment | I | Biological Sampling Area I | 2 Oct | 0830 | 15 | 15 |
| | II | Biological Sampling Area II | 3 Oct | 1000 | 25 | 25 |
| | S8 | Same as Water Sample 8 | 3 Oct | 1100 | Shoreline | -- |

* Diver stated that water had a petroleum product taste

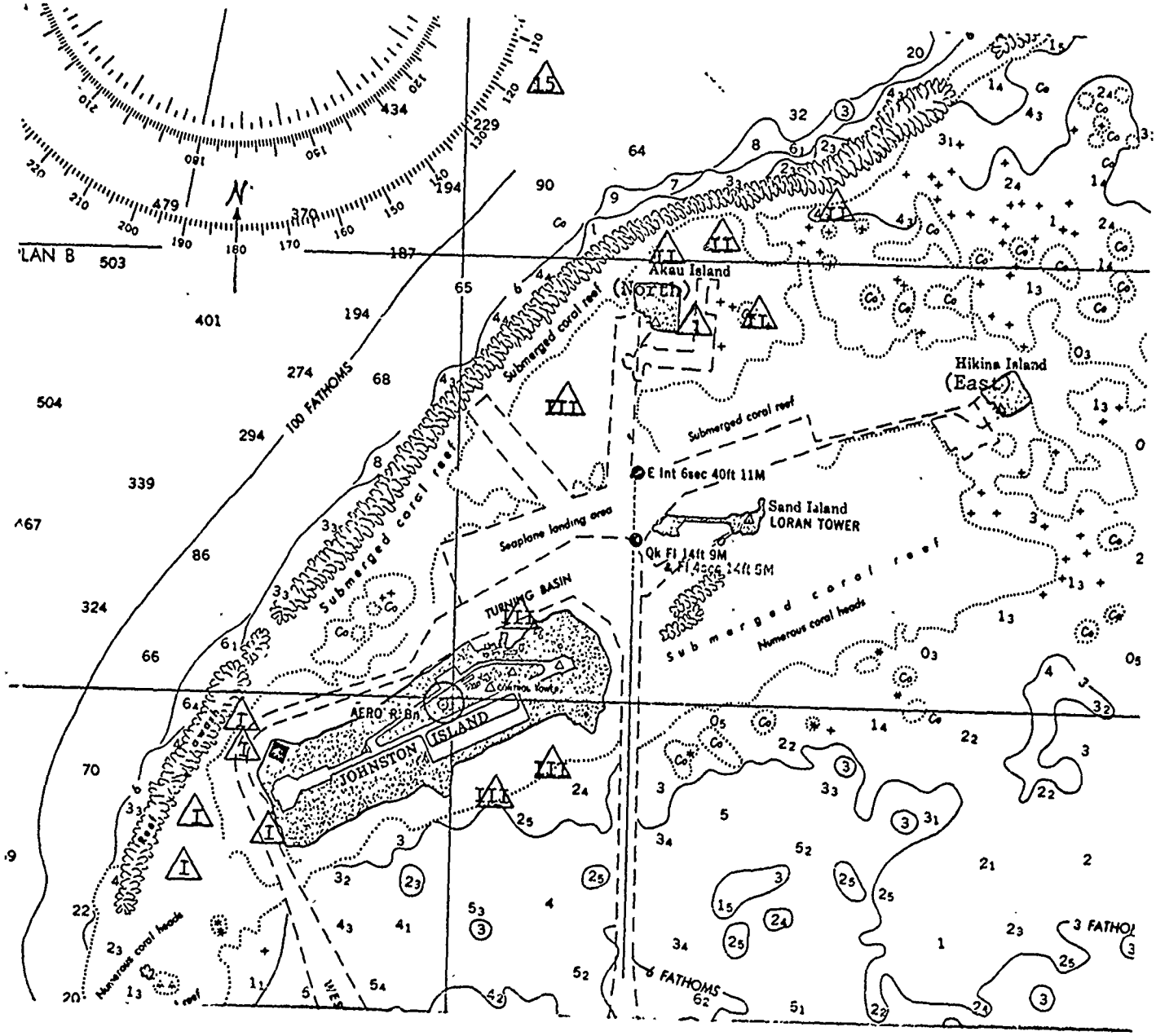



FIGURE III-2 MARINE SAMPLING LOCATIONS
EHL(K) FIELD TRIP, JOHNSTON ATOLL, OCT 73.

I Sampling locations offshore from Orange Herbicide storage area.

II Control sampling locations north and east of North (Akau) Island.

III Miscellaneous control sampling locations.

1 15 Control locations for marine water samples.

■ Orange Herbicide Storage Area.

TABLE III-2 MARINE BIOLOGICAL SPECIMENS

EHL(K) FIELD TRIP, JOHNSTON ISLAND, OCT 1973

| SPECIMEN* | COLLECTION AREA** I | II | III |
|---|---|---|---|
| A. White-tipped reef shark, Triaenodon obesus | x (liver) x (muscle) | | |
| Gray reef shark, Charcharinus amblyrhyncos | | | x (liver)† x (muscle) |
| B. Moray eel, Gymnothorax javanicus | x (body)† section) | | |
| C. Sand eel, (Anguilliformes) | x | | |
| D. Green sea turtle, Chelonia mydas (?) | | | x (liver) x (muscle) |
| E. Surgeon fish, Acanthurus nigroris (?) | | | x |
| F. Surgeon fish, Acanthurus achilles | x† | x† | |
| G. Squirrel fish, Adioryx spinifer | x | x | x |
| H. Parrot fish, (Scaridae) | x | x | |
| I. Sea Cucumber, Holothurea atra & other species | x† | x† | |
| J. Mushroom (razor) coral, Fungia scutaria | x | | x |
| K. Staghorn coral, Acropora sp | x | x | |
| L. Algae species #1 Schizothrix calicola mixed with other species | x | x | |
| M. Algae species #2, Halimeda Discoidea | | x | |
| N. Algae species #3, Bryopsis sp. | | | x |

*Sample is composed of whole specimen(s) unless otherwise noted
**Collection areas are indicated on attached map, Figure 2
†Specimens sent to Dow Chemical for dioxin analysis

Laboratory at Bay St Louis MS for preparation with subsequent TCDD analysis at the EPA Laboratory at Perrine FL. The remaining biological samples were retained at EHL(K) for 2,4-D and 2,4,5-T analysis.

(3) Sediment: One set of sediment samples was delivered to the EPA Laboratory at Bay St Louis MS for subsequent dioxin analysis at Perrine FL. The second set was analyzed at EHL(K) for 2,4-D and 2,4,5-T.

e. Results of Analysis

(1) Water: As shown in Table III-3 no TCDD was found in any water samples. Acids of 2,4-D and 2,4,5-T were found at the shoreline adjacent to the storage area and in the test wells in the storage area as seen in Table III-4. The well openings are at grade and the presence of the acid is probably from water-carried (rain) drainage of leaked herbicide into the wells. The shoreline station was just below the redrumming area so it also could receive leaked herbicide.

(2) Marine Biological and Sediment: Table III-5 shows no TCDD in any of the marine samples analyzed except for sample I-I, Sea Cucumber which is reported as 2.2 ppt (by weight). The analysis which resulted in this concentration was the second analyses conducted on sample I-I by the EPA. The first analyses resulted in a "non-detectable" report but the recovery was low resulting in a TCDD detection limit of 64 ppt. A portion of sample I-I was one of the six samples which was forwarded to the Dow Chemical Company for analyses. Dow split the sample into "flesh" and "internal organs" and the analyses of each portion resulted in a non-detectable concentration of TCDD at a detection limit of 1 ppt. The remaining samples forwarded to the Dow Chemical Company were also negative for TCDD with detection limits ranging from 1 to <11 ppt. The latter limit, <11 ppt, was for sample III-A, the grey reef shark liver, and was attributed to an interfering substance present in the sample. Table III-6 shows that all samples were negative for 2,4-D and 2,4,5-T; the detection limits ranged from 0.07 to 2.0 µg/kg for the biological samples and was 5.0 µg/kg for the sediment samples.

f. Conclusions: From the results of analyses of ocean water, drinking water, marine biological and sediment samples collected in October 1973 by the survey team from EHL(K), it was concluded that there was no evidence of Orange herbicide pollution or environmental effects.

g. Analytical Procedures: See Appendix J.

TABLE III-3 TCDD RESULTS
EPA LABORATORY, BAY ST LOUIS MS AND PERRINE FL

| Sample Code | Location | TCDD Detection Limit (PPT) | Remarks |
|---|---|---|---|
| 1 | East of North Island - Inside Reef | 0.10 | ND |
| 2 | Distillation Plant Intake | 0.11 | ND |
| 3 | North Shore | 0.14 | ND |
| 4 | Garbage Chute - 10 yds from shore | 0.15 | ND |
| 5 | Sea Turtle Area | 0.23 | ND |
| 6 | Northwest of Herbicide Area | 0.31 | ND |
| 7 | East End of Runway | 0.37 | ND |
| 8 | West of Herbicide Area - Shoreline | 0.60 | 16% Recovery, ND |
| 15 | 1.2 Miles Northwest of North Island Outside Reef | 0.19 | ND |
| 10 | Salt Water Reservoir | 0.85 | 14% Recovery, ND |
| 11 | Distillation Unit Discharge | 0.27 | ND |
| 12 | Potable Water Reservoir | 0.16 | ND |
| 13 | Dining Hall (Sink Tap) | 0.20 | ND |
| 14 | Distillation Unit Brine | 0.23 | ND |
| 17 | JOC Bldg (Sink Tap) | 0.26 | ND |
| 9 | Well Hole - Center Herbicide Area | 0.37 | ND |
| 16 | Well Hole West Side Herbicide Area | 0.24 | ND |
| 8 | Sediment | - | Contained contaminant |
| I | Sediment | 1.7 | ND |
| II | Sediment | 0.88 | ND |

TABLE III-4 WATER SAMPLE ANALYSES RESULTS (EHL(M))

| General Location | Sample # | Specific Location | Analyses Results, ng/l | | | | |
|---|---|---|---|---|---|---|---|
| | | | 2,4-D | | 2,4,5-T | | |
| | | | Ester 200* | Acid 100* | Ester 50* | Acid 20* | Aroclor 700* |
| OCEAN SAMPLES | 1 | East of North Island - Inside Reef (Control Sample) | ND** | ND | ND | ND | ND |
| | 2 | Distillation Plant Intake | ND | ND | ND | ND | ND |
| | 3 | North Shore | ND | -*** | ND | - | ND |
| | 4 | Garbage Chute - 10 yds from shore | ND | ND | ND | ND | ND |
| | 5 | Sea Turtle Area | ND | ND | ND | ND | ND |
| | 6 | Northwest of Herbicide Area | ND | ND | ND | ND | ND |
| | 7 | East End of Runway | ND | ND | ND | ND | ND |
| | 8 | West of Herbicide Area - Shoreline | ND | 1170 | ND | 910 | ND |
| | 15 | ~1.2 Miles Northwest of North Island Outside Reef (Control Sample) | ND | ND | ND | ND | ND |
| POTABLE WATER | 10 | Salt Water Reservoir | ND | ND | ND | ND | ND |
| | 11 | Distillation Unit Discharge (Sample Tap) | ND | ND | ND | ND | ND |
| | 12 | Potable Water Reservoir | ND | ND | ND | ND | 900 |
| | 13 | Dining Hall (Sink Tap) | ND | ND | ND | ND | 700 |
| | 14 | Distillation Unit Brine | ND | ND | ND | ND | |
| | 17 | JOC Bldg (Sink Tap) | ND | ND | ND | ND | 900 |
| TEST WELLS | 9 | Well Hole - Center of Herbicide Area | ND | 44,000 | ND | 1,200 | ND |
| | 16 | Well Hole - West Side of Herbicide Area | ND | 77,000 | ND | 3,600 | ND |

*Detection Limits, ng/l
**Less than the detectable limit
***Analyses not accomplished

TABLE III-5 TCDD RESULTS
EPA LABORATORY, BAY ST LOUIS MS AND PERRINE FL

| Johnston Island Collection Area | Specimen | TCDD Detection Limit (ppt) | TCDD Concentration (ppt) |
|---|---|---|---|
| I-A | White-Tipped Reef Shark Liver | 56 | ND |
| I-A | White-Tipped Reef Shark Muscle | 9.5 | ND |
| I-B | Moray Eel | 6.0 | ND |
| I-C | Sand Eel | 3.7 | ND |
| I-F | Surgeon Fish | 8.7 | ND |
| I-G | Squirrel Fish | 20.1 | ND |
| I-H | Parrot Fish | 78.7 | ND |
| I-I | Sea Cucumber | 1.9 | 2.2 |
| I-J | Mushroom Coral | - | Contaminated Extract |
| I-K | Staghorn Coral | - | Contaminated Extract |
| I-L | Algae #1 | 1100 | ND |
| II-F | Surgeon Fish | 14.3 | ND |
| II-G | Squirrel Fish | 20.7 | ND |
| II-H | Parrot Fish | 27.4 | ND |
| II-I | Sea Cucumber | 1.3 | ND |
| II-K | Staghorn Coral | - | Contaminated Extract |
| II-L | Algae #1 | 7.1 | ND |
| II-M | Algae #2 | 13.1 | ND |
| III-A | Grey Reef Shark Liver | 9.3 | ND |
| III-A | Grey Reef Shark Muscle | 6.7 | ND |
| III-D | Green Sea Turtle Liver | 4.0 | ND |
| III-D | Green Sea Turtle Muscle | 8.7 | ND |
| III-E | Surgeon Fish | 5.0 | ND |
| III-G | Squirrel Fish | 2.2 | ND |
| III-J | Mushroom Coral | - | Contaminated Extract |
| III-N | Algae #3 | 8.3 | ND |

TABLE III-6 RESULTS OF BIOLOGICAL AND SEDIMENT SAMPLE ANALYSES BY EHL(K)*

| Johnston Island Collection Area | Specimen | 2,4-D | 2,4,5-T | Detection Limit Microgram/Kg |
|---|---|---|---|---|
| I-A | Shark Liver | N.D. | N.D. | 0.25 |
| I-A | Shark Muscle | N.D. | N.D. | 0.33 |
| I-B | Moray Eel | N.D. | N.D. | 0.15 |
| A-I-C | Sand Eel | N.D. | N.D. | 2.00 |
| I-F | Surgeon Fish | N.D. | N.D. | 2.00 |
| I-G | Squirrel Fish | N.D. | N.D. | 0.67 |
| I-H | Parrot Fish | N.D. | N.D. | 0.67 |
| I-I | Sea Cucumber | N.D. | N.D. | 0.20 |
| I-J | Mushroom (Razor) Coral | N.D. | N.D. | 0.07 |
| I-K | Staghorn Coral | N.D. | N.D. | 0.10 |
| I-L | Algae Species #1(Blue Green) | N.D. | N.D. | 1.00 |
| II-F | Surgeon Fish | N.D. | N.D. | 2.00 |
| II-G | Squirrel Fish | N.D. | N.D. | 0.67 |
| II-H | Parrot Fish | N.D. | N.D. | 0.40 |
| II-I | Sea Cucumber | N.D. | N.D. | 0.67 |
| II-K | Staghorn Coral | N.D. | N.D. | 0.04 |
| II-L | Algae Species #1(Blue Green) | N.D. | N.D. | 1.00 |
| II-M | Algae Species #2 | N.D. | N.D. | 1.00 |
| III-A | Grey Reef Shark Liver | N.D. | N.D. | 0.50 |
| III-A | Grey Reef Shark Muscle | N.D. | N.D. | 1.00 |
| III-D | Green Sea Turtle Liver | N.D. | N.D. | 1.00 |
| III-D | Green Sea Turtle Muscle | N.D. | N.D. | 0.50 |
| III-E | Surgeon Fish | N.D. | N.D. | 0.67 |
| III-G | Squirrel Fish | N.D. | N.D. | 1.00 |
| III-J | Mushroom (Razor) Coral | N.D. | N.D. | 0.07 |
| III-N | Algae Species #3 (Green) | N.D. | N.D. | 1.00 |
| #8 | Sediment | N.D. | N.D. | 5.00 |
| I | Sediment | N.D. | N.D. | 5.00 |
| II | Sediment | N.D. | N.D. | 5.00 |

N.D. - None Detected

*Samples were analyzed for the components of Orange herbicide by Gas Chromatography with Electron Capture detector. Two columns of different polarity were used. Fifteen of the 29 samples analyzed were found to be suspect since they had peaks with the same relative retention time, on both columns, as the methyl esters of 2,4-D and 2,4,5-T. These samples required confirmation of the compounds. The fifteen samples were then analyzed by Gas Chromatography/Mass Spectrometry. The suspected compounds were not confirmed by this technique. Therefore, it was concluded that Orange herbicide was not present in any samples.

2. MOVEMENT: The present Orange storage site is on the northwest corner of Johnston Island, and from a meteorology standpoint, the incineration facility should be sited at the same location (dominant east to west wind). There will be a potential for admittance of Orange into the ocean at this location due to accidents resulting in spillage during handling and transfer of the Orange for incineration. However, stringent precautions to prevent accidental spillage and to contain any such spillage will be accomplished. The determination of a location for the programmed long term discharge of scrubber water in the ocean was evaluated to demonstrate the environmental impact of the scrubber water. Selection of a suitable location is complicated by the difference in ocean water circulation and turbid water outflows from Johnston Island. The most detailed work on water patterns in and around the reef complex at Johnston Island has been accomplished by Kopenski and Wennekens (1965). Most of the information to follow is from this reference; the Smithsonian Report, Appendix A, also includes a summary of Kopenski-Wennekens report. During the study by Kopenski and Wennekens, the investigators were able to utilize turbid water, caused by current and wave action on the island's coral shore, as a tracer. Observation of turbid water, documented by aerial photography, was utilized in both the winter and summer surveys to show the transport of turbid water from the island's environment to the main ocean. In addition, parachute drogues, current meters, and dye studies were also conducted. Johnston Island is a projection of a shallow platform (80 square nautical miles) which is nearly submerged. This shallow platform is a truncated portion of a submarine mountain. A reef and extensive coral shoals occupy most of the northwestern section of the platform. The island is located in the Northwest Trade Belt and is in the North Equatorial Current. The above stated natural geographical factors disrupt the ocean's flow, and the extensions to Johnston Island and the dredging of ship channels have had an affect on the local (island's) flow patterns. In addition, the flow is dependent upon: tidal currents, wave-driven flow over the reef, and the North Pacific Equatorial Current, which during the Kopenski-Wennekens study was fairly strong and steady from the east in the winter but weak and variable in the summer. The flow patterns about Johnston Island for these conditions are shown in Figures III-3, 4, and 5, which were taken from the Kopenski-Wennekens Report. Inspection of these figures reveals that the Orange storage site is generally satisfactorily located as regards water transport of any Orange which may be accidentally spilled into the ocean at the site. Transport is to the south from the west ship channel in both the Winter Survey, Figure III-3 and the Summer Survey - Easterly Flow, Figure III-4. Transport is to the north with the outlet through the reef cut for the Summer Survey - Westerly Flow, Figure III-5. It is this summer flow condition that is responsible for the sluggish action of sanitary sewage discharge commented on in the referenced report. The summer fluctuation is due to tides which occur twice daily and therefore increase the residence time of water in the lagoon on the north side of the island. Transport from the lagoon to the ocean is therefore greater in the winter than in the summer. Under the three flow conditions shown, the west reef below the reef cut is the primary reef area affected by the turbidity transport, and this turbidity has already had a detrimental effect upon the reef (Brock, et al, 1965).

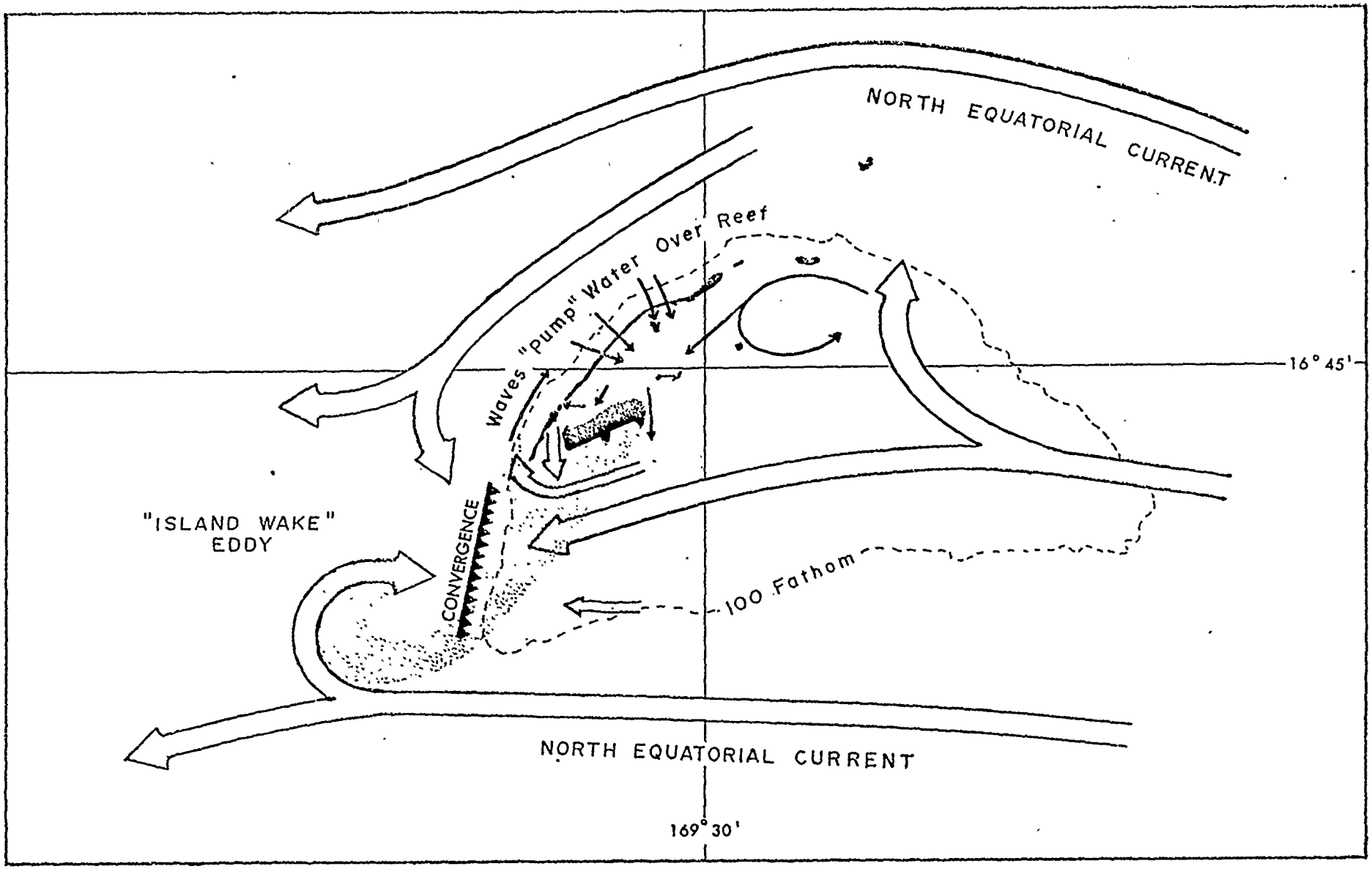



FIGURE III-3 JOHNSTON ISLAND-INFERRED CIRCULATION, JANUARY-FEBRUARY 1965 (KOPENSKI AND WENNEKENS 1965)

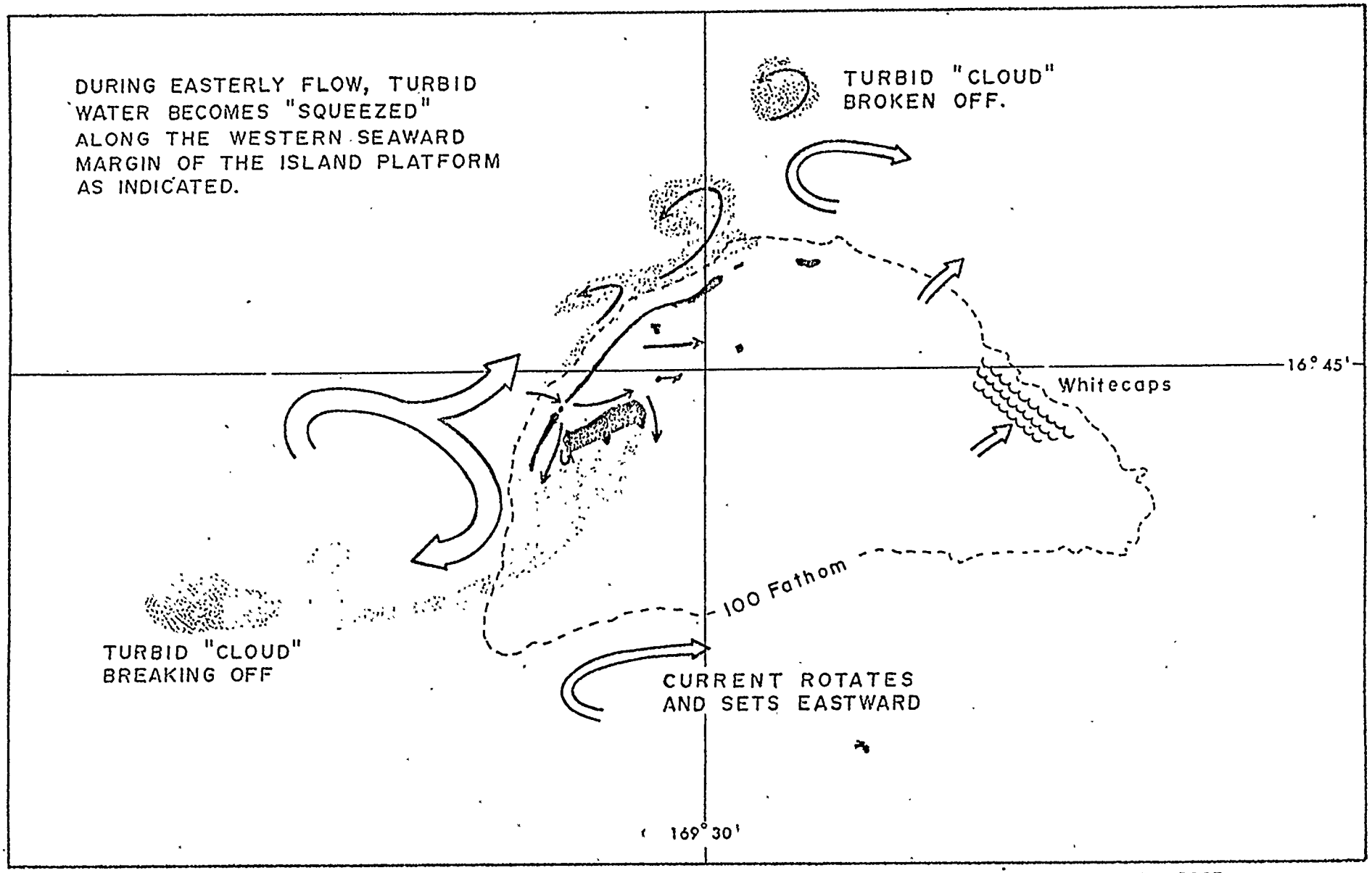



FIGURE III- 4 . JOHNSTON ISLAND-EASTERLY FLOW, INFERRED CIRCULATION AND TURBID OUTFLOW, JULY-AUGUST 1965 (KOPENSKI AND WENNEKENS 1965)

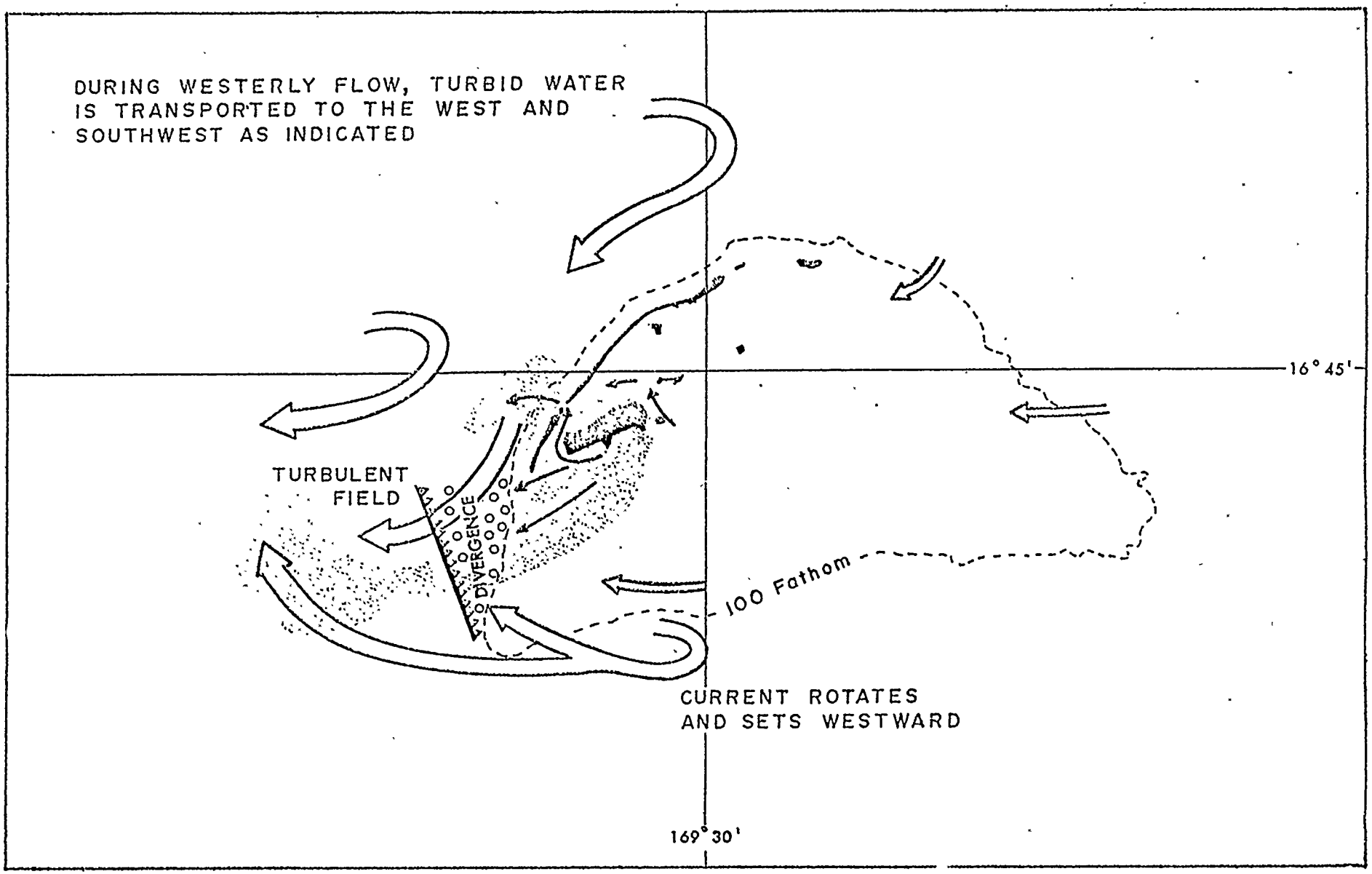



FIGURE III-5 JOHNSTON ISLAND-WESTERLY FLOW, INFERRED CIRCULATION AND TURBID OUTFLOW, JULY-AUGUST 1965 (KOPENSKI AND WENNEKENS 1965)

3. PERSISTENCE

a. General: The composition of the liquid discharge from an incinerator operation may include sodium chloride, calcium chloride, hydrogen chloride, particulates (primarily elemental carbon), chloride residual, hydrocarbons (uncombusted or partially combusted Orange) and heat. Excluding the hydrocarbons, only the particulates represents a material which is persistent or which will not be dissipated by the receiving water. Essentially complete destruction of the herbicide and TCDD is anticipated in the combustion process; however, for the sake of completeness, the interactions of this material with the water environment is discussed. Any herbicide which enters the ocean would be subject to various phenomena including: hydrolysis, photodecomposition, sorption, and biodegradation.

b. Hydrolysis: The herbicide esters are hydrolyzed to 2,4-D and 2,4,5-T acid and butyl alcohol when subjected to aqueous alkaline conditions; the acid is obtained as its salt and can be liberated by the addition of mineral acid. The ester and acid are not soluble in water, but the salt is water soluble. Aly and Faust (1964), in a study on the fate of 2,4-D and ester derivatives in natural surface waters, have found the solubility of the calcium and magnesium salts of 2,4-D in distilled water at 25°C to be 4,000 and 1,000 mg/l respectively. An alkaline scrubber using sodium or calcium hydroxide would readily convert very low concentration of ester in the combustion gases (should they occur) to the sodium or calcium salts. Smith (1972) found the hydrolysis of 2,4-D ester to be extremely fast in a 0.1N sodium hydroxide solution - greater than 50 percent of the ester being hydrolyzed in less than one minute, and negligible hydrolysis was noted in distilled water over a five-hour period. The Environmental Health Laboratory, Kelly AFB, is presently conducting studies in the hydrolysis of Orange herbicide in aqueous sodium hydroxide solutions and in ocean water. Preliminary data analysis indicates good comparison with Smith's results for the hydroxide solutions, and for the ocean water studies, 90% of the Orange esters were hydrolyzed within 7 days.

c. Photodecomposition: The phenomena of photodecomposition of 2,4-D has been studied by several investigators. Crosby and Tutass (1966) conducted an experimental study to compare the effect of sunlight on aqueous 2,4-D solutions and to identify any major decomposition products. They concluded:

> "2,4-D acid decomposes rapidly in the presence of water and ultraviolet light. This decomposition results in the formation of 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzenetrol, and, finally, polymeric humic acids. The results with artificial light and with sunlight are essentially identical."

In tests under field conditions, Penfound and Minyard (1947) investigated the relationship of light intensity to the effect of the herbicide on water hyacinth and kidney bean and observed more necrosis and greater epinasty in shaded plants than in those in sunlight. TCDD is known to be photosensitive in alcohol to the extent that analytical standards are protected from sunlight by storage in amber glass. Crosby, et al. (1971) stated as a result of

experiments "Abstract. The toxic herbicide impurity 2,3,7,8-tetrachlorodibenzo-p-dioxin and its homologs decomposed rapidly in alcohol under artificial light and natural sunlight, the rate of decomposition depending upon the degree of chlorination. However, photodecomposition was negligible in aqueous suspensions and on wet or dry soil," (Emphasis added).

d. Sorption: Aly and Faust (1973) performed studies on the sorption of 2,4-D ester and sodium salt on three clay minerals, bentonite, illite, and kaolinite; the amounts sorbed were 0.02 to 0.14 mg per gram which was considered to be small and insignificant. The primary cause of turbidity in the ocean near Johnston Island is the coral which is eroded from the shore. Dry coral is a very good absorber of Orange and handling procedures call for the absorption of spilled Orange with coral or calcium carbonate. No data are available on the release of herbicide from contaminated coral particles which may enter the ocean, nor on the absorption/adsorption of herbicide salts or acids which may be in the ocean water.

e. Biological Degradation: Aly and Faust (1964) performed studies on the biological degradation of 2,4-D compounds in lake waters and in bottom muds. 2,4-D ester concentrations of 50 mg/l were placed in biochemical oxygen demand (BOD) dilution water seeded with 5% settled sewage. Oxygen utilization exceeded that of the control, but each ester concentration was not changed after nine days, suggesting biological hydrolysis into the free 2,4-D acid and corresponding alcohol. The oxygen uptake was attributed to biodegradation of the alcohol moieties. Concentrations of 2,4-D sodium salts at 20, 80 and 150 mg/l were prepared in 50 and 100 percent solutions of settled domestic sewage and oxygen uptake measured over nine days. The oxygen uptake was not different from the control, and no biodegradation of the 2,4-D was concluded. In lake water studies, solutions of 3 mg/l of 2,4-D sodium salt prepared at various pH's and aerated over a period of 120 days showed no change in the original 2,4-D concentration. In lake mud studies, initial concentrations of 2,4-D of 20 to 30 mg/l were decomposed biologically from 81 to 85 percent within 24 hours, but only after extensive microbial adaptation techniques. No data are available on biological degradation in sea water but based on the above it is not felt that such action would be significant in very low concentrations in the ocean environment.

f. Summary: The phenomena discussed above would tend to indicate that small amounts of herbicide esters discharged to the ocean would be hydrolyzed and exist as the water soluble sodium salt. This compound would be considered persistent because of the lack of removal mechanisms except for photodecomposition. The persistence of TCDD in the ocean cannot be accurately predicted. Baughman and Meselson (1973) have reported TCDD concentrations in fish and shellfish collected in 1970 in Viet Nam from the Dong Hai and Saigon Rivers and along the Can Guo Coast. The Vietnamese fish contained from 18 to 814 ppt TCDD, and a Cape Cod butterfish used for comparison contained not more than 3 ppt TCDD. The rivers from which the samples were collected drained areas on which 45,000 tons of Orange were sprayed between 1962 and 1970. This information is more appropriate to a discussion of biological sampling and analyses for TCDD; however, it attests indirectly to the persistence of TCDD in an aquatic ecosystem.

4. MONITORING METHODOLOGY: Monitoring of the water environment around Johnston Island can be readily and accurately accomplished. The water sampling program would consist of periodic grab samples. Grab samples collected by authorized personnel in specially prepared glass containers with teflon-lined lids are preferred over a continuous sampler arrangement. Samples can be collected along any of the shoreline of Johnston Island, and throughout the lagoon utilizing a motorized catamaran platform. Scuba divers are available on Johnston Island for sample collection within the water column. In addition to water samples, sediment samples, high food chain predators, reef and shoreline scavengers, bottom feeders (sea cucumbers), algae and coral can be readily sampled. Ocean water samples can also be collected beyond the reef, in a limited range, by a vessel which is located at Johnston Island. The rationale for selection of the location of the sampling points would include consideration of: storage and incinerator location, outfall location and ocean currents, impact on the reef and its community, and the island drinking water supply. The analysis of these samples would be performed by approved analytical chemistry procedures utilizing extraction techniques and gas chromatography-mass spectrometer instrumentation (Appendix J).

## 5. ENVIRONMENTAL IMPACT

### a. General

(1) The environmental impact on the water environment will be discussed for the proposed action and the principal alternative described in Part II. Incineration on Johnston Island will be discussed in terms of no combustion gas scrubber; however, an alkaline scrubber and a sea water scrubber are discussed for completeness and to demonstrate the potential for impact due to any scrubber water discharge. For either incineration at sea or incineration on Johnston Island, the destruction of the herbicide and TCDD will be essentially complete as a result of the incineration process. Quality control and failsafe procedures are incorporated into both cases to insure that the Orange is incinerated only under optimal conditions. Since either action involves activities at Johnston Island, the impact upon the island's water supply (lagoon) and the fringing reef is of paramount importance. In this regard, either the proposed action, or the principal alternative which does not include combustion gas treatment, are favorable since neither includes the discharge of scrubber water to the ocean. Of the two, incineration at sea is most favorable since there is literally no chance of impact upon the Johnston Island environment as a result of the incineration process. Potential impact on the island's drinking water supply from the shipboard method is limited to any accidental spillage while loading Orange on the ship for subsequent incineration at sea. This possibility will be remote because stringent precautions will be taken to preclude any accidental spillage. Incineration on Johnston Island has potential for the combustion gas plume to impact on the waters just west of the island. If either alkali or sea water scrubbers were used, the spent scrubber waters would discharge into the water environment. This scrubbing would also include major expenses in treatment unit, chemical procurement, shipment, handling and the ocean outfall. In the analyses that follows there is no consideration for TCDD because, even if it were present in the combustion gases, its concentration would be at least an order of magnitude below its typical detectable limits of 0.2 nanograms/l. As for the possibility of bioaccumulation of TCDD, incineration at sea would be the better option in that if bioaccumulation does occur, the possibility of occurrence would be slight in the sparsely populated ecosystem of the open tropical sea. At Johnston Island, no evidence of bioaccumulation was revealed during the ecological survey previously discussed.

(2) As noted under Part II.D. Failsafe, it is possible to dump the waste cargo if the safety of the crew/vessel is threatened. Also, the possibility of the vessel's sinking while loaded with waste is an environmental as well as personnel concern. Both of these contingencies were considered early in the planning for incineration at sea, and the low probability of occurrence was acceptable when compared with other positive aspects of this proposed action. The vessel has been approved by the U.S. Coast Guard for operations from U.S. ports and will follow all applicable maritime regulations. The vessel has operated for about two years without encountering a situation which required cargo jettison. The loading and conveyance via barge or ship of toxic or ecologically harmful cargo (chlorine, petroleum, fertilizer, etc.) is a normal occurrence. Quantification of the impact of cargo jettison or ship sinkage is not prudent because of the many assumptions required. Such an event in the harbor at Gulfport or at Johnston Island would present a very grave situation as regards environmental

resources. At Johnston Island, the island's water supply (ocean water for distillation), portions of the fringing reef and the biological reef communities would be very adversely affected. Cargo jettison or vessel sinkage in the open tropical ocean is not anticipated to be environmentally disastrous. Any effects would be generally localized and not persistent. The tremendous dilution afforded by the ocean, the physical chemical properties of Orange, i.e. hydrolysis to the less toxic acid, settling due to specific gravity and insolubility, biodegradation and photodecomposition of residual concentration would all tend to reduce the hazard of a large scale release of Orange into the ocean. It is noted that the Orange herbicide stock on Johnston Island was transported there via vessel and that the Orange in Gulfport would be transported to Johnston Island by vessel if the incineration occurred on Johnston Island.

b. Incineration at Sea

(1) Potential for Impact

(a) Evaluation of the environmental impact of incineration of Orange herbicide at sea requires the consideration of six major emission components: 1) unburned or pyrolyzates of Orange herbicide, 2) hydrogen chloride, 3) particulate carbon, 4) carbon monoxide, 5) carbon dioxide, and 6) heat.

(b) In order to calculate the quantities of these materials emitted to the atmosphere and ocean during incineration, a set of "worst case" conditions was established, and emission/dilution values were determined. Based on technical literature concerning the operation of the incinerator ship, an incineration efficiency of 99.9 percent for chlorinated hydrocarbon chemicals was used in these calculations. For perspective, the analyses was also accomplished for incinerator efficiencies of 99.0 and 95.0 percent. The service speed of the ship is 13 knots, but in these calculations a figure of 10 knots was used. The average monthly wind velocity in the vicinity of Johnston Atoll is 15 mph (13 knots), although the calculations used a condition of calm, with the combustion gas plume dispersing directly behind the ship and the plume dispersing to no greater width than the 14.4 meter beam of the ship. Ocean currents were not added to the dispersive forces in the following computations, although mass water movement would certainly play a positive role in the total dilution of the incinerative emissions contacting the water. An effective mixing depth of two meters was assumed for these calculations. This depth was an estimated figure that attempts to include such factors as mixing in the wake of the ship, chemical interaction of emission products with sea water, and the possible effects of toxic products on marine organisms, especially phytoplankton, which are the most prevalent life form.

(c) The biological aspects of the open sea require further discussion because these waters are generally poor in nutrients, and therefore the marine life (from plankton through the food web to large fish and mammals) is scarce when compared to that found in coastal areas or near localized upwellings due to islands. This lack of nutrients, and therefore, lack of productivity, is compounded in tropical/subtropical seas where vertical mixing of water due to seasonal changes is minimal. The clear waters of the tropical

ocean will thus contain relatively small amounts of phytoplankton per unit volume, but these populations may occur to a depth of 100 meters due to light penetration (Kinne, 1970). Similarly, most phytoplankton are not found at the surface of the water, but are located at variable depths, dependent on their specific limitations and requirements regarding light wave lengths, temperature and other physical/chemical factors. Thus, incinerative emissions from the ship which interface with the water will require some degree of mixing to establish substantial contact with the marine biota. However, the greater the amount of mixing, the greater the dilution and hydrolysis of chemical compounds. Therefore, the compromise figure of a two meter mixing depth is quite conservative for dilution and toxicity calculations.

(d) The beneficial uses of the open sea are generally limited to commercial fishing, and this utilization is even more limited in tropical/subtropical latitudes due in large part to the low primary productivity discussed above. The only major ecosystems that have lower gross per unit area primary productivity than the open ocean are desert and tundra (Odum, 1971). Therefore, the only commercially important organisms that might occur in the vicinity of the ship during the incineration process would be scattered unpredictable populations of transient biota. As will be discussed below in paragraph (2)(a), even the oxygen production of the phytoplankton community should not be impaired by the incinerative emissions.

(e) Included in Appendix N is a report prepared by the Center of Biological Studies and Research and of Oceanographic Medicine,Nice, France on "Effect on the Marine Environment of the Combustion at Sea of Some Industrial Waste." The objective of the study was to obtain data on environmental aspects during incinerator ship operations in the North Sea and then to make judgments on the effects of such operation in the Mediterranean Sea. The data acquisition was environmental in nature and did not include monitoring of the incineration process directly (stack samples). This study was of short duration but quite comprehensive. Areas of study include: smoke plume effects, pH, salinity, plankton, toxicity tests (for combustion gas collected 5 meters from the incinerator stack), food chain test and chemical and biological analyses. A conclusion of the report is: "In the present state of our knowledge, it seems that the process of incineration does not cause, certainly not short term, any special harm to the oceanic environment". This conclusion is conditional in that it may not hold for the long term and is only for the specific waste being incinerated. While the wastes incinerated were not Orange herbicide, the satisfactory results obtained certainly support the case for incineration of Orange at sea.

(2) Probable Impact

(a) Application of the above set of "worst case" conditions to an evaluation of the impact of the unburned or pyrolyzates of herbicide on the marine environment yields the following results. An incinerative efficiency of 99.9 percent allows 0.576 ton of herbicide to escape the stacks per day (24 hour incineration day) (5.76 tons at 99.0% and 28.8 tons at 95.0%). The speed of the ship as discussed would be 10 knots or 18.5 km/hour, producing a dispersal distance in one dimension of 444 km (444,000 meters) per day. The minimal

lateral dispersal as discussed would be 14.4 meters, and the mixing depth is calculated as two meters. The volume of the dispersion zone, on a daily basis, is 12.6 x $10^6$ cubic meters. Complete mixing of the 0.576 ton of unburned herbicide produces an average concentration of 0.041 mg/l in the sea water mixing zone (0.41 mg/l at 99.0% and 2.05 mg/l at 95.0%). Walsh (1972) found that oxygen production in four species of marine algae was decreased by 50 percent when the algae were exposed for a period of 90 minutes to 50-60 ppm of the technical acid of 2,4-D (author's terminology), 100-200 ppm of the butoxy-ethanol ester of 2,4-D, and 50-150 ppm of the technical acid of 2,4,5-T. Walsh found very similar results when measuring the effects of the same herbicides on the growth rates of the four algal species. Algal bioassays at the USAF Environmental Health Laboratory at Kelly AFB similarly showed Orange herbicide to inhibit growth at concentrations of 50-100 mg/l. Comparison of bioassay results with the above emission calculation for 99.9 percent incinerative efficiency illustrates that under "worst case" conditions there will exist a safety factor of three orders of magnitude before moderate toxicity effects would occur in the phytoplankton populations. (Reference Part II.F.4. of this statement for further toxicity data and literature.) In several of the referenced cases, Orange herbicide or its components showed greater toxicity (1-10 ppm) to organisms other than phytoplankton; however, the small floating plants of the euphotic zone were chosen for detailed discussion due to their much greater likelihood of exposure to any unburned herbicide fraction. Regardless of the organisms chosen for sensitivity studies, the safety factor involved continues to be at least 2-3 orders of magnitude with a 99.9 percent efficiency of incineration. It must be emphasized that "worst case" analyses is very extreme in that all of exhaust stack emission is considered to be transferred to the ocean directly behind the vessel and mixed to a depth of only two meters. In reality, it is expected that some of the unburned Orange would remain airborne for a considerable time period and that the ocean mixing zone would be much greater than that selected. Therefore, it is felt that even the concentration of unburned as pyrolyzates of herbicide after a 95.0 percent incinerative efficiency would be acceptable, particularly in view of the short duration of the incineration period.

(b) Hydrogen chloride production and discharge rate from the ship will be about 178 ton/day. Assuming this total daily amount enters the ocean, an average concentration of 12.8 mg hydrogen chloride would be added to each liter of sea water in the previously defined mixing zone. The pH excursion resulting from the addition of this amount of hydrogen chloride to sea water was calculated to be not greater than 0.5 pH units. This calculation was based on buffer capacity equations in which the carbonate system was the primary buffer. The predicted results were confirmed in the laboratory by the addition of hydrochloric acid to sea water. Any transitory effects produced by the hydrogen chloride emission should have very little disturbance on planktonic organisms and certainly no long-term effect on these populations.

(c) Calculation of particulate carbon emissions was based on about 0.5 percent of the incinerated herbicide going to the carbon form. An estimated 3.0 ton/day of carbon would be produced in this process, with an average concentration of 0.22 mg/l in the ocean mixing zone. The carbon emissions should produce no detrimental effect on the ocean environment.

(d) Carbon monoxide and carbon dioxide mass emissions to the atmosphere were calculated/estimated to be about 50 and 1000 tons per day, respectively. While these compounds are major combustion products, their mass emissions should produce no environmentally detrimental effect.

(e) Heat production from the ship incineration process was calculated on the basis of a caloric value of 10,000 BTU per pound of undiluted herbicide. A daily amount of heat equal to $1.15 \times 10^{10}$ BTU will be produced during incineration. The emission of heat can be considered in a similar context with particulate carbon and carbon dioxide (as well as the water produced by hydrocarbon combustion); i.e., these products are major components of the combustion of standard ship fuel oils. Thus, in terms of the environmental impact of these inorganic products, the ship can simply be considered to have two additional engine exhaust plumes for the duration of the incineration period.

(3) Environmental Monitoring at Sea: The above discussion of environmental impact indicates a very minimal and transient effect resulting from the shipboard incineration of Orange herbicide on the open tropical sea. The "worst case" analysis is quite conservative, and realistic incorporation of normal wind and ocean current dispersal factors will further reduce even these minimal environmental effects. In view of these facts, and the short duration and nature of the proposed operation, off-ship environmental monitoring of the ocean and air is considered unnecessary and lacking feasibility to adequately detect any transient environmental changes that may occur.

c. Principal Alternative - Incineration at Johnston Island

(1) No Combustion Gas Treatment: The remote location on Johnston Island and its meteorology indicates that the discharge of untreated combustion gases directly into the atmosphere would not result in any irreversible detrimental environmental impact to the air environment, see Part III. B. The immediate Johnston Island environment is the major concern and meteorological constraints may be required to insure that Johnston Island, the atoll, and the other islands are not affected due to changes in the normal weather pattern. There is a fringing reef to the west of Johnston Island, and this reef has been seriously damaged by turbidity from past dredging operations and continues to be affected by turbidity from erosion of the island's shoreline. Although the condition of the west reef would appear to be of the least significance to the maintenance of the atoll, it is imperative that the reef not be further degraded by fallout of constituents of the stack gas.

(a) Potentials for Impact: The constituents of concern as regards deposition from the stack plume, and reaction at the plume/ocean interface are unburned Orange and pyrolyzates, hydrogen chloride, and particulates. For the analyses that follows, the daily discharge rates are 1.2 pounds of unburned Orange and pyrolyzates, 18.5 tons of hydrogen chloride and 0.3 tons of particulates. The above discharge rate for the unburned Orange and pyrolyzates is approximately 3 times greater than that reported in Appendix E, in which the Orange constituents were undetectable and reported as less than 0.00095 pounds per day, and the pyrolyzates are 0.387 pounds per day.

(b) Probable Impact: This discussion is in two parts, impact upon the open ocean and impact upon the lagoon (primarily as related to interference with the development of the reef).

1. Open Ocean: As a "worst case" situation, it is assumed that the entire mass of each of the above combustion gas constituents is deposited onto a very small area of the ocean surface. The area has been selected to be plume shaped with a major axis of 1,000 feet and a minor axis of 100 feet. The mixing depth is conservatively estimated to be six feet, thus providing about 300 thousand cubic feet as a mixing zone. It is further assumed that ocean current in this impact area is 0.5 knots and that this condition would provide for the mixing zone to be replenished about 72 times per day. Therefore, an effective mixing volume of about 21.6 million cubic feet of ocean water can be considered to receive the deposition/reaction of the constituents of the plume. The average daily mass concentration of the unburned Orange and pyrolyzate, the hydrogen chloride, and the particulates in deep ocean water would be 0.0009 mg/l, 28 mg/l, and 0.45 mg/l, respectively. From a comparison of these concentrations with the concentrations and predicted effects on the ocean discussed under the proposed action, it is concluded that the discharge of the combustion gases into the atmosphere with resultant deposition on the open ocean surface would not cause any detrimental environmental impact in the water environment.

2. Reef Area: The major concern of this analysis is the impact of hydrogen chloride deposition on the pH of ocean water in the reef area and thus on possible inhibition of the deposition/precipitation of calcium carbonate by the reef community. The discussion will consist of a comparison of two approaches to "worst case" analysis of this discharge with a format as follows: Case 1 - assume a "worst case" deposition (that is, deposition of the entire discharge) in the general area of the reef, calculate the resulting concentration of hydrogen chloride, and comment on the significance of this calculated concentration; Case 2 - predict (utilizing the meteorological model, Appendix K) the mass of hydrogen chloride which is present in the atmosphere above the reef impact area, and comment on the significance of the deposition of the entire predicted mass.

a. Case 1: Entire Discharge-Reef Area: It is assumed that the entire daily hydrogen chloride discharge is deposited into the ocean over a square area (0.25 sq. mile) with the reef running through the center of the area. For a mixing depth of 1 meter (based on depth at the edge of the reef), the average additional concentration of hydrogen chloride from the stack discharge would be about 26 mg/l per day. The water in the impact zone is not stagnant, as assumed in the above calculation. The current can be conservatively estimated at 0.1 knot thus providing for replacement of the water in the impact zone about five times per day. This replacement factor would adjust the calculated addition of hydrogen chloride to about 5 mg/l in the ocean water. This would cause a reduction of less than one-half pH unit which would be acceptable for practically any ecosystem except possibly a living reef. Although not considered in the above calculations, the natural buffer capacity of the water in the zone described is higher than normal ocean water due to the

presence of turbidity in the form of coral (calcium carbonate) which has been eroded from Johnston Island. Therefore, even under "worst case" situation, the extent of damage on an acute basis to the reef in the localized impact zone may be quite minimal. However, the damage to the reef on a chronic basis over the duration of the disposal project cannot be predicted and continuous discharge with the deposition described under this "worst case" situation would not be recommended.

b. Case 2: Predicted Discharge-Reef Area: In actuality, the deposition of hydrogen chloride in the general area of the reef will be much less than under the above "worst case" situation. The sea level concentration of hydrogen chloride below the centerline of the stack discharge plume, at points 0.25 miles inshore of the reef, at the reef, and 0.25 miles beyond the reef are predicted under "worst case" sea level conditions to be 0.78 $ppm_{v/v}$, 0.12 $ppm_{v/v}$, and 0.05 $ppm_{v/v}$ respectively. The isopleths shown in Appendix K are for these sea level concentrations. The concentrations in the vertical direction can also be calculated. The results of the meteorological model represent a steady state solution showing the distribution of the mass of hydrogen chloride on a daily basis. The model results were applied to determine the quantity of hydrogen chloride which is present on a daily basis in the space above the impact area (0.25 sq. mile) to a height of 100 meters. This mass has been calculated to be 0.082 tons and represents 0.44 percent of the daily discharge. For determination of the average concentration within the zone, the highest level found by the meteorological model, 0.78 $ppm_{v/v}$ was applied. This value is very conservative. If the entire predicted available mass under this "worst case" approach were deposited into the ocean impact zone (1 meter deep), the average daily concentration of hydrogen chloride would be increased by 0.12 mg/l. Application of the ocean water replacement factor of five would result in a lowering of this concentration. The pH depression in this case would be negligible and, therefore, would not cause any acute or chronic damage to the reef. Comparison of above concentrations of hydrogen chloride calculated under both Case 1 and 2 with those calculated for the "worst case" situation described under the "open ocean" above indicates that the respective values of Orange and pyrolyzates and carbon particles would not cause any signifcant detrimental environmental impact.

(c) Monitoring: Monitoring of the ocean area is not necessary from an environmental standpoint. Monitoring of the Johnston Atoll would be accomplished to insure that the local area was not to be affected by disposal operation.

(2) Combustion Gas Scrubbers

(a) Alkaline Scrubber

1. Potentials for Impact: The constituents of the spent scrubber water which may have an environmental effect include: heat, chlorine residue, total dissolved solids, suspended solids, and hydrocarbons. The heat and chlorine residual would constitute major pollutant loads and, therefore these constituents are to be reduced by an appropriate treatment device, i.e.

cooling tower, spray pond, etc. Such treatment would also reduce the suspended solids concentration in the discharge. The hydrocarbon content is a minor fraction of the scrubber water and the discharge rate would consist of: undetectable Orange constituents <0.00036 pounds per day, pyrolyzates and hydrolyzates at 0.021 and 0.005 pounds per day, respectively (Appendix E). The major substance in the scrubber water will be the total dissolved solids. Although not specifically addressed, the alkaline scrubber will be operated so that the pH of the spent scrubber water will be about 8.5 units.

2. Probable Impact: The spent scrubber water will be discharged to the marine environment on the south side of the island via the sanitary sewage outfall. The mass transport of the sea water and its suspended matter (turbidity) from the sewage outfall is generally to the southwest and therefore, the remainder of the island's aquatic environment is minimally involved. However, during certain conditions, summer season and easterly regional flow, sluggish circulation has been observed along the southern shore of the island. This has resulted in a long residence time and very limited mixing for the sewage discharge (Kopenski and Wennekens, 1965). The reef area which would be primarily affected by this flow situation is located on the west side of the island. The disruption and extensive silt production from the major dredging operation in the early 1960's and the characteristic of the ocean currents (high turbidity from erosion of the south side of the island) have already resulted in a depauperate reef community on the island's west shore (Brock et al., 1965). The high total dissolved solids concentration of the spent scrubber water will cause a relatively small mixing zone in the area of the discharge where the specific gravity will be adjusted. Calculations show that one million gallons of ocean water will be more than enough to adjust the specific gravity of one day's flow of spent scrubber water to a specific gravity which is essentially the same as that of the ocean. For an ocean current of 0.25 knots and a dispersal pattern 10 feet wide and 10 feet deep, approximately one million gallons of ocean water would be available to adjust the specific gravity of one hour's spent scrubber water flow (8,300 gallons). In addition, a major part of the total dissolved solids is sodium chloride ~35,800 mg/l (chloride ~22,000 mg/l), with the normal ocean chloride concentration being ~20,000 mg/l. Therefore, under the above conditions, the mixing zone should not extend farther than 3,000 feet from the outfall line. The suspended solids (80-100 mg/l), some of which may be removed in the treatment processes, represents a discharge of solids. The suspended solids are primarily elemental carbon, see Appendix E, and at a maximum of about 200 pounds per 200,000 gallons are not considered significant. The turbidity present in the Johnston Island aquatic environment, particularly south and southwest of the island, would tend to negate the impact of a wastewater discharge containing suspended solids. The minor fraction of hydrocarbons would be further diluted in the receiving water and not be significant from an environmental standpoint. The environmental impact of this alternative is minimal and would be manifested in a small mixing zone near the wastewater outfall.

3. Monitoring: This alternative is excellent from the monitoring aspect in that water, sediment, and marine biological samples in the impact area can be readily collected. The discharge occurs in the lagoon ecosystem and extensive analytical chemistry and biomonitoring of spent scrubber water prior to discharge will be required.

(b) Sea Water Scrubber

1. Potential for Impact: The constituents of the spent scrubber water which would have environmental impact include: heat, chlorine residue, hydrogen chloride (hydrochloric acid), suspended solids and a minor hydrocarbon fraction. Of primary concern are the heat, chlorine residue, and the dissolved hydrogen chloride. A daily discharge of 500,000 gallons of spent scrubber water would contain some 37,000 pounds (~1.0%) of hydrogen chloride, and have a temperature of ~160°F and a chlorine content of ~250 mg/l. The hydrocarbon content would be similar in magnitude to that stated above for the alkaline scrubber.

2. Probable Impact: Although the environmental impact of this wastewater stream could be significant, the major constituents are not considered as persistent pollutants; the heat and chlorine residual will be dissipated and the hydrochloric acid is readily absorbed in the ocean. The buffer capacity of ocean water and its regenerative natural forces make the ocean an acceptable sink for certain acids, particularly hydrochloric acid. On a mass basis, the discharge of 18.5 tons of hydrogen chloride into the ocean is insignificant; however, the impact of such a discharge on the pH in the discharge zone must be considered. Buffer calculations, using the carbonate species as the only buffer, reveal that if 75 million gallons of ocean water are mixed with one burn day's discharge that the pH excursion would be from 8.3 to 6.5 units. It is noted that the pH change will be temporary and the normal ocean pH will be rapidly established. On a mass basis, the chloride added to this volume (75 million gallons) is 58 mg/l which is of minor consequence when compared to the usual concentration of ~20,000 mg/l. The ocean water required to dissipate the heat and chlorine residual is less than that required for absorption of the hydrogen chloride. To determine a mixing zone, the rate and method of waste stream discharge and the flow of the receiving water is required. If an ocean flow of 0.25 knots and a dispersal zone of 10 feet wide by 10 feet deep is assumed, then in one hour some one million gallons of water will flow by the outfall. Since approximately three million gallons are required for neutralization of one hour's wastewater discharge, the mixing zone may extend to 6,000 feet from the discharge point. This relatively long mixing zone will require that the outfall be placed so that the acidity of the discharge does not affect the reef during the time duration of the project. The ability of the ocean to accommodate acid waste on a "slug" discharge basis has been documented. The following is from Technical Memorandum No.39, U.S. Army Corp of Engineers: "The permissible pH range for the coastal waters of New York and New Jersey, according to water quality criteria (EPA, 1972), should be from 6.5 to 8.5. The pH range observed in the vicinity of the dumping grounds of the N.Y. Bight, ranges from 7.10 to 8.40, and does not exceed the prescribed limits. The only drop in pH would be observed in the waters of the acid dumping grounds, immediately after an acid dump. The low pH value in this area would occur for brief periods. As discussed earlier, Redfield and Walford (1951) have shown that the pH of the water from the wake of an acid dumping barge was above 6.0 in all samples collected more than 3 minutes after dumping and a pH of 7 was reached about 3.5 minutes after dumping." The daily discharge of 500,000 gallons of spent scrubber water containing 18.5 tons of hydrogen chloride represents a

stream of sufficient acidity to cause certain detrimental environmental effects. In addition, the heat and chlorine residual of this stream are sufficient to cause localized detrimental effects. The suspended solids and the minor hydrocarbon fraction of the wastewater are, as previously described, not considered significant as regards environmental impact. It is imperative that this stream not be discharged into the ocean where there are beneficial uses, i.e., swimming, fishing, reefs, water supply within the mixing zone.

3. Monitoring: The discharge point would be located within the vicinity of Johnston Island, either in an area further off-shore than the present sanitary sewage discharge or in an area to the southwest of the island. In either case, ecological monitoring, primarily in the form of water samples and other samples which can be collected from a boat, can be readily accomplished within the impact zone.

D. MARINE FLORA AND FAUNA ON JOHNSTON ISLAND

1. SCOPE OF CONSIDERATIONS: The potential for adverse effects on marine ecosystems is greater with incineration on Johnston Island than with incineration on the open ocean. The fertile waters of the atoll yield a biomass many times greater than that of the relatively nutrient deficient open ocean. The potential effects of the incineration of Orange herbicide on both marine flora and fauna of Johnston Atoll are considered together in this section since the potential for harmful effects will originate from the same source and will concern the same areas of the underwater atoll. The distribution of fish on the atoll is divided into three zones: 1) the northern peripheral reef area, 2) the southern shoal reef area and 3) the bank or lagoon shoals. The "northern reef area" is characterized by pelagic species of fish such as the shark on the seaward side of the reef and by inshore types of fish on the lagoon side of the reef. The "southern reef area" has fewer numbers and varieties of fish. The "bank shoals" or lagoon area is characterized by large numbers of inshore types of fish. In all, 194 species of inshore fish have been identified on the atoll. Gosline (1965) classifies the Johnston Atoll fish fauna into 4 components: 1) endemics, 2) fish that have made Johnston a stopping point on their migrations north, 3) fish that have made Johnston a stopping point in their southward travels, and 4) the pelagic fish to whom Johnston is of little or no significance. Only two species of Johnston fishes have not been taken elsewhere. These are Centropyge nigriocellus and C. flammeus, both butterfly fishes; neither are abundant at Johnston. A total of 175 species of marine arthropods inhabit the lagoon water together with 37 species of Echinodermata and 18 species of Cnidaria (e.g. jellyfish, corals). Dredging operations in 1964 directly destroyed 700 acres of living coral. The silt from the operation seriously affected much larger areas of coral. A parallel reduction in the number of associated invertebrate species and fish also occurred (Amerson, 1973). A large portion of the southwestern reef was seriously affected and remains so today. The algae were also damaged by the increased silt in the dredging operation. Also, the dredging affected the distribution of the 67 benthic marine algae identified on the atoll. At least 58 species of mollusca and 12 species of annelida inhabit the atoll. The ocean currents approaching the atoll have a relatively sparse plankton population.

2. POTENTIALS FOR IMPACT ON AQUATIC PLANTS AND ANIMALS: It is obvious that contamination of the waters of Johnston Atoll with large amounts of Orange herbicide would result in disastrous effects upon the biota of the lagoon and reef. Thus, the storage of the herbicide and the proposed incineration site was so situated that any unenvisioned, catastrophic accident would not affect the majority of the barrier reef and lagoon. The use of a scrubber system to treat combustion gas would produce a certain localized and controlled amount of water pollution in the down-current area of the outfall. The use of no scrubber system would be expected to affect a larger area where the exhaust gases contact the ocean. However, meteorological models, Part III, C., indicate that combustion gas components at the plume/ocean interface would be in such low concentrations that there would be minimal effect on the marine ecosystem.

3. PROBABLE ENVIRONMENTAL IMPACT ON AQUATIC PLANTS AND ANIMALS

a. Toxic Chemical and Acid-Base Effects

(1) Incomplete Combustion Products: Possible toxic chemicals from incomplete combustion would include Orange herbicide components and their pyro-

lytic products. However, the test incinerations and bioassays (see Appendix E) proved that Orange herbicide can be incinerated without the production of highly toxic effluents. Continuous analytical monitoring, biomonitoring and failsafe mechanisms described in this report will safely protect against the release of harmful toxic chemicals. Therefore, environmental effects from incomplete combustion products are not considered probable. Biomonitoring would detect very minute amounts of unoxidized herbicide.

(2) Complete Combustion Products: Environmental effects could result from the planned, efficient combustion of Orange herbicide which will produce potentially harmful corrosive gases, carbon particles, heat and a minor fraction of hydrocarbons. Two situations are considered where no treatment (scrubbing) of the gases would be used: 1) incineration on the boat would have no impact on the waters around Johnston Island, especially because of wind and distance factors, and 2) incineration on Johnston Island using no scrubber would be expected to impact on the waters west of the island in a manner quantitatively similar to that predicted for incineration at sea. The major difference between the two is the increased numbers of plants and animals in the waters on, and closely surrounding the atoll. If the saltwater scrubber were to be used, the scrubber water must be delivered into the ocean far enough beyond the reef to provide sufficient dilution in deep water and to insure that the diluted effluent does not flow back onto the reef. The alkaline scrubber system would neutralize the acidic elements' potential toxicity by conversion to their salt forms. Other treatments described earlier would remove chlorine and produce cooling of spent scrubber water. Therefore, probable environmental impact will be confined to a small, definitive mixing zone. The salinity changes would be expected to be of minimum consequence in the warm surface water which has a normal salinity between 34.6% and 34.8%.

b. Thermal Pollution: The size and position of the thermal mixing zone will affect the extent of the environmental impact of thermal pollution from the incineration of Orange herbicide. Normally, the extent of a mixing zone is directly related to requirements for maintaining free passage of migrating aquatic organisms in the body of water. In contrast, the major concern for Johnston Atoll was to select a mixing area away from the lagoon and reef. The location required that currents would direct the effluent away from the atoll in the most efficient manner available. The current sewer outfall on the south side of Johnston Island would be the optimum site for the alkaline scrubber water outfall. This already-proven site would place the thermal mixing zone in an area where a mixing zone already exists and ecological alterations have already occurred. Thus, the major expected impact would be the resulting shift to more heat tolerable species of plants and animals inhabiting the mixing zone. The warm-water inshore fishes of the lagoon and migrating fishes can easily avoid the mixing zone without harmful effects from the increased warmth of the water. Since the salt water scrubber effluent would entail a much larger mixing zone, the outfall would be placed southeast of the reef. This will place the effluent mixing zone in deeper, colder water in an area where currents will direct it away from the reef. The effects of the heat should be rapidly dissipated.

c. Carbon Particle Effects: Fine carbon particles, suspended solids, in the effluent could produce damage to living coral. Suspended fine particles from earlier dredging operations and sediment-laden water from the shoals have severely affected the coral on the southwest portion of the reef. Carbon particles from the incineration operation are not expected to contact the living coral

reef. The observations made during the test burn of Orange herbicide indicate that these particles will rapidly settle out. However, the situation will have to be monitored to determine any impact on living coral. Again, the alternative salt water scrubber effluent would be placed so that currents would carry the carbon particles away from the reef. The use of no scrubber system would result in such a widespread dispersion of the particles as to be of no ecological significance.

## E. TERRESTRIAL FLORA AND FAUNA

### 1. FLORA OF ISLANDS

a. Scope of Considerations: Terrestrial vegetation is relatively sparse on the 4 islands of Johnston Atoll. Only three species of native, vascular plants existed in 1923. However, the activities of man upon the islands have been responsible for most of the intentional or accidental introduction of 124 other species. Many species are ornamental and exist only by benefit of special care. Other introduced species or adventive types have adapted to the coral soil and climatic conditions. Damage to the terrestrial flora on Johnston Atoll, is not expected to occur due to Orange disposal.

b. Potentials for Impact

(1) Complete Combustion of Orange herbicide resulting in the production of corrosive hydrogen chloride and chlorine in the exhaust gases.

(2) Incomplete Combustion resulting in escape of unoxidized herbicide and other pyrolytic products in exhaust gases.

(3) Accidental Spills of liquid herbicide on land producing localized effects on terrestrial plants.

c. Probable Impact: No detrimental effects to terrestrial vegetation would be expected from the incineration of Orange herbicide on Johnston Island. Meteorological constraints would be utilized to insure that the effluent gases from the unscrubbed stack gases do not impact on the islands in harmful concentrations. The incinerator operation under the principal alternative would contain sufficient safeguards to protect against incomplete combustion or accidental spills. However, should even these safeguards fail and the unlikely event of an atmospheric contamination occurs, the physical position of the operation on the atoll in relation to prevailing winds would protect the flora on the four islands from atmospheric exposure.

d. Monitoring Methodology for Air Contamination: With incineration aboard ship no products of combustion would ever reach the atoll area so that monitoring will not be necessary. For the principal alternative of incineration on Johnston Island both analytical and biological monitoring for air pollution would be used. Biological monitoring using highly sensitive indicator plants would signal trace air contamination with herbicides or corrosive chemicals in time to prevent extensive damage to other plants should man-made safeguards fail.

2. FAUNA OF ISLANDS

a. Scope of Considerations: Except for man, seabirds are the most ecologically important species on the four islands of Johnston Atoll. There were originally no mammals on the islands and only one species of reptile. Man introduced the dog and cat, rodents and three species of geckos. Also, sixty-eight species of arthropods are associated with and distributed in relation to the bird populations on the islands. All the terrestrial animals on the atoll are of relatively little importance in relation to the considerations that must be given to protect the large number of seabirds that use the islands for breeding and nesting rounds. Sand Island is the major island of importance to the birds. Man's activities on the other islands limit the size of their bird populations.

b. Potentials for Impact: Exposure of the animals on the atoll's islands to atmospheric contamination from improper functioning of the incinerator could result in harmful effects related to the concentration-dose of such theoretical contamination. The noise and activity of the incineration operation could discourage seabirds' nesting activities if placed too close to the nesting areas. Damage to the birds' food supply would also be detrimental if it should occur.

c. Probable Impact: No impact on the terrestrial fauna of Johnston atoll is expected from the incineration of Orange herbicide. Any atmospheric contamination would be signaled early by indicator plant damage at concentrations low enough to forestall damaging doses to animal life should any incineration safeguard systems fail. Most certainly, incineration of the herbicide on shipboard, downwind from the atoll, poses the least chance of all of exposing the animals of the atoll to combustion gases. With the option of incineration on Johnston Island, the proposed location of the incinerator on the southwestern tip of the island is purposely positioned so that any air contaminants will be carried away from the other islands. Winds are from between northeast and east 85% of the time on the yearly average. Also, the site of the incinerator will be far enough from Sand Island to prevent any disturbance of the birds there. Sand Island is 2-1/2 nautical miles from the proposed incinerator site. The seabirds feed from the ocean in a 100 mile radius around Johnston Atoll rather than from the shallow waters of the atoll. Thus, their food supply could not be affected by the incineration operations. As noted earlier, studies with phenoxy herbicides indicate that they are not highly toxic to birds. Also, these herbicides do not accumulate in the food chain.

F. SOIL (CORAL AND SAND)

1. MOVEMENT: There are no research data on the movement of the herbicide Orange in compacted coral. However, it is known that $CaCO_3$ rapidly "fixes" herbicide Orange and in fact has been suggested as a chemical compound to "clean up" spills of the herbicide. Based on observations made on Johnston Island, spills of the herbicide are readily and rapidly contained. After 2,4-D, 2,4,5-T and TCDD reach the soil each moves through the biosphere and accumulates or degrades according to its own chemical and physical properties (Advisory Committee, 1971). Once the herbicides and TCDD reach the soil they become immediately subjected to physical and chemical actions that continually reduce the amount remaining at the site of application. These actions include degradation by soil microorganisms, leaching and surface movement by water, volatilization, movement by wind and photochemical decomposition (Amerson, 1973).

2. PERSISTENCE: There are no available data on the persistence of 2,4-D and 2,4,5-T in compacted coral. However, the limited diurnal and annual variation of the relatively high temperatures - annual mean of 79.3°F with daily variations of only 7-8°F - and of the high relative humidity (annual mean is 75%) (Amerson et al., 1973) should favor the rapid decomposition of the herbicide. The persistence of 2,4,5-T, influenced by its rate of application, climatic conditions and other factors, occurs most rapidly under conditions that are optimal for the growth of soil bacteria (Zelinski and Fishbein, 1967). Loss of all phytotoxicity of 2,4,5-T applied to the soil was reported to occur in 3 - 6 months after application (Kearney and Negh, 1972).

G. THE ECOLOGICAL SIGNIFICANCE OF JOHNSTON ISLAND: AUTHORITATIVE OPINIONS.

Amerson (1973) states in the "Ecological Baseline Survey of Johnston Atoll, Central Pacific Ocean" that the document was reviewed by four well known ecologists in various fields. The purpose of the reviews was to assess the ecological significance of Johnston Atoll. Their opinions have been summarized as follows:

1. Ray Dasman of the International Union for Conservation of Nature states: "Because of its small size, and extreme isolation Johnston Atoll was originally of considerable ecological interest as an area in which it would have been possible to follow the slow process of colonization and establishment of species on oceanic islands and to study over the years the processes that may have led to the development of new races or species in its limited biota. The opportunity was lost with the exploitation of the island and later with its development as a naval and air base. However, human occupancy of the island followed by the introduction and establishment of many new species of plants and animals has created an equally interesting ecological situation in which the interactions among its still limited biota could profitably be studied. Such situations, however, occur on many other isolated oceanic islands, and Johnston cannot be considered as particularly unusual or of outstanding interest from this point of view."

"Considering the dry land area of Johnston Atoll, the greatest concentration of ecological interest is to be found on the remaining natural island, the ten acres of the western portion of Sand Island. This is the principal breeding area for seabirds and appears to support the most complex terrestrial biota. Sand Island is of major importance for its breeding population of Sooty Terns and of significant importance for breeding populations of Red-footed Boobies, Brown Noddies, Wedge-tailed Shearwaters and Great Frigatebirds. It is significant also as a wintering area for shorebirds, notably the Golden Plover and Ruddy Turnstone. Every effort should be made to minimize disturbance of this area in the future and to maintain it as a refuge for seabirds. With protection and freedom from disturbance its value as a seabird breeding center can be expected to increase, and it will achieve greater value as a site for ecological studies. By contrast, the ecological interest of the eastern, man-made portion of Sand Island, of Johnston Island, of Akau and of Hikina Islands is slight at the present time, although if disturbance of these areas were to be greatly reduced in the future, they would no doubt be colonized in time by breeding populations of seabirds." (Emphasis Added)

"The marine area of Johnston Atoll can be considered of equal interest to the terrestrial area. Although the marine biota has not been thoroughly studied, the inshore fish population appears to be of considerable biological interest and it is likely that further studies will reveal a higher degree of endemism than is now reported, particularly among the marine invertebrates. Considerable damage to the marine fauna has resulted from past dredging and filling operations. Future activities of this nature, when necessary, should be conducted with greater precautions to minimize damage to reef and lagoon fauna."

"Considering that Johnston Atoll may continue to be used for a variety of purposes in the future it is recommended that particular attention be given to protection of the western portion of Sand Island for the purpose of maintaining the seabird breeding colonies and their associated biota and to maintaining

the reef and lagoon biota in a healthy state, allowing for its recovery from past disturbance. Avoidance of pollution and siltation of the reef-lagoon complex should be given priority."

2. Robert E. Jenkins of The Nature Conservancy states:

"Of particular importance to Johnston Atoll is the recurring theme of its seabirds. In spite of all of the "reconstruction" which has severely changed the original natural environments in the area, there is still a tremendous seabird population using the near-shore feeding grounds or breeding--primarily on Sand Island. The information collected on these birds forms a truly impressive body of data. The monumental accomplishment of having banded over 300,000 individual birds in the course of 6 years has already added greatly to our knowledge of population dynamics, distribution, faunal exchange, site constancy, breeding systems, species composition, etc., and in the years ahead should add even more to our understanding of some important components of the oceanic system."

"There have also been fairly extensive studies made on the effect of the dramatic and pervasive human alteration of Johnston Atoll. A continuation of these studies will give us new insight into the effect of dredging on the physical and biological environment of coral reefs, the effects of greatly enlarging the terrestrial mass in the area through the creation of entirely new superaquatic platforms from native materials, and the effects of stocking these (however haphazardly) with a large number of exotic species of plants and animals. The increase in the vascular plant flora from three species in 1923 to 127 in 1973 provides us with a very interesting case in point. In the last few years, the relatively young discipline of island biogeography has been yielding new insights on a number of ecological and evolutionary phenomena such as colonization, competition, extinction, community stability, genetic adaptation, ecological exclusion, niche dimensions, etc., and the Johnston Atoll situation represents a unique experiment in this field which could richly reward intense scrutiny. Aside from the population and community phenomena which are favorably isolated for investigation, the effects of the biota in modifying the raw, new substrates over time should be carefully observed and documented. Within the aquatic environment, the same processes of ecological recovery from the effects of dredging and filling provide us similar opportunities."

3. Lee M. Talbot, Senior Scientist, Council on Environmental Quality states:

"Johnston Atoll has high ecological significance for two primary reasons. The first derives from its isolated location in the central Pacific Ocean. Study of the organisms found there can contribute significantly to the understanding of migration and distribution mechanisms and evolutionary ecology of a variety of types of organisms. The inshore fishes are exemplary of this in connection with the distribution, dispersion, and introduction of warm-water fishes."

"Another allied source of ecological significance to this isolated Atoll derives from what studies based there can indicate about the migratory movements of birds, their parasites and pathogens, marine mammals, reptiles, and fishes. The bird studies have been the most extensive to-date, of course, and the detail in this paper reflects that."

"The other, and in my opinion more important reason for its significance, derives from the history and nature of the Atoll. In its present form it is very largely man-made. Even those parts that have not literally been constructed by man have been very significantly modified. This history is well documented with scientific collections, descriptions, and maps and with extensive photographs. At the same time, it is a relatively simple ecosystem from the standpoint of topography and other physical aspects. A high percentage of the terrestrial organisms have been introduced by man (e.g., 124 out of 127 species of vascular plants, and all of the terrestrial mammals and reptiles). Since most of these introductions are of comparatively recent origin and many can be reasonably well dated, the Atoll provides an almost unique laboratory in which the mechanisms of dispersion, introduction, adaptation, and development of an ecosystem and its component species can be studied. The uniformity and simplicity of a substrate further facilitates study and comprehension of the mechanisms and isolation and understanding of the dynamic processes involved."

4. George W. Watson, Curator of Birds, National Museum of Natural History states:

"The birds frequenting the atoll may be classified according to activity into breeders, offseason or prebreeding migrants, and vagrants. The ecological significance of the last is nil. The island does not play any role in the survival of the species and perhaps very little role in the long-term survival of the errant individual. Far and away the most important breeding bird is the Sooty Tern which produces about 50,000 chicks a year on Johnston Atoll. Lesser numbers of Brown Noddies and Wedge-tailed Shearwaters use the island for breeding as do relatively insignificant numbers of other species. None of these species is restricted to Johnston Atoll nor is the population on Johnston Atoll a significant fraction of the Pacific Ocean population of the species. There are no endemic landbirds or seabirds restricted to the islands."

"The same is true of the five species of shorebirds that regularly visit the islands on migration. Most of these are wide-ranging and scatter from their largely arctic breeding grounds over much of the tropical oceans of the world. One species, the Bristle-thighed Curlew is considered rare and endangered on its breeding grounds in Alaska. It disperses so extensively to islands in the tropical Pacific Ocean, however, that even if the Johnston Atoll birds were eliminated, the total species population would not be jeopardized."

"What still remains unknown is the importance of seabirds in the overall marine environment. Obviously in the waters near the island concentrations of birds can exert predation pressure on small fish, crustaceans and squid and thus limit populations in relatively infertile tropical waters. There is little feeding by seabirds in the lagoon or other waters near the atoll. (Emphasis Added) Sooty Terns are probably feeding at up to a full day's flight away from the atoll. Some of the other species may also have great daily flight ranges. Nor is it known exactly where most of the individuals that breed on the island go during the period when they are not breeding. It is known that the island serves as resting or roosting ground for numbers of birds that breed elsewhere, particularly boobies from islands to the north in the tropical Pacific Ocean."

H. HUMAN WELFARE: The discharge of effluent streams resulting from the incineration of Orange at sea or on Johnston Island will not endanger the health of any personnel either aboard ship or on Johnston Island. The data contained in Appendices D and E attest to the essentially complete destruction of herbicide by the incineration process. For the proposed action of incineration at sea, only those personnel who are directly involved in the disposal project, that is the ship's crew, will be subject to any of the project's risks. The potential for exposure of personnel aboard the ship to herbicide will be very minimal. The Orange storage tanks are enclosed and the exhaust gases from the ship's incinerators will be carried away from the ship. In addition, there is no means possible for contamination of the ship's drinking water supply with Orange. The relatively few personnel involved, the fact that all personnel involved are actually working on the project, and the complete lack of a means of exposure of personnel to the incinerator effluent stream, makes incineration at sea highly favorable from the human welfare standpoint. For incineration on Johnston Island, consideration must be given to all of the personnel employed on Johnston Island both from the standpoint of potential air and drinking water contamination. The exhaust stack will be located on the west side of the island so that the normal and dominant winds will carry the combustion gases away from the atoll. Drinking water is provided for Johnston Island via distillation and the water intake is located on the north side of the island. The scrubber water discharge, if a scrubber was to be used, would have to be constantly monitored, and the discharge point would have to be selected so as to minimize any potential for contamination of the water supply. If a scrubber was not used, the water supply will still be constantly monitored to insure that any impact by fallout of stack gases will be detected. In addition, the stack height will be such that the majority of the exhaust gas will not fallout in the atoll. The principal alternative - incineration on Johnston Island - while acceptable as regards human welfare is not as favorable as the proposed action - incineration at sea. This is due to the proximity of personnel not directly related to the project and of the source of the island's water supply. In addition, the proposed action is more favorable since it minimizes exposure time of personnel who will be involved in handling and transfer operations. While proper industrial hygiene procedures will be required, incineration at sea can be completed much faster than incineration on Johnston Island and, therefore, any exposure time will be reduced. The safety and industrial hygiene aspects of each option have not been discussed, but any contractor working on this project will be required to concur with all applicable legislative criteria.

I. BENEFICIAL ASPECTS OF THE PROPOSED ACTION: There are no beneficial aspects, in the absolute sense, for the proposed disposal action. However, there are very important benefits to be obtained by performing the disposal action in a timely manner. These benefits include: 1) minimizing the cost involved in maintenance of the Orange storage areas, 2) making the land in the current storage areas available for other use, and 3) eliminating potential contamination/pollution of the Johnston Island lagoon. The present storage of the Orange at Johnston Island is in 55-gallon drums at a site adjacent to the lagoon which is not a desirable situation from these three aspects. Routine maintenance of the storage site is accomplished to identify leaking drums, fix or redrum the leakers, and contain (by absorption in coral) any spillage resulting from the leakers or the redrumming operation. This operation is quite expensive. The land area which comprises the storage site on Johnston Island is high value property and its dedication for long term storage of Orange represents a constraint on future plans and activities on the island. The normal operation of the storage site represents a low level potential for contamination of the lagoon water. However, a catastrophic event affecting the herbicide storage area could cause massive spillage and could result in pollution of the lagoon, possible contamination of the drinking water supply, and possible damage to the reef. Incineration at sea is favorable from these considerations in that the Orange herbicide would be quickly and totally removed from the Johnston Island environment. The removal of Orange at Johnston Island would require two loadings of the ship, which means that all of the Orange could be removed from Johnston Island in less than one month from the start of the project. Incineration on Johnston Island would require that operations involving Orange handling and transfer be continued for the duration of the incineration process. It would also probably require use of even more land, for installation of the incinerator, than is currently used for storage. The time period for incineration on Johnston Island has not been fixed since an incineration scheme has not been decided as yet; however, it is felt that, in a trade off between facilities and manpower cost, about one year would be required. Another somewhat indirect benefit which can be discussed on the basis of the time and place of the incineration project is the costs associated with ecological and technical monitoring associated with the project. Monitoring programs are very expensive as regards equipment, manhours, travel requirements, chemical analyses, and data analyses. Incineration at sea which does not require ecological monitoring would be more favorable than the principal alternative of incineration on Johnston Island, in which an extensive monitoring program will be required during and for a distinct time period after completion of the project. In summary, there are very important beneficial aspects which can be attained by the timely completion of the disposal project and these are best served by incineration at sea.

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PART IV ADVERSE ENVIRONMENTAL IMPACT WHICH CANNOT BE AVOIDED: There will be no adverse envrionmental effects from the disposal of Orange herbicide by the proposed incineration. A manufactured product, which cannot be utilized for the purpose for which it was manufactured and purchased, is to be disposed of via incineration which converts it into the basic chemical compounds: carbon dioxide, water, and hydrogen chloride. The incineration process will discharge these compounds in exhaust streams into the environment. Their discharge will result in a minimal impact of a transient nature in a relatively small zone near the point of discharge; however, these compounds are compatible with the atmosphere and ocean environment of the open tropical sea. It is feasible to destroy at least 99.9 percent of all the herbicide and its TCDD content, see Appendices D and E. Any pyrolytic hydrocarbon products of undetectable herbicide feed constituents in the combustion gases will not be of sufficient magnitude to be environmentally significant, see Appendix E. Less than one percent of the herbicide will be converted to particulate material, primarily elemental carbon, which will be discharged with the exhaust stream. These particulates will not be of sufficient magnitude to result in other than minimal localized environmental effects.

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# PART V ALTERNATES TO THE PROPOSED ACTION


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A. PRINCIPAL ALTERNATIVE - INCINERATION ON JOHNSTON ISLAND: The Air Force proposes the destruction of Orange herbicide via incineration on a ship at sea. However, this action is dependent on the EPA issuing a permit in accordance with the Marine Protection, Research and Sanctuaries Act of 1972. If the EPA administrator decides not to issue a permit, the Air Force will pursue the principal alternative of incineration in a facility which would be constructed on the west side of Johnston Island. A detailed description of the incineration parameters and the environmental analyses of the operation are presented in Parts II and III. The facility on Johnston Island would probably be designed to incinerate about 206 drums of herbicide per day. At this rate, approximately 200 burn days would be required to incinerate all 2.3 million gallons of the Orange stocks. If a portion of the herbicide is registered by EPA, then the project time would be shortened or a smaller facility would be constructed. The incineration facility on Johnston Island would provide essentially complete destruction of undiluted Orange herbicide, and the environmental impact of the facility would be minimal. The potential impact on the delicate ecosystem of Johnston Atoll and lengthy project duration make this alternative less desirable than the proposed action.

B. CONVENTIONAL INCINERATION IN THE CONUS

1. LIQUID WASTE INCINERATORS

a. General: The term "conventional" is used to describe incineration systems which have a refractory lined combustion chamber and afterburner section and use a "flame" concept of combustion. These systems can handle a wide range of waste volumes from 1,000 to 10,000 pounds per hour. The normal design termperature range is 1800 to 2100°F; above 2100°F construction material becomes an operational and economic problem. The temperature attained in a given incinerator is a function of the physical unit, i.e. size, shape, construction materials, the caloric value of the waste fuel, and the fuel to air ratio. To insure efficient combustion, at least 20 percent excess air is required . The means of conditioning and injecting of the fuel are also important factors in incineration efficiency. A turbulent environment is desired in the combustion zone to insure exposure of the fuel to the heat sink and to prevent insulation of fuel particles by other fuel particles. Fuel injection systems are designed to insure intimate mixing in the combustion chamber; the viscosity and atomization of the fuel must be controlled to insure thorough vaporization and combustion before being exhausted from the incinerator. Atomization can be accomplished mechanically (nozzles), by two phase flow (fuel/air mixture) or by a combination of both methods. For atomization, the liquid waste should have a maximum viscosity of about 160 centipoises. At greater viscosities, atomization may not be fine enough and the resultant droplets of unburned liquid may cause smoke or other unburned particles to leave the unit. Viscosity is usually controlled by heating the liquid with tank coils or in-line heaters. Another important factor in system efficiency is the "stay time," i.e. the time duration in which a fuel particle remains in the combustion zone. The longer the "stay time" for a fuel particle the better its chance for combustion. The stay time, around three seconds for conventional incinerators, is limited by system size, air flow, turbulence, and gas dynamics. A conventional incinerator is best operated on a continuous basis as the cooling and heating of refractory material must be done properly to insure that such materials are

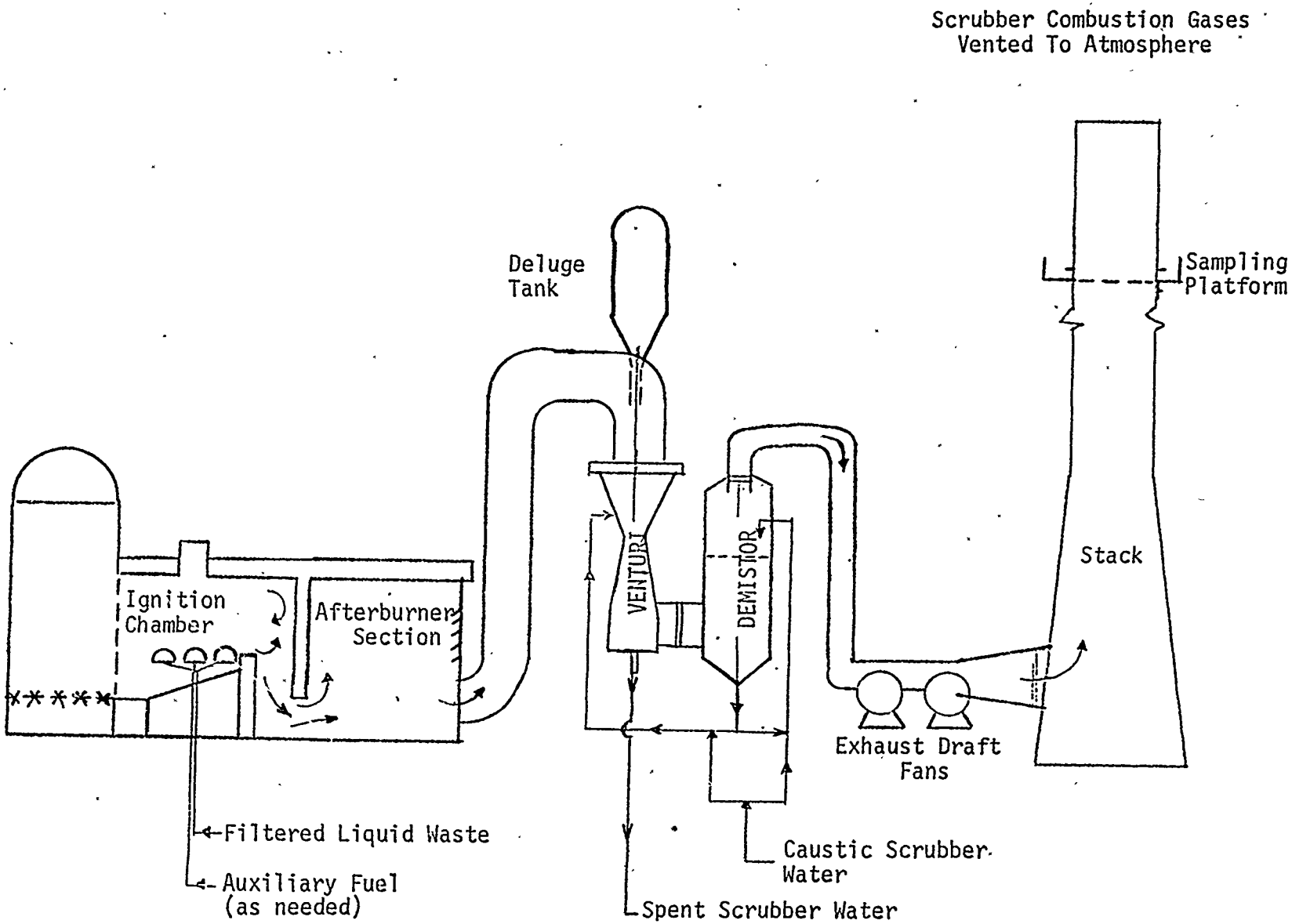



FIGURE V-1: SCHEMATIC OF COMMERCIAL INCINERATOR FACILITY

not damaged. This situation makes the conventional incinerator more appropriate to long term burning projects as opposed to projects which require frequent start/stop procedures. In addition, the size of the units and the type of construction are not generally conducive to transportation and construction on a portable or semi-permanent basis.

b. Diagram: A schematic of a commercial incinerator system is shown in Fig V-1. Incineration of chlorinated hydrocarbon fuels such as Orange will result in hydrogen chloride in the combustion gas; the hydrogen chloride is removed by the venturi scrubber which uses a caustic scrubbing liquid. The scrubber water may require neutralization prior to discharge to a natural water system. The incinerator system also includes gas analysis equipment, accessory fuel storage/feed systems, and process control systems.

2. INCINERATION AT ROCKY MOUNTAIN ARSENAL

a. Introduction: An incineration system has been constructed, installed, and operated at the U.S. Army Rocky Mountain Arsenal (RMA) in Colorado which, by technical investigation, appears to be capable of incinerating the Orange in an environmentally safe manner. The RMA incinerator is used to destroy mustard agent and many of the problems associated with the incineration of mustard and Orange are similar. The problems arise from the similarity between mustard and Orange as regards certain physical and chemical properties and environmental impact. These problems include: fuel conditioning, high temperature incineration, acceptable effluents, real time monitoring and drum disposal. The problems are handled at RMA; but, the facility is necessarily of considerable value, and the waste feed rate of ~2 gallons per minute (gpm) requires considerable time to incinerate a given quantity of material. The information below regarding the RMA facility has not been reviewed by U.S. Army, nor has any action been taken to contract the RMA facility for Orange incineration. This proposal is presented to show that incineration in the CONUS is a viable technical and environmental option. For additional information on the RMA facility the reader is directed to "Final Environmental - Impact Statement for Project Eagle - Phase I, The Disposal of Chemical Agent Mustard at Rocky Mountain Arsenal, Denver Colorado, Headquarters, Department of the Army, Washington 25, D.C."

b. System Description: The system consists essentially of fuel feed tanks, incinerator, packed tower scrubbers, electrostatic precipitator, a spray drier, and a "thaw house" for temperature control of the fuel. The combustion gases are passed through a packed column liquid scrubber which utilizes sodium hydroxide for acid gases removal, and then through at electrostatic precipitator for particle removal. The gases are then discharged to the atmosphere through a stack; there is a stack gas monitoring system; and RMA has established monitoring stations on the facility's perimeter. The scrubber water is spray evaporated, and a sodium salt is produced as a residue. There is no liquid effluent from the system, but the solids generated in the precipitator and evaporator require final disposal. Fifty-five gallon drums can be treated by being "burned-out" in two special furnaces which are adjacent to the main incinerator. The exhaust from these furnaces is treated in the same manner as

that from the incinerator unit. The heat destroys the integrity of the drums and they are sold as scrap. Paragraphs 4 and 5 of Tab C to the Final Environmental Impact Statement for Project Eagle - Phase I concern the combustion of mustard in a bench scale unit which does not include effluent gas scrubbing. Mustard agent, as the sole fuel, was destructed to 99.9999994 percent in the laboratory unit under conditions less than the design criteria for the full scale RMA facility: shorter residence time, no atomization of fuel, lower air supply, lower temperature, and less turbulence. Personal communications with a representative of RMA revealed that no combustion gas samples (prescrubber) have been collected, but that scrubbed gas samples are collected and analyzed on a continuous basis. To date, Jul 74, no mustard has been detected in these samples, and the detection limit is 0.03 mg/cbm. In addition, RMA representatives were of the opinion that mustard agent would not be removed in the scrubber process. Therefore, based on the detection limit and an input of 2 gallons per minute the calculated destruction efficiency is 99.9887 percent. The chemical/physical similarities between Orange and mustard considered with the demostrated capability of Orange combustion and the very efficient combustion of mustard accomplished at RMA indicate that the facility could adequately destruct the Orange.

c. Proposed Incineration - RMA: Incineration of 2.3 million gallons would require approximately 27 months. The system can operate at >2,000°F with a stay time of 2-6 seconds. Although no actual Orange incineration data is available, it is felt that the experimental data, Appendix D and E, show that such operating conditions will adequately destroy the herbicide and TCDD. In addition, the caustic scrubber will provide additional treatment of the combustion gas. The elimination of the liquid discharge, the slow rate of incineration, the combustion gas treatment, the monitoring systems installed, and the drum cleaning capability make this option extremely attractive.

d. Exhaust Gas Discharge: The exhaust gas is discharged through a 55 feet stack located near the center of the RMA facility. The stack gas will contain essentially no herbicide esters and acids, TCDD, and particulates. The amount of hydrocarbons, based on comparison with data from Orange incineration projects, in the stack gas will be extremely small (fractional microgram per liter concentration).

3. APPLICATION TO ORANGE: Based on technical and environmental considerations, incineration in the CONUS in units such as the RMA facility could be safely accomplished. Unfortunately incineration units of sufficient capacity are located near centers of population and industry, and these areas are already marginally acceptable from a pollution viewpoint because of presently occurring degrees of air pollution. Furthermore, local and state governments are generally opposed to the importation of waste for disposal within their areas of jurisdiction. For the above reasons, incineration in the CONUS is not a viable alternative.

C. USE

1. DESCRIPTION OF ACTION

a. General

(1) Orange herbicide is not an EPA registered pesticide and cannot be domestically used or sold. The Orange herbicide stock to be destroyed by the action proposed in this environmental statement represents a resource of considerable monetary value. The safe and appropriate utilization of all or part of this resource would certainly be a beneficial action. The Air Force has been and is continuing to pursue the possibility of EPA registration of portions of the Orange herbicide stock. Affirmative action on registration prior to the contractual initiation of the proposed action, incineration at sea, or the principal alternative, incineration on Johnston Island, would insure that the stock which is registered would not be destroyed. Orange herbicide has a potential use on Federal lands as well as on privately owned lands; however, any use would require registration. The prudent disposition of Orange herbicide for use on privately owned or governmentally owned lands may have a tremendous impact on increasing the availability of certain natural resources, e.g. rangelands and forests.

(2) Undesirable weed and brush species are widespread in every region of the United States. Their combined impact on rangelands and production of commercial timber is enormous. Approximately half of the total land area of the United States is used for pasture and grazing purposes, and weeds and brush are a problem on nearly all these forage lands. Economic losses from weeds on forage lands are virtually incalculable and include low yield of forage and animal products per unit area, reduced livestock gains, and livestock poisoning. Although herbaceous weeds are found on all rangelands in the United States and result in forage losses, brush is the primary problem. Various brush species dominate an estimated 320 million acres of rangelands (Palm, 1968). More than 80 percent of 107 million acres of grazing land in Texas alone is infested to some extent with brush. Once established, woody plants such as mesquite (Prosopis spp.), juniper (Juniperus spp.), oak (Quercus spp.), and Sagebrush (Artemisia spp.) cannot be eliminated by good grazing practices alone. Measures must be taken to convert brush-dominated rangeland to more productive types of vegetation. Good brush control and striking improvements in the grazing capacity of rangeland may be obtained most economically by low-rate and low-volume applications of phenoxy herbicides (Kirch, 1967).

(3) Commercial forest land in the United States is estimated at 509 million acres. Although much of this land is not under any form of planned management for production of forest products, management for an increased productivity will soon become essential to meet the needs of the United States population (Palm, 1968). Walker (1973) summarized the total area of forest lands supporting important amounts of undesirable vegetation at some 300 million acres, or a land area of potentially commercial timberland equal to roughly the combined areas of Texas, California, and Washington. Gratkowski, Hopkins and Lauterback (1973) have estimated that there are some 4.7 million acres of commercial forest land in western Oregon and Washington on which the land is occupied by vegetation whose presence precludes reestablishment of conifers. Much of the area is in the highest productivity class for growth of forest products.

(4) Concepts of selective brush control have been developed for reforestation with the aid of commercial formulations of 2,4-D and 2,4,5-T. There are presently some 100,000 acres being treated each year with various formulations of these materials, all as the low-volatile esters. Success has been good, especially in operations on the slower-growing brush species (Lauterback, 1967) (Theisen, 1967).

b. Purpose: The purpose for using herbicide Orange on rangelands and reforestation is to reduce the amount of undesirable vegetation that dominates in selected regions of the United States because of past disturbances and improper grazing and/or timber practices. With the use of herbicide Orange, a more diversified and desirable variety of plant species may become established. This in turn will have a substantial impact on increasing productivity of these regions.

2. ENVIRONMENTAL IMPACT: The environmental impact of using herbicide Orange for chemical brush control will vary from region to region and whether it is for range or forest use. However, regardless of the region of use,or for rangeland or reforestation, critical assessments of effects on vegetation, wildlife, domestic livestock, soil microorganism, aquatic life, rangeland or forest waters, and man must be evaluated. Young et al. (1974) have evaluated the ecological consequences of massive quantities of 2,4-D and 2,4,5-T, i.e., Orange. Their five-year study documents the persistence, degradation, and/or disappearance of the herbicides from soils and drainage waters of an approximately one square mile area that had received 345,117 pounds of herbicide. Moreover, ecological assessments were made of the herbicides' subsequent effects (direct and indirect) upon the vegetative, faunal, and microbial communities. The summary of their five year field study is included as Appendix F.

D. RETURN TO MANUFACTURERS: In March 1972, seven manufacturers of herbicide Orange were contacted regarding the possibility of chemically reprocessing Orange herbicide whereby all impurities, including dioxin, would be extracted or destroyed. Results from all manufacturers were essentially the same; i.e., they did not feel that they were capable of reprocessing the product without extensive investment in equipment and/or development of new processes. Lead time for this type of action would require in excess of 18 months before large scale reprocessing could begin. As a result of EPA's action on 24 Jun 74 to cancel hearings on the possible further restriction of 2,4,5-T, the manufacturers have again been contacted (Aug 74) via letter to determine if their position may have changed. Manufacturers have indicated that they do not have the capability to reprocess Orange without major research efforts and capital expenditures.

E. DEEP (INJECTION) WELL DISPOSAL: This process involves injection of the herbicide into a deep sub-surface formation. This well hole down into the formation is lined with casing which has been cemented into place to prevent fluids from rising to the surface outside of the casing. A packer tube runs from the surface inside the casing to a permeable geologic formation. The herbicide drums are emptied into tanks or vats on the surface where the Orange is diluted and then pumped down the tubing to the permeable formation. The packer tool prevents fluid from returning to the surface inside the casing and impermeable upper and lower formations adjacent to the permeable formation restrict vertical movement. This process has not been approved by state agencies, or the EPA, and deep well injection is not considered environmentally safe or desirable disposal method for waste materials. The policy is to oppose all storage or disposal of wastes in deep wells without strict controls and a clear demonstration that such disposal will not: a) interfere with present or potential use of sub-surface water supplies, b) contaminate interconnected surface waters, or c) otherwise damage the environment. Little concrete information is available on what degradation of the Orange would occur at the depths, temperatures, and pressures encountered in deep wells. This coupled with the possibility of sub-surface disturbance at a later date allow Orange to migrate into formations leading to water supplies or other valuable formations, has prevented any of the firms interested in disposing of Orange in deep wells from obtaining state or Federal permits.

F. BURIAL IN UNDERGROUND NUCLEAR TEST CAVITIES: The Atomic Energy Commission was contacted regarding the possibility of disposing of the Orange by burying it in an earth cavity formed during underground nuclear testing. They advised that a major research, development, and experimentation effort would be required to prove the practicality of this alternative. In view of the time required for this effort, it is not considered a feasible alternative.

G. SLUDGE BURIAL

1. GENERAL: This technique offered definite promise, but there was a lack of interested and qualified industries to undertake the necessary preliminary investigations. This process involves one concept of destroying the Orange through bacterial action. The proposal envisions constructing trenches in geologically suited formations on isolated government land. The type of formations picked for the trenches would preclude vertical and lateral movement of the Orange. The trenches would be filled with drums containing the Orange and would then be surrounded by secondary sewage plant sludge, which would provide a growth medium for the bacteria. The tops of the drums would be holed to allow a controlled release of the Orange. The trenches would then be mounded with dirt fill and aggregate. Depending upon the type of bacteria selected to decompose the Orange, vents might also be required. This process is not considered acceptable because of the time to completely destroy the herbicide is quite lengthy, possibly as long as 10 to 25 years, and because a system of monitoring would be required throughout this time period. The earth covering would require maintenance and additional time would also be required to develop a strain of bacteria suitable for use with Orange.

2. ENVIRONMENTAL IMPACT:

a. General Impact: Environmental impact of a sludge burial proposal will be concentrated for the most part in the approximately 30 acres of land utilized for the operation. The most significant impact of this proposal is the denial of land for reclamation or recreational uses for a period ranging from 15 to 25 years. Other effects include alteration of the soil profile and structure, temporary destruction of all vegetation, and disturbance and possible destruction of ecosystems in the area. The impact on air and water quality of the site is anticipated as minimal, providing site selection criteria and proposed burial procedures are followed.

b. Impact on Air Quality: The biological degradation of organic matter results in the formulation of various gaseous products including, in this case, phenol, carbon dioxide, methane, and the volatile fraction of the normal butyl ester of the herbicide. Dependent upon various parameters, these products may exist in significant quantities. To contain the fractions, five feet of compacted earth cover is proposed with an additional two feet of earth placed at the center line of each drum row. Indications are that this cover will be adequate to preclude escape of gases into the atmosphere. It should be noted that two feet of compacted earth is used as final cover for a sanitary landfill. Odor problems will be prevalent during the dumping of the sludge into the trenches. Volatilization of the normal butyl ester will occur to some extent prior to covering of the drums. The extent of volatilization will depend upon atmospheric conditions at the time, the number and size of holes punched into the drums, and the time period during which the punched drums are uncovered. To a lesser degree, air pollutants in the form of dust and emissions from the excavating equipment will be emitted during "construction" of the trenches. Significant degradation of air quality during this phase is not anticipated.

c. Impact on Water Quality: The site selected for sludge burial will be either a portion of a flat dry lake bed where the depth to the water table is several hundred feet, or on an alluvial fan bordering a saline playa where the water table beneath the fan is also several hundred feet deep. In either case, several hundred feet of unsaturated earth exists between the bottom of the trenches and the water table. Precipitation in both of these settings

would tend to be insufficient (less than five inches per year) for unchanneled water to penetrate through the unsaturated materials and reach the water table. Prior to the selection of a suitable site, data must be gathered describing the parent material and underlying rock formations with indications of possible discontinuities, including a geological profile and information on the existence of faults or fissures. Having satisfied these requirements, the selected site would have no significant adverse effect on the water quality of the area selected.

d. Land Use: A significant impact of a sludge burial disposal alternative is denial of land for a significant length of time. Approximately 30 acres of land will be denied for reclamation or recreational uses for a period ranging from 15-25 years.

e. Soil: The sludge burial proposal involves construction of trenches. These trenches will vary in number and dimensions. Trench depths of 10 to 15 feet minimum will be required for the operation. Excavation of these trenches will cause complete destruction of vegetation and the soil profile, disturbance and possible destruction of wildlife habitat, and disturbance of the bioecology of the particular area. The total environmental impact can only be determined if base line data is gathered prior to construction. This data should include an accurate description of (1) permanent inhabitants (2) migratory inhabitants and (3) the identification of any endangered species which may occupy the site.

f. Vegetation: Approximately 30 acres of vegetation would be destroyed if the proposal were implemented. Depending upon the geographic location of the site, natural vegetation will begin to reestablish itself within a year with weed species being the first to invade.

## H. MICROBIAL REDUCTION

### 1. DESCRIPTION OF ACTION

a. General: This process involves the biological degradation of the herbicide through fermentation. It requires the development of a microorganism to "feed" on the herbicide. From the literature, it seems apparent that microorganisms have developed unbelievable capabilities for handling organic compounds. However, two factors severely complicate the biological degradation of this refractive material: 1) its insolubility in water and 2) its chemical structure (specifically the number and position of chlorine atoms attached to the aromatic ring). Many investigators have showed that 2,4-D is rapidly decomposed in soils, and that high concentrations of the material have no appreciable effect on the soil population of bacteria, fungi, and actinomycetes (Stojanovic, 1972). The persistence of 2,4,5-T is usually two to three times longer than 2,4-D (DeRose, 1947) and very few microorganisms have been identified as having the ability to break down the 2,4,5-T molecules (Aly, 1964). Leopold, VanSchaik, and Neal (1960) found that increasing chlorination of phenoxyacetic acid decreased its water solubility while increasing its absorption onto activated carbon and organic matter, thus making less available for microbial degradation. Stojanovic et al. (1972) added a mixture of 2,4-D and 2,4,5-T to soil at a concentration of 5 tons/A (5,000 ppm in top 6 inches). It appeared that mixtures of 2,4,5-T were more rapidly degraded than were the single compounds. Very little work has been done on the microbial degradation of TCDD; however, Matsumura and Benezet (1973), have studied the problem. Using 100 microbial strains, they found that only 5 strains showed some ability to degrade the compound. Thus far, Matsumura and Benezet have not been able to manipulate cultural conditions to increase the rate of degradation of TCDD in any of the microorganisms. Worne (1972) reported in a paper presented at Ghent, Belgium, that he has developed mutated organisms which have the capability to cause 100 percent disruption of the aromatic ring of several chlorinated phenols. He reported a detention time of 52 hours for concentrations of 200 ppm.

b. Treatment Methodology: Detoxification of the herbicide would be accomplished utilizing one of many conventional systems, including lined stabilization ponds, activated sludge, anaerobic digestion, or complete mixing activated sludge. The latter method offers many advantages. A plant in Canada uses complete mixing activated sludge (Besselievre, 1969) to treat phenol bearing wastes containing up to 3,000 ppm phenol, the effluent containing .04 ppm. Utilizing a 20 MGD conventional activated sludge facility with treatment capability of 200 ppm, the herbicide would be treated in a period of 2 years. Plant cost would approach $2 million. The feasibility of and using microbial fermentation as a disposal alternative is largely contingent upon the concentration of waste to be treated. Treatment of concentrations of between 1,000 to 3,000 ppm herbicide would make this alternative attractive.

2. ENVIRONMENTAL IMPACT: The environmental impact of a microbial reduction method is dependent upon the fate of TCDD in a biological treatment facility. It must be established that no TCDD is remaining in the effluent, or a problem of enormous consequences can occur. Thus far no data are available on the fate of TCDD in a biological system. All other aspects of such an alternative can be controlled and minimized to an acceptable level. Monitoring methodology and a failsafe system would be required. Until more data are developed the

particular environmental aspects cannot be evaluated. More specific information concerning the process, size of facility, land acreage required, and effluent parameters are needed.

I. FRACTIONATION: Fractionation is the process of converting Orange into its acid ingredients by means of distillation. This would separate the normal butyl esters of 2,4-D and 2,4,5-T and its contaminant TCDD. The 2,4-D and 2,4,5-T would be reformulated for commercial use. TCDD would then be destroyed by chemical, biological or incineration techniques. Actual distillation efficiencies theoretically could approach 90-95%. One investigator stated that any TCDD residue could be destroyed by splitting the ether bonds of the molecule. In the process of fractionation, the dioxin would be isolated or destroyed. A small scale study was funded, but the results were inconclusive. Fractionation is not acceptable because: a) the fate of the dioxin has not been demonstrated, b) in the process, 3% of the Orange processed could not be accounted for, c) standards to control and monitor vapor and fluid emissions into the environment have not been identified. Further discussion is contained in paragraph J.

J. CHLORINOLYSIS

1. From the theoretical engineering point of view, chlorinolysis offers an efficient, controlled, and safe method for disposal of the herbicide, as well as other hydrocarbon formulations. Chlorinolysis is a process that breaks down the molecule and adds a chlorine molecule to produce carbon tetrachloride, phosgene, and anhydrous hydrogen chloride, all of which have established commercial value.

2. Chlorinolysis as a means to dispose of Orange herbicide was evaluated over a period of almost two years. In July of 1972, discussions and correspondence with the Environmental Protection Agency (EPA) committed the Air Force to pursue the testing and research program necessary to determine the feasibility of converting Orange to salable products by chlorinolysis. In September 1972 a Memorandum of Agreement between the EPA and the Air Force was initiated. The objective of the agreement was the development of a laboratory program to evaluate the practicality of the application of chlorinolysis for the disposal of Orange. The investigation was also to determine the extent of destruction of the impurity dioxin. The information and data obtained in this research was to be utilized by the Air Force to determine whether the proposed concept could be applied and used to dispose of Orange and by the Environmental Protection Agency to determine if it could contribute toward solving the disposal problems of the petrochemical industry. It was agreed that the EPA would manage the research and provide a report containing all data collected, together with conclusions and recommendations. The Air Force agreed to fund the effort in the amount of $35,000. An additional $10,000 was provided for analysis of dioxin. Three drums of Orange containing 14 ppm dioxin (analysis by Dow Chemical Company) were provided by the Air Force.

3. Reports received in November 1972 indicated that no dioxin was detected (sensitivity level of 100 ppb) in the carbon tetrachloride extracted during the first run. A later report of analysis indicated no dioxin at a sensitivity of less than 10 ppt of dioxin in carbon tetrachloride subjected to improved distillation. 2,4-D which was fractionally distilled from Orange by the Diamond Shamrock Company contained less than 1 ppb of dioxin. The material remaining after distillation is predominantly 2,4,5-T and dioxin. After fractionation the residual must still be disposed of by an acceptable method.

4. In December 1972 a presentation was made by EPA to the Air Force regarding total and partial chlorinolysis (fractionation of 2,4-D followed by chlorinolysis of the 2,4,5-T and dioxin residual). It was explained by EPA that to convert 26.5 million pounds of Orange to carbon tetrachloride, phosgene and hydrogen chloride would require about 170 million pounds of chlorine. For a 10-ton per day chlorinolysis plant, the cost to the Air Force for the worst case commercial sale value of the produced products would be about $9.1 million. For the best case sales, the cost would be about $2.4 million. A cost uncertainty of $6.7 million results. One of the disadvantages pointed out by EPA was that quartz lined reactors of the size needed do not exist and that development of a large scale reactor would be required. It was estimated that 18 to 24 months

would be needed to design and construct a plant after a 6 month pre-engineering study. It was further estimated that 24 to 30 months would be needed to process the Orange. A total time of 38 to 60 months would thus be required.

5. In January 1973 Air Force officials, accompanied by two consultants, visited the Diamond Shamrock facilities and essentially confirmed the cost estimates and time frames previously presented by the EPA. It was confirmed that some 85,000 tons of chlorine would be needed. The Diamond Shamrock officials discussed a commercial operation by a German firm which had been successfully processing hydrocarbons by chlorinolysis using a higher pressure process than that of Diamond Shamrock. An advantage of the German process was that a quartz reactor was not necessary.

6. The EPA investigated the German plant for the possibility of chlorinating Orange herbicide. Two drums of Orange were provided by the USAF to the EPA for testing purposes in Germany. EPA officials visited the German facilities in July 1973. In September 1973 EPA officials reported that because Orange is approximately 16 percent oxygen (by weight), corrosion of the reaction vessel was feared. Bench scale tests indicated 20-30 percent greater corrosion than observed when hydrocarbons containing no oxygen were tested. This observation may have occurred due to the problem of test size as the full scale plant has not experienced any corrosion processing hydrocarbons which do not contain oxygen. Nevertheless, additional tests were thought to be needed prior to conducting a full scale evaluation. The reaction kinetics and thermodynamic differences between the Diamond Shamrock process of high temperature/low pressure and the German process of low temperature/high pressure also needed to be understood according to the EPA before any full scale test. During the bench scale tests $CO_2$ was unexpectedly produced. The reason for its formation was not known and further testing was indicated as being required. Further tests and another visit were planned for December 1973. It was indicated that a final report containing the Diamond Shamrock, German, and EPA data would be provided shortly.

7. In April 1974, the EPA, in discussing chlorinolysis in a newsletter indicated that "The process...has been proven on a small scale and research is continuing to demonstrate its usefulness on a large industrial scale."

8. The EPA report, "Study of Feasibility of Herbicide Orange Chlorinolysis" (EPA-600/2-74-006, July 1974), covering only the work of Diamond Shamrock Company was delivered on 2 Oct 1974. A limited number are also available for loan from the USAF Environmental Health Laboratory, Kelly AFB Texas 78241. The report covers the results of bench scale tests and concludes, based on these bench scale tests, that chlorinolysis under the proper conditions effectively converts Orange herbicide and its TCDD contaminant to carbon tetrachloride, carbonyl chloride and hydrogen chloride. Destruction of the TCDD was complete, and preliminary toxicology tests of the recovered carbon tetrachloride on rabbits showed no evidence of TCDD contamination. The report also contains cost estimates which include credit for the sale of chemicals from a 25 ton/day plant. The cost in the worst case is shown to be $11 million and in the best $4 million.

9. Owing to the uncertainties associated with developing this technique to a full scale plant capable of processing 2.3 million gallons of Orange in a timely and economic manner, partial or total chlorinolysis was not selected as the method of disposal even though it is satisfactory from an environmental point of view.

## K. SOIL BIODEGRADATION

### 1. DESCRIPTION OF ACTION

#### a. General

(1) Soil biodegradation is a soil incorporation technique based on the premise that high concentrations of the Orange herbicide and the contaminant TCDD will be degraded to innocuous products by the combined action of soil microorganisms and soil chemical hydrolysis. The rationale for soil incorporation of herbicide as an ecologically-safe disposal method comes from pertinent laboratory and field studies.

(2) When soil microorganisms are exposed to high concentrations of a herbicide, there is usually a lag period before utilization of the material begins. This lag period represents the time required for the microorganisms to become adapted. Once breakdown of the herbicide is initiated and completed, the soil microorganisms retain an enhanced capacity for degradation of that herbicide. For example, Audus (1960) treated a soil with 100 ppm 2,4-D and 20 days were required for 80% detoxification, but when the soil was treated again only three days were required for 80% detoxification. Colmer (1953) found that 5,000 ppm 2,4-D were at first inhibitory to a bacterium, but after subculturing three times the organisms grew rapidly in the 5,000 ppm concentration. Stojanovic, Kennedy, and Shuman (1972) added a mixture of 2,4-D and 2,4,5-T (similar to the formulation of herbicide Orange) to soil at a concentration of 5 tons/acre (5,000 ppm in top 6 inches of soil). Seventy-eight percent of the herbicide carbon was given off as carbon dioxide in 56 days. It also appeared that mixtures of the herbicides were more rapidly degraded than were single compounds.

(3) In the laboratory, Shennan and Fletcher (1965) subjected 38 species of soil bacteria fungi, actinomycetes to 2,4-D and 2,4,5-T at concentrations of 100 to 10,000 ppm in the soil, respectively. Twenty-six species were not inhibited by 10,000 ppm 2,4-D. Twenty-four organisms required 10,000 ppm 2,4,5-T for growth restriction to occur. In the study by Stojanovic, Kennedy, and Shuman (1972), 5,000 ppm of an equal mixture 2,4-D and 2,4,5-T inhibited growth of bacteria and actinomycetes but the total number of fungi increased during the 56-day incubation period. Kearney, Woolson, and Ellington (1972) in the laboratory studied the persistence of TCDD in two soils, Lakeland sand and Hagerstown silty clay loam, at three rates of application (1, 10, and 100 ppm) for 360 days. The soils represented extremes in biological activity and in physical and chemical properties. The soils were maintained at 28 to 30°C with a moisture content equivalent to 70% of field capacity. After 1 year, 56 and 63% of the originally applied TCDD was recovered in the Hagerstown and Lakeland soils, respectively. As Kearney *et al.* (1972) pointed out, however, a concentration of 1 ppm of TCDD in soils is $10^6$ times greater than the residues likely to be encountered in a 2 pound/acre (lb/A) application of 2,4,5-T containing 1 ppm TCDD. However, Young *et al.* (1974) has reported soil persistence of TCDD in Lakeland sand which had received 947 pounds/acre 2,4,5-T nine years earlier (1962-1964). A TCDD concentration of 0.71 parts per billion (ppb) was found in the 0-6 inches of soil profile, see Appendix G.

(4) It seems apparent from laboratory studies that microorganisms have developed extensive capabilities for handling organic compounds. Moreover,

most organisms seem to have a latent ability for decomposition of halogenated hydrocarbons. However, the amount of active herbicide applied to soil may diminish by means other than biological decomposition; e.g., chemical degradation, absorption, volatilization, leaching, and photodecomposition.

(5) Lutz, Byers, and Sheets (1973) studied the persistence and movement of 2,4,5-T in soils of a western North Carolina watershed. They found that at 50 and 100 days following applications of 2 lb/A 2,4,5-T less than 10 ppb remained at depth below 7.5 cm (3 inches). O'Connor and Wierenga (1973) studied the persistence of 2,4,5-T in greenhouse lysimeter studies. They found 3 ppm 2,4,5-T at a depth of 24 cm (14 inches) in soil cores following 3 irrigations with 80 ppm 2,4,5-T (10.5 months elapsed time from first to the third irrigation). Total degradation time for 2,4,5-T was calculated to be 85 days for this pretreatment and concentration. Hanks (1946) has shown that 2,4-D was much more resistant to leaching from alkali soil than from a peat soil.

(6) Until recently there was very little information concerning the breakdown of 2,4-D or 2,4,5-T in a soil incorporation site. However, Goulding (1973) has conducted field experiments on the use of soil incorporation as a method of disposing of massive quantities (approximately 1-1/4 million gallons) of 2,4-D and waste by-products. Goulding found that when he employed a trenching technique, simulating subsurface injection, he could place 500 lb/A 2,4-D (plus waste) at a depth of 10 inches into 5-inch bands on two-foot centers. With this placement the actual concentration of herbicide within these bands was approximately 1250 ppm. Samples taken between trenches and in soil profile segments from the surface down through the point of application indicated minimal vertical and horizontal movement of the herbicide (or phenolic waste) from the site of initial deposition. Results from this experiment indicated little differences in rates of degradation in the trenched plots or a surface application of 500 lb/A: 95% degradation in 540 days.

(7) Young, Arnold and Wachinski (1974) have studied the persistence and movement of herbicide Orange (and TCDD) following soil incorporation at rates of 1,000, 2,000 and 4,000 pounds active ingredient 2,4-D and 2,4,5-T/acre (lb ai/A). The percent loss of herbicide over a 330 day sampling period was 78.2%, 75.2% and 60.8% for the 1,000, 2,000 and 4,000 lb ai/A plots, respectively. They calculated that the half-life of herbicide Orange in alkaline (pH = 7.8) desert soils was approximate 150 days at these massive rates. Data on soil penetration indicated that less than 3.7% of the herbicide was found at depths greater than 18 inches 282 days after soil incorporation of 4,000 lb ai/A. Preliminary data based on levels of TCDD in the formulation (3.7 ppm) and those encountered in the soil profile 265 days following soil incorporation suggested that under these environmental conditions the half-life of TCDD was 88 days. A copy of this report is attached as Appendix G.

b. Site Criteria for Soil Biodegradation: It is important that the criteria for selection of a site for soil biodegradation include certain physical, biological, and managerial factors.

(1) Physical Factors: From the standpoint of just physical consideration, the soil incorporation technique provides an array of alternatives as to the selection of site. In general:

(a) A minimum of 2,000 acres must be available.

(b) The site must be remote. It cannot be adjacent to land currently in agronomic production.

(c) The land must have a low-use potential, i.e., it should be marginal land. Moreover, the land should not be considered land that will be significantly productive in the foreseeable future.

(d) Water resources must be sufficiently far away so as not to be contaminated.

(e) The topography of the land must be relatively flat with a uniform surface.

(f) The texture of the soil should be sandy-loam or silty-loam with a pH of approximately 8.0.

(g) The area should not be characterized by rock outcrops or areas of marked deflation or dunes. The area should also have minimal surface erosion.

(h) Data should be available on subsurface geology and hydrology.

(2) Biological Factors: The vegetation that characterizes the particular site must be uniform with a ground cover of at least 10-15%. Such a plant community will provide the organic matter and microclimate that supports the growth and maintenance of the microflora (e.g., fungi and bacteria). Ideally, the vegetation should be low-growing shrubs, forbs and grasses to facilitate the incorporation equipment.

(3) Management Factors: The management factors that will influence the selection of the site are:

(a) The requirement for established all weather roadbeds to and within the disposal site.

(b) The distance to the disposal site from an off-loading station (e.g., rail to truck).

(c) The requirement for security of the disposal site.

(d) Availability of personnel facilities.

(e) Adequate storage space at the disposal site.

c. Method of Incorporation: A subsurface injection system will be used to incorporate the herbicide into the soil at a depth of 6-10 inches. The injection would be done by using a conventional agricultural subsoiler, drawn by a heavy industrial tractor. The subsoiler would consist of a vertical blade on which a chisel, or foot, is mounted at an angle of approximately 15° from horizontal. A piece of metal tubing will be attached to the blade (and terminating at the base of the chisel) in such a manner that a piece of hose from the injection pump could be inserted to permit deposition of the herbicide immediately behind the chisel. The equipment, with eight injectors (shanks), should be calibrated to apply 4000 lb/A of Orange. The eight shanks should be on 20-inch centers. During the process of application the overlying vegetative structure will be damaged. To prevent the loss of soil moisture and to reseal the soil (thus minimizing volatility and damage from wind), a soil compacter (cultipacker) will be required and a drought resistant, salt tolerant grass will be planted.

2. ENVIRONMENTAL IMPACT

a. General: The environmental impact of soil biodegradation will be expressed in two major areas; the most significant of which is the denial of a 1,000 - 2,000 acre tract of land for reclamation or recreation use for a 3 - 5 year period during biodegradation. The proposed site would require continuous monitoring during the lifetime of the project. Also occurring will be damage and/or kill of the overlying vegetative structure in the immediate disposal area, drastic alteration of the soil structure, and disturbance and/or temporary destruction of local ecosystems. Adherence to the above site criteria and incorporation method will optimize the soil biodegradation procedure and minimize adverse environmental impact.

b. Air Quality: Impact on air quality will be confined to the period of incorporation. Some volitalization of the n-butyl esters will occur during loading of the incorporation equipment. To a lesser degree volitalization may occur while actually injecting the herbicide into the soil. Air pollutants in the form of dust and emissions from the incorporation equipment will be emitted during the treatment of the site.

c. Impact on Water Quality: The impact on water quality will be minimal. Actual field data for soil incorporation at 4,000 lb ai/A herbicide Orange indicated only minimal leaching (in alkaline soils) below 18 inches of depth. However, the incorporation site should be in an area of sufficiently deep soil to prevent unchanneled water from penetrating through the unsaturated materials.

d. Vegetative and Animal Communities: The soil biodegradation method would disrupt and/or kill the vegetation on a minimum of 1,000 acres of land. This would significantly influence the animal community dependent on this vegetation. However, if a site is selected that fits the criteria, the animal population will be minimal. Immediate action to establish salt-tolerant grasses will minimize potential long-term damage to the animal community.

L. NO DISPOSAL ACTION

1. INTRODUCTION: If none of the disposal methods listed above can be employed at the present time because: 1) they are not ecologically acceptable, 2) technology not sufficiently far advanced, 3) excessive capital investment required, 4) unacceptable time delay, and 5) socio-political opposition, it is possible to put herbicide Orange into "permanent" storage in an above ground steel storage tank on Johnston Island. The required capacity of the tank would be approximately 1.8 million gallons. This volume is an estimate based on the assumption that about 500,000 gallons having a TCDD content of 0.1 ppm or less and presently in storage at the NCBC, Gulfport MI will be registered. The estimated cost of construction of a storage tank with a capacity of 1.8 - 2.3 million gallons on Johnston Island is $875,000 - $1,000,000. The transportation of the drums presently stored at the NCBC, Gulfport MI to Johnston Island would probably add another $450,000 to the total cost increasing it to about $1.35 to $1.45 million dollars. There are several methods of treatment available which could be used to prevent external corrosion of the tank. Pitting or abrasion of the paint or other coating due to blowing sand might constitute a problem. Orange and dioxin are inert to mild steel and, in the absence of water, internal corrosion should not be a problem. This "permanent" storage offers several advantages as follows: 1) it would eliminate the cost of continuing redrumming on Johnston Island where redrumming is a major problem and would also eliminate the same problem at the NCBC, Gulfport MI where the problem is not as acute, 2) during the period of storage advances in technology would occur, 3) the cost of certain closed systems, i.e., chlorinolysis, microbial degradation, etc., would be technologically advanced and probably reduced in cost. If for any reason the construction of a tank or tanks is not considered feasible on Johnston Island, storage in already existing tanks or other Pacific islands might be considered.

2. ENVIRONMENTAL IMPACT: Only during the construction phase would there be any impact on the environment. If it became necessary for any reason to provide additional land area for the construction (placement) of the storage tank, dredging would be necessary. However, it is believed that sufficient land area is available on the southwest corner of the island to permit the construction of a storage tank with a capacity of 2 to 2.3 million gallons. The land area for a storage tank of the above stated capacity and the necessary impoundment area and dikes would be about 2 acres. This area includes a part of the storage site where drums of Orange are currently stored and it would be necessary, probably, to move some and perhaps all of these drums. Extensive construction has been conducted on Johnston Atoll in the past. This work has involved drilling and blasting; the use of heavy earth moving equipment and dredging. Explosive devices have been detonated in the area and nuclear devices have been fired at high altitude. Except for dredging which almost certainly altered the ecosystem of the lagoon and nearby waters, changed the direction and velocity of the currents, altered tidal and wave actions, increased the land area of the island, resulted in the creation of two man-made islets and altered the shoreline of all islands, none of these activities has resulted in the permanent disturbance of the ecosystems of the atoll. While space may be available for tank construction at this time, the available land on the island is very limited and competing missions must be considered. Storage has been continuous for a number of years since the cessation of use. The alternative simply prolongs storage at great expense but does not dispose of the material. Ultimate disposal of the Orange is only delayed and for no purpose as an acceptable disposal method has been identified.

PART VI. RELATIONSHIP BETWEEN LOCAL SHORT-TERM USE OF MAN'S ENVIRONMENT AND THE MAINTENANCE AND ENHANCEMENT OF LONG-TERM PRODUCTIVITY: Bioaccumulation in the environment has been proposed as an adverse environmental consequence of using 2,4,5-T as a defoliant. This Orange herbicide disposal action is not expected to contribute to the bioaccumulation of TCDD in the biosphere on or near Johnston Island because of the high efficiency of the proposed incinerator and the sparsely populated ecosystem of the open tropical sea. The destruction by incineration would eliminate the short- and long-term risks that may be involved with continued storage of the material. Incineration under the controls and precautions to be included in the final contract would not narrow the range of beneficial uses of the environment or pose long-term risks to health or safety.

PART VII. IRREVERSIBLE AND IRRETRIEVABLE COMMITMENTS OF RESOURCES WHICH WOULD BE INVOLVED IN THE PROPOSED ACTION IF IMPLEMENTED: This action would not involve the irrevocable use of resources other than the small amount of fuel required to bring the incinerator to proper operating temperature. The action would not involve changes in land use, destruction of archaeological or historical sites, or unalterable disruptions in ecosystems. It will not curtail the beneficial uses of the environment.

# APPENDIX A

# ECOLOGICAL BASELINE SURVEY OF JOHNSTON ATOLL CENTRAL PACIFIC OCEAN

by

A. Binion Amerson, Jr.

Ecology Program
Office of Environmental Sciences
The Smithsonian Institution
Washington DC 20560

17 December 1973

(The document consists of over 300 pages. For the sake of space conservation, the Table of Contents and Summary only are included here. Copies of the document are available on a loan basis to qualified interested parties and may be obtained by request from USAF Environmental Health Laboratory, Kelly AFB Texas 78241.)

## SUMMARY

Johnston Atoll, located between the Hawaiian Islands and the Line and Phoenix Islands, is one of the most isolated coral atolls in the world. Military activity has greatly altered the atoll: two of the four islands are man-made and the original two have been greatly changed. Since World War II, the atoll has been a military base. The wildlife on the atoll is protected under a little-known 1926 Executive Order.

The flora of Johnston Atoll is well known. There are 67 species of benthic marine algae known from the lagoon. Increased silt from dredging activities in 1963 and 1964 decreased the number of algal species in the dredged areas. Three vascular plants occurred on the original two islands; man has apparently introduced 124 species since 1923.

The invertebrate fauna is not well known and dredging has further reduced or eliminated some species. The known groups are: 18 species of Cnidaria (Coelenterata), 58 species of Mollusca, 12 species of Annelida, 75 species of marine Arthropoda, 85 species of terrestrial Arthropoda (including 2 tick species, 7 chiggers, 23 biting lice, and 2 louse flies), and 37 species of Echinodermata.

The vertebrates are well known. There are at least two species of pelagic fishes and 194 species of inshore fishes. Dredging operations have drastically reduced the fish population in certain

lagoon areas. Ciguatera is prevalent among the inshore fishes, with the moray eel, white-tipped reef shark and grey sand shark being most toxic. Five species of reptiles are known; all but one were introduced by man. Likewise, no mammals are native to the atoll; however, man has introduced six species. Fifty-six species of birds, whose total population ranges upward to 600,000, are known from the atoll. Of the 22 seabird species, 12 species are breeders, 3 are former breeders, and 7 are visitors. Of the 34 species of waterfowl, marsh, and land birds, 7 species are regular migrants, 6 are irregular visitors, 2 are stragglers, 16 are accidentals, and 3 are introductions. Analysis of 60,932 returns of 303,901 birds comprising 21 species banded at Johnston Atoll reveals that the atoll is the major focal point for interisland movements in the north-central Pacific. A total of 733 individual banded birds have moved to or from Johnston Atoll; most interisland movement involves the northwestern Hawaiian Islands.

Johnston Atoll is perhaps the most scientifically studied atoll in the central Pacific. Despite man's disturbance, the atoll is ecologically significant because of its isolation and from the standpoint of its opportunities for island ecological research. Although much ecological research has been accomplished, the potential of additional ecological understanding of the atoll is great.

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# APPENDIX B

## EXECUTIVE ORDERS (NOS. 4467, 6935, & 8682) ESTABLISHING JURISDICTION OVER JOHNSTON ISLAND

# Executive Order

It is hereby ordered that two small islands known as Johnston island and Sand island, located in the Pacific Ocean, approximately in latitude 16° 44′ 45″ North and longitude 169° 30′ 30″ West from Greenwich, as segregated by the broken line upon the diagram hereto attached and made a part of this order, be and the same are hereby reserved and set apart for the use of the Department of Agriculture as a refuge and breeding ground for native birds.

It is unlawful for any person to hunt, trap, capture, wilfully disturb or kill any bird of any kind whatever, or take the eggs of such bird within the limits of this reserve, except under such rules and regulations as may be prescribed by the Secretary of Agriculture.

Warning is expressly given to all persons not to commit any of the acts herein enumerated, under the penalties prescribed by Section 84 of the U. S. Penal Code, approved March 4, 1909 (35 Stat., 1088), as amended by the Act approved April 15, 1924 (43 Stat., 98).

This reservation to be known as Johnston Island Reservation.

CALVIN COOLIDGE

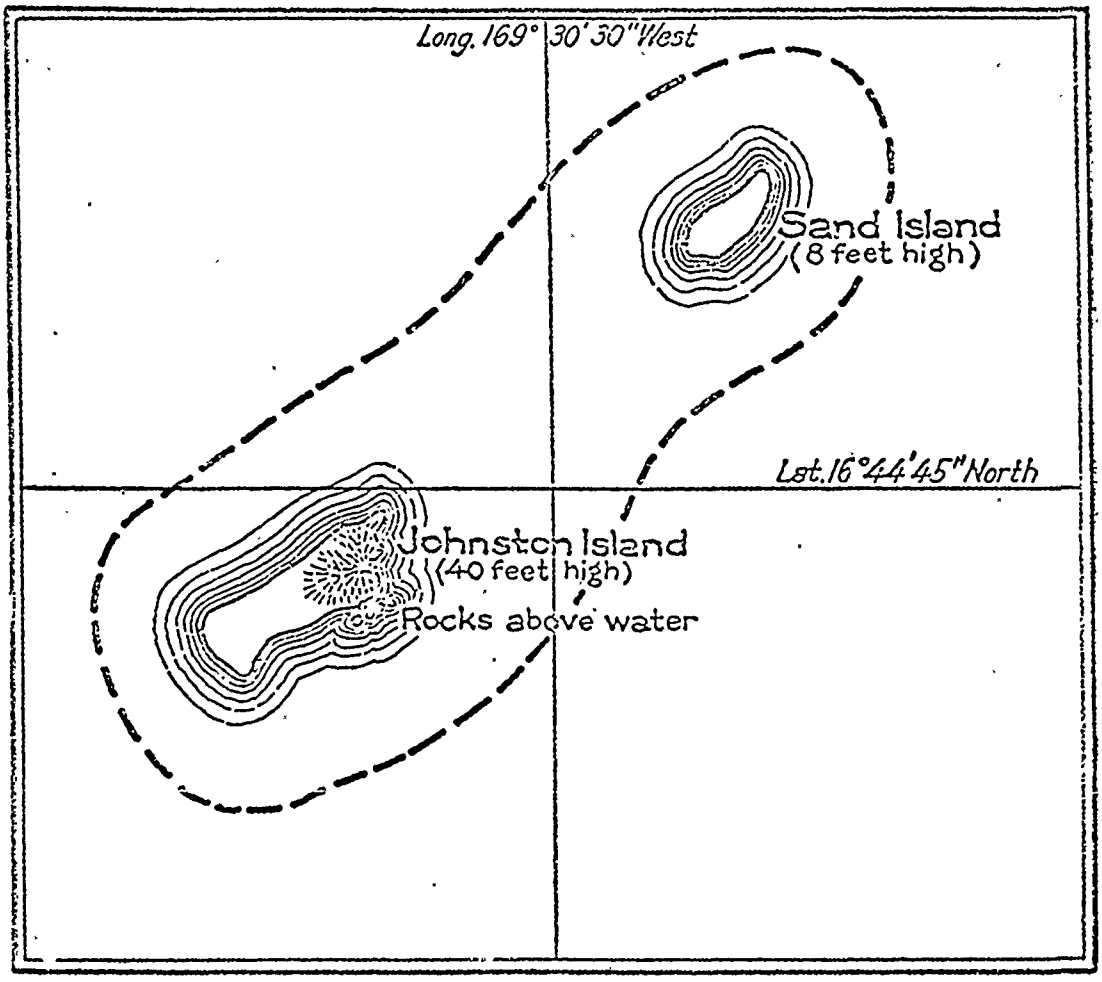
THE WHITE HOUSE,
*June 29, 1926.*

[No. 4467]

# JOHNSTON ISLAND RESERVATION

## For the Protection of Native Birds

*Embracing two small islands known as Johnston Island and Sand Island located in the Pacific Ocean approximately in Latitude 16°44'45" North, Longitude 169°30'30" West.*




DEPARTMENT OF THE INTERIOR

Hubert Work, Secretary

GENERAL LAND OFFICE

William Spry, Commissioner

GOVERNMENT PRINTING OFFICE

# Executive Order

## Placing Certain Islands in the Pacific Ocean Under the Control and Jurisdiction of the Secretary of the Navy

### Wake Island, Kingman Reef, and Johnston and Sand Islands

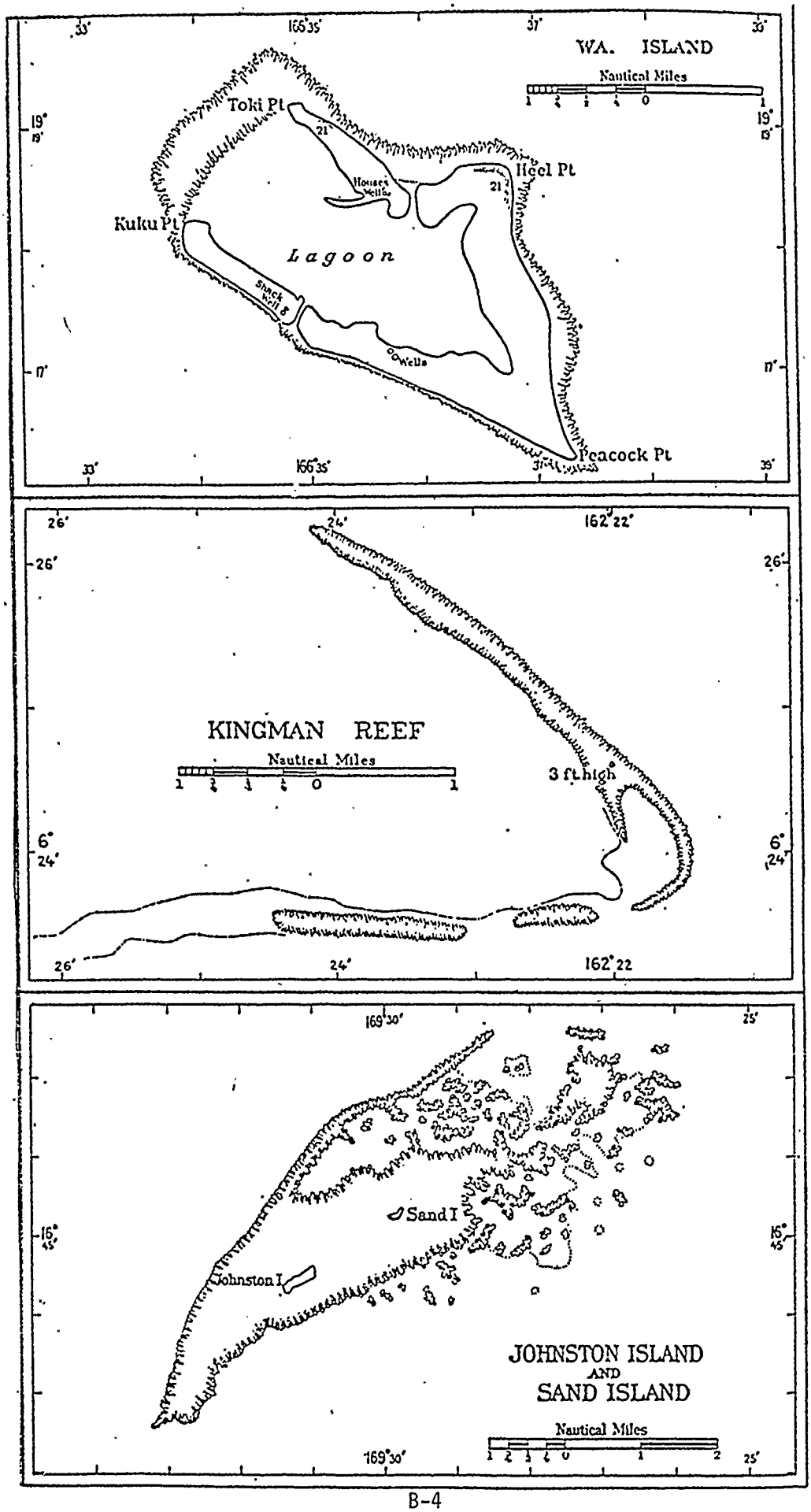
By virtue of and pursuant to the authority vested in me by the act of June 25, 1910, ch. 421, 36 Stat. 847, as amended by the act of August 24, 1912, ch. 369, 37 Stat. 497, and as President of the United States, it is ordered that Wake Island located in the Pacific Ocean approximately in latitude 19°17′28″ N. and longitude 166°34′42″ E. from Greenwich, Kingman Reef located in the Pacific Ocean approximately in latitude 6°24′37″ N. and longitude 162°22′ W. from Greenwich, and Johnston and Sand Islands located in the Pacific Ocean approximately in latitude 16°44′32″ N. and longitude 169°30′59″ W. from Greenwich, together with the reefs surrounding all the aforesaid islands, as indicated upon the diagram hereto attached and made a part of this order, be, and they are hereby, reserved, set aside, and placed under the control and jurisdiction of the Secretary of the Navy for administrative purposes, subject, however, to the use of the said Johnston and Sand Islands by the Department of Agriculture as a refuge and breeding ground for native birds as provided by Executive Order No. 4467 of June 29, 1926.

This order shall continue in full force and effect unless and until revoked by the President or by act of Congress.

FRANKLIN D ROOSEVELT

The White House,
*December 29, 1934.*

[No. 6935]


WA. ISLAND
Nautical Miles
Toki Pt
Heel Pt
Kuku Pt
Lagoon
Peacock Pt
KINGMAN REEF
Nautical Miles
3 ft high
JOHNSTON ISLAND
AND
SAND ISLAND
Nautical Miles
Sand I
Johnston I

## EXECUTIVE ORDER 8682

ESTABLISHING NAVAL DEFENSIVE SEA AREAS AROUND AND NAVAL AIRSPACE RESERVATIONS OVER THE ISLANDS OF PALMYRA, JOHNSTON, MIDWAY, WAKE, AND KINGMAN REEF

PACIFIC OCEAN

By virtue of the authority vested in me by the provisions of section 44 of the Criminal Code, as amended (U.S.C., title 18, sec. 96), and section 4 of the Air Commerce Act approved May 20, 1926 (44 Stat. 570, U.S.C., title 49, sec. 174), the territorial waters between the extreme high-water marks in the three-mile marine boundaries surrounding the islands of Palmyra, Johnston, Midway, Wake, and Kingman Reef, in the Pacific Ocean, are hereby established and reserved as naval defensive sea areas for purposes of national defense, such areas to be known, respectively, as "Palmyra Island Naval Defensive Sea Area", "Johnston Island Naval Defensive Sea Area", "Midway Island Naval Defensive Sea Area", "Wake Island Naval Defensive Sea Area", and "Kingman Reef Naval Defensive Sea Area"; and the airspaces over the said territorial waters and islands are hereby set apart and reserved as naval airspace reservations for purposes of national defense, such reservations to be known, respectively, as "Palmyra Island Naval Airspace Reservation", "Johnston Island Naval Airspace Reservation", "Midway Island Naval Airspace Reservation", "Wake Island Naval Airspace Reservation", and "Kingman Reef Naval Airspace Reservation".

At no time shall any person, other than persons on public vessels of the United States, enter any of the naval defensive sea areas herein set apart and reserved, nor shall any vessel or other craft, other than public vessels of the United States, be navigated into any of said areas, unless authorized by the Secretary of the Navy.

At no time shall any aircraft, other than public aircraft of the United States, be navigated into any of the naval airspace reservations herein set apart and reserved, unless authorized by the Secretary of the Navy.

The provisions of the preceding paragraphs shall be enforced by the Secretary of the Navy, with the cooperation of the local law enforcement officers of the United States and of the Territory of Hawaii; and the Secretary of the Navy is hereby authorized to prescribe such regulations as may be necessary to carry out such provisions.

Any person violating any of the provisions of this order relating to the above-named naval defensive sea areas shall be subject to the penalties provided by section 44 of the Criminal Code as amended (U.S.C., title 18, sec. 96), and any person violating any of the provisions of this order relating to the above-named naval airspace reservations shall be subject to the penalties prescribed by the Civil Aeronautics Act of 1938 (52 Stat. 973).

This order shall take effect ninety days after date hereof.

FRANKLIN D ROOSEVELT

THE WHITE HOUSE,

*February 14, 1941.*

## EXECUTIVE ORDER 8683

ESTABLISHING NAVAL DEFENSIVE SEA AREAS AROUND AND NAVAL AIRSPACE RESERVATIONS OVER THE ISLANDS OF ROSE, TUTUILA, AND GUAM

PACIFIC OCEAN

By virtue of the authority vested in me by the provisions of section 44 of the Criminal Code, as amended (U.S.C., title 18, sec. 96), and section 4 of the Air Commerce Act approved May 20, 1926 (44 Stat. 570, U.S.C., title 49, sec. 174), the territorial waters between the extreme high-water marks in the three-mile marine boundaries surrounding the islands of Rose, Tutuila, and Guam, in the Pacific Ocean, are hereby established and reserved as naval defensive sea areas for purposes of national defense, such areas to be known, respectively, as "Rose Island Naval Defensive Sea Area", "Tutuila Island Naval Defensive Sea Area", and "Guam Island Naval Defensive Sea Area"; and the airspaces over the said territorial waters and islands are hereby set apart and reserved as naval airspace reservations for purposes of national defense, such reservations to be known, respectively, as "Rose Island Naval Airspace Reservation", "Tutuila Island Naval

# APPENDIX C

## SAILING DIRECTIONS FOR THE PACIFIC ISLANDS

Vol III, The South-Central Groups,
6th Ed. 1952, pp. 354-357

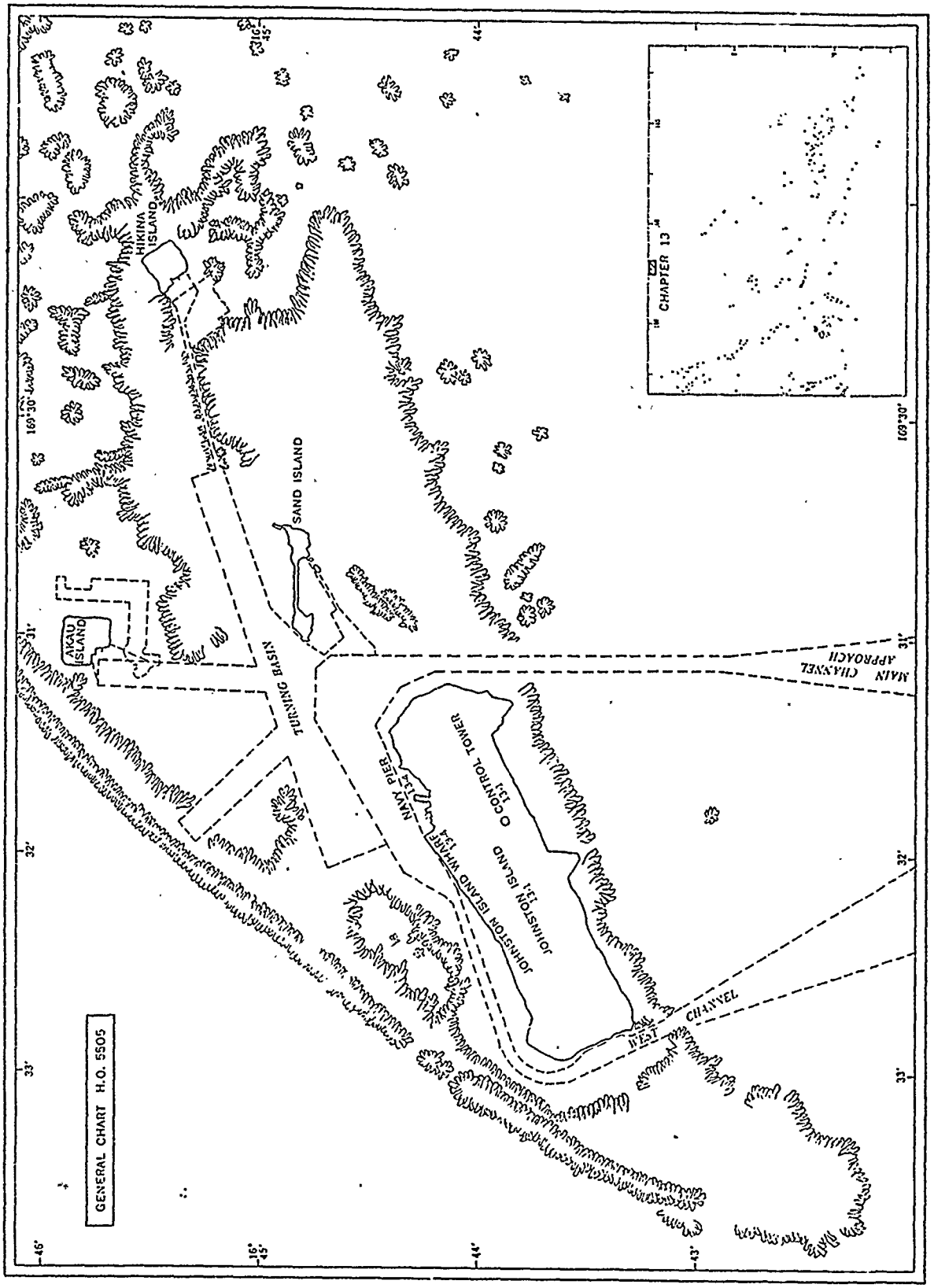



Chart limits shown are of the best scale charts issued to naval vessels by the U.S. Naval Oceanographic Office.
Section numbers refer to the place in the text where a description of the designated locality begins.

## CHAPTER 13—GRAPHIC INDEX

CHAPTER 13

JOHNSTON ATOLL

13-1 JOHNSTON ISLAND (Johnston Atoll) (16°45'N., 169°31'W.), a possession of the United States, consists of four islets that lie on a reef about 9 miles long in a northeast and southwest direction. The southwesternmost of the islets, known as Johnston Island, is about 3,500 yards long in a northeast and southwest direction, and about 700 to 1,200 yards wide. The smaller island, about 3/4 of a mile to the northeastward is known as Sand Island. An airfield is located on Johnston Island. Two small artifical islands, known as Akau and Hikina Island, are located at about 1 1/2 miles northward and 2 1/3 miles east-northeastward, respectively, of the east end of Johnston Island.

Johnston Island is a Naval Defense Sea Area and Airspace Reservation and is closed to the public. The airspace entry control has been suspended, but is subject to immediate reinstatement without notice. The administration of Johnston Island is under the jurisdiction of the Joint Chiefs of Staff, Defense Atomic Support Agency and Joint Task Force Eight.

Johnston Island Air Force Base is closed to all traffic except emergency landings and flights directed or approved by Commander Joint Task Force Eight, or by the island commander, Commander, Joint Group 8.6.

No vessels, except those authorized by Commander, Joint Task Force Eight or Commander, Joint Task Group 8.6, shall be navigated within the three-mile limit. For merchant vessel entrance procedure see section 1-22. In addition to these procedures authorities at Johnston Atoll must receive ship visit requests a minimum of 5 days in advance, and include certifications of masters' and ships' crew security clearances in the request.

WINDS—WEATHER.—Weather is usually excellent for navigation.

Winds average 10 to 15 knots in summer, and 15 to 25 knots in winter. They are from east to northeast about 90% of the time. During kona weather, the occasional Hawaiian Island storms are characterized by stormy southerly or southwesterly winds and heavy rains.

Brief showers occur frequently, but protracted bad weather is rare. Average rainfall varies from 30 to 50 inches.

Visibility is good, usually over 12 miles. There is no fog.

TIDES.—The high-water interval at full and change is 3h. 15m. The mean range of the tide is 1.8 feet.

DEPTHS—DANGERS.—A barrier reef extends in an arc from west to northeast of the islands. Depths outside the reef line drop off to 182.9m (100 fm.) in about 700 yards. With heavy breakers on the reef, a 0.6m (2 ft.) to 0.9m (3 ft.) surge exists in the lagoon. From northeast, via south, to southwest is a foul area with very irregular bottom. The 182.9m (100 fm.) curve lies 4 miles due south of the center of Johnston Island proper, however, there are 10.4m (34 ft.) shoals lying as close as 550 yards inside the curve and to the southeastward of the island. From south of Johnston Island the 182.9m (100 fm.) curve extends to the eastward about 083° about 11 miles, thence veering off northwestward. From this same point, 4 miles due south of the center of Johnston Island, the 182.9m (100 fm.) curve continues on about 248° for a distance of least 2 1/2 miles.

LANDMARKS.—The control tower and aviation beacon on Johnston Island and the towers on Sand Island are prominent. A tank, with a dish antenna, marked by an obstruction light and located on the northeast side of Johnston Island, is prominent.

The 640-foot loran tower on Sand Island was reported visible at 27 miles. The towers and buildings on this island show as separate radar targets. The outline of the island does not show until within 10 miles of the island.

HARBOR.—The harbor consists of a turning basin within the lagoon about midway between Sand Island and Johnston Island. The turning basin and harbor area are dredged to 10.7m (35 ft.). The berthing area alongside the main pier has been dredged to 9.1m (30 ft.) 1968. Vessels may anchor in the turning basin or berth at Johnston Island Navy Pier or Main Wharf. Mooring buoys are moored in the turning basin between 550 yards and 1,000 yards northeastward of the pier head.

The main entrance channel is entered southeastward of Johnston Island and is indicated on the chart by dashed lines. The channel, which bears true north and south, was dredged (1964) to a depth of 10.7m (35 ft.). Maximum draft for vessels entering the harbor under normal conditions is 8.5m (28 ft.) (1968). The navigable width of the channel is 400 feet. The largest ship that has entered and docked (1966) was 523 feet in length with a beam of 68 feet.

The channel to Sand Island narrows from about 200 feet to 100 feet as the dock is approached. Sand Island dock, approximately 60 feet long, is suitable only for small craft.

A channel with a least depth of 4.6m (15 ft.) (1967) has been dredged from the southwestern corner of the turning basin through the reef close westward and close southwestward of Johnston Island.

13-2 NAVIGATIONAL AIDS.—Johnston Atoll Fairway Entrance Buoy, equipped with a radar reflector and painted in black and white vertical stripes, is moored in about 36 feet in position 16°41′54.5″N., 169°-31′07.3″W. Johnson Atoll Channel Entrance Lighted Buoy 2 is moored in approximately 16°43′N., 169°31′W. and is equipped with a radar reflector. Channel Lighted Buoy 3, is moored about 1/2 mile northward of Buoy 2, on the west side of the channel. Channel Buoy 4, moored 150 yards eastward of Buoy 3, is equipped with a red reflector. The remainder of the channel to the turning basin is marked as follows: the west side by square concrete pile beacons fitted with green reflectors; the east side by square concrete pile beacons fitted with red reflectors. the beacons are at the channel limits. Several beacons have lights.

The channel from the turning basin to Johnston Dock is marked by buoys.

Range lights, marking the entrance channel are shown from rectangular-shaped daymarks; the front beacon is located at the northeastern corner of the turning basin; the rear beacon is 360° from the front beacon, distant about 640 yards.

A light is shown from the northeast end of the island.

A light is shown on the seaward end of the breakwater on Johnston Island.

A light is shown near the northeastern corner of the Navy Pier.

Obstruction lights are shown from the loran tower on Sand Island.

An aeronautical radiobeacon transmits from a tower near the center of Johnston Island.

REGULATIONS.—The following regulations are in effect:

As of April 1968, entrance to the harbor is not recommended at night. Ships are requested to night steam or anchor 3 miles southward of Johnston Island to wait for daylight.

Observe carefully rules and regulations prescribed by the Commandant for navigation in harbors and anchorages of Johnston Island, and have on board an officer familiar with these waters while underway in these areas.

All persons on board shall be U.S. citizens.

No photographs will be taken from the vessel. All cameras will be kept in the custody of the Master so long as the vessel is within waters contiguous to Johnston Island.

While anchored the vessel will maintain steam up and be prepared to get underway.

Dogs, cats, and other animals shall be confined on board.

Plants and fruits will not be imported without specific authority of the Commander of Johnston Island.

No garbage or ashes will be dumped overboard within three miles of Johnston Island. Ships will normally dump garbage before entering the channel. During the stay in port garbage and trash removal will be arranged.

Rat guards will be placed promptly on all lines, chains, hawsers, etc., used to make fast.

No oil or oily bilges may be pumped while in the harbor.

CAUTION.—An explosives dumping area has been established southwestward of Johnston Island, between the parallels of 16°25′ N., and 16°35′N., and between the meridians of 169°45′W., and 169°55′W.

13-3 ANCHORAGES.—It is suggested that vessels drawing more than 8.5m (28 ft.) anchor in the channel approach area south of the channel entrance.

Emergency Anchorage can be taken in the turning basin. As soon as practicable ships will be moved pierside or to a mooring buoy. The bottom in the turning basin is sand and coral, poor holding ground.

CAUTIONS.—A submarine cable is laid from the east end of Johnston Island southward down the main channel for about 2 1/4 miles.

Submarine cables are laid between Johnston Island, Sand Island, and Akau Island. Submarine cables are laid between the latter island and Hikina Island. (See H.O. Chart 5505.).

PILOTS.—No licensed pilots are available. Ships normally may not enter at night or when cross-channel winds exceed 25 knots. The harbormaster will board ships at the fairway entrance buoy with current information as to channel and harbor conditions. A navy tug is available for docking.

DIRECTIONS.—Vessels bound for Johnston Island ship channel should approach the channel from southward passing through position 16°41'00"N., 169°31'08"W., thence proceed northward to the fairway entrance buoy. When abeam the fairway entrance buoy they should heave to and await the boarding officer. While have to, a drift to the westward will usually be experienced. This drift must be checked, because the exact limits of the foul area on the port hand are not determined. There is usually a current in the channel, determined by tidal conditions. During the rising tide the current flows north and during the falling tide it flows south. It attains a rate of 1 knot to 2 knots. At low tide transition (low plus or minus 1 1/2 hours) the current flows southwestward at a rate of about 1 knot. At high tide transition (high plus or minus 1 hour) the current flows northward but is weak. Vessels with low power or with a relatively high wind area should favor the eastern side of the channel. A minimum speed of 8 knots should be maintained to overcome the effect of wind and current and increased proportionally with unusual conditions. During periods of heavy swell on the barrier reef, a strong easterly set may be encountered at the junction of the entrance channel and the turning basin, particularly during ebb tide.

13-4 FACILITIES.—Johnston Island Naval Pier is 400 feet long by 50 feet wide with pierhead of 186°, and has a timber deck supported by steel piling. Ships tie up starboard side to. The pier will accommodate ships with a maximum draft of 4.6m (15 ft.) Diesel oil pipelines are installed on the dock.

Johnston island Main Pier, 570 feet in length with pierhead of 236° is constructed of steel piling with concrete cap and has a depth of about 9.1m (30 ft.) alongside.

There is a small boat dock with five 50-foot slips. It has a depth of 2.4m (8 ft.) alongside, and is located westward of the Navy Pier.

At Sand Island there is a 60-foot long lumber quay wall, which is used only by station craft.

Cargo handling facilities include one 60-ton capacity crane and two 45-ton capacity cranes.

Fresh Water can be furnished to transient ships.

Repair facilities are available for local small craft.

COMMUNICATIONS with the island is under military control. When ships are within 100 miles, they are requested to contact the harbor master by voice radio on 2716 kc. The voice call Johnston Control is used and this frequency has a 24 hour guard. Radio contact can also be established on other marine frequencies if prior arrangements are made. The island uses zone +10 time.

13-5 OFF-LYING BANKS.—A bank with a depth of 12.8m (7 fm.) to 14.6m (8 fm.) over it, lies at a distance of about 7 3/4 miles eastward from the eastern end of Johnston Island.

NOVELTY SHOAL.—Captain F. Herriman, master of the schooner Novelty, reported in 1897 that with the eastern end of Johnston Island bearing 257°, distant 12 miles; in approximately 16°49'N. latitude, 169°14'W. longitude, he obtained soundings of 5 1/2 fathoms, rocky coral bottom. The bottom was visible for half an hour after taking the soundings while the vessel ran north 2 miles. Light breakers were seen about 3 miles to the eastward while the vessel was passing over the shoal.

# APPENDIX D

# INCINERATION OF ORANGE HERBICIDE

# APPENDIX D

## INCINERATION OF ORANGE HERBICIDE

A. GENERAL INFORMATION: The purpose of this appendix is to provide basic information concerning the combustion of Orange herbicide, to review all previous Orange herbicide incineration studies, and to comment on the applicability of incineration as a method of Orange herbicide disposal. It is noted that an incineration method known as "molten salt incineration" is not included in the review of previous studies contained in paragraph C. This method has been favorably applied to certain pesticide incineration studies; however, the method has not been applied to Orange herbicide incineration and therefore no Orange incineration data is available. The limited data on this system preclude any judgment as to its application to the large scale disposal of Orange. In addition, the fate of TCDD in this system will require investigation in view of concern over possible TCDD production at the temperature, pressure, and in the sodium environment in which the reactions occur (Baughman and Meselson b, 1973).

1. COMPLETE COMBUSTION: The theoretical products of combustion of Orange herbicide are carbon dioxide, hydrogen chloride, and water. Fifty pounds of normal butyl 2,4-D and 50 pounds of normal butyl 2,4,5-T would require 74 pounds and 67 pounds of oxygen, respectively, for complete combustion. Therefore, approximately 141 pounds of oxygen is required for the complete combustion of 100 pounds of herbicide. With the oxygen supplied in air, 610 pounds or 8200 cubic feet of air at 25°C, 760 mm is required for the combustion of 100 pounds of herbicide.

2. TEMPERATURE REQUIREMENTS: The Mississippi State, U.S. Department of Agriculture Report on Thermal Decomposition of Orange Herbicide, referenced in paragraph B, 1, reports the temperatures required for the complete combustion of Orange herbicide. The analysis was accomplished by the differential thermal analysis method utilizing a "Deltatherm" Model D2000, Technical Equipment Corporation, differential thermal analyses aparatus. The following is quoted from the referenced report: "The results show that both 2,4-D and 2,4,5-T analytical standard materials (free acids) are readily combusted between 330 and 360°C (Table 2). Esterified materials, i.e., normal butyl esters of 2,4-D and 2,4,5-T and the isooctyl ester of 2,4,5-T, on the other hand, require roughly twice as high a temperature for degradation as do their counterpart free acids. All three esters are combusted between 550 and 700°C. Dioxin (TCDD) is completely combusted between 980 and 1000°C. The bulk of the TCDD molecule, however, appears to be disintegrated at 850°C as indicated by an extremely large exothermic peak on the DTA curve (Figure 7). It is estimated (please note estimated) that about 70% of the TCDD molecule is degraded at that temperature alone. Two small exothermic peaks are shown at the completion of burning at 955 and 975°C with complete burning taking place at 980 to 1000°C. Similarly Orange and Orange II herbicides are completely combusted between 960 and 980°C. The normal butyl 2,4,5-trichlorophenoxyacetate containing 0.1 ppm dioxin (TCDD) is thermograded in the same temperature range as the esters without TCDD. Apparently the TCDD concentration was too small to be of any consequence, although it was conspicuous with Orange and Orange II herbicides." The caloric value of the Orange is 10,000 Btu per pound. This data was obtained on the basis of 200 samples collected at random from the Gulfport stock and analyzed at the Aerospace Fuels Laboratory, Wright-Patterson AFB, Ohio. The theoretical adiabatic flame temperature for complete combustion, under the test conditions described in Appen-

dix E, i.e., 1.55 pounds per second of air at 520°F and 0.185 pounds of herbicide per second at 77°F, is calculated to be greater than 3,000°F.

B. PREVIOUS STUDIES ON ORANGE INCINERATION

1. MISSISSIPPI STATE UNIVERSITY AND THE U.S. DEPARTMENT OF AGRICULTURE, STATE COLLEGE, MS.

a. Report: Technical Report on Thermal Decomposition of Orange Herbicide under the Amendment No.2 to the U.S.D.A. Cooperative Agreement No. 12-14-100-10, 673(34); submitted by Mississippi Agricultural and Forestry Experiment Station and Plant Science Research Division of the United States Department of Agriculture to the Department of the Air Force, Headquarters San Antonio Air Material Area (AFLC) Directorate of Aerospace Fuels, Kelly Air Force Base, Texas 78241; June 1, 1972 State College, Mississippi 39762. This report was prepared by Mr. B.J. Stojanovic, Mr. M.V. Kennedy and Mr. W.C. Shaw.

b. Objectives: The objectives as quoted from the report are: "The objective of this laboratory study was to determine temperatures required for complete thermal degradation, the degradation products, and the volatile gases of Orange herbicides containing dioxin (TCDD) and evaluate suitable scrubbing agents to remove toxicants from the effluent. Another phase of this project was to determine the biological activity (phytotoxicity) of the residues resulting from Orange herbicide incineration."

c. Type of Incineration: Herbicide samples were placed in ceramic combustion boats which were placed in a Vycor glass combustion tube (length 121 cm, O.D. 2.5 cm). The tube was placed in a resistance-type furnace; the total heated length of the tube was 80 cm. A silica combustion tube (30" x 1" I.D.) replaced the Vycor tube after some initial experiments. Commercial oxygen or air was passed through the combustion tube at a prescribed rate.

d. Quantity of Orange Incinerated: A series of experiments were conducted at various temperatures, 700 to 1000°C to determine chloride recovery, particulate recovery, scrubber efficiency, and carbon monoxide and carbon dioxide recovery. Experiments were conducted for mass spectograph analysis of exhaust gas samples and extracts of particulate filters. Experiments were also conducted for phytotoxicity analysis. Herbicide and TCDD analyses were accomplished throughout these experiments. The ceramic combustion boat was usually loaded with 100 mg of test material for each experiment; in all, approximately 5-6 grams of Orange and Orange II (isooctyl ester) were incinerated.

e. Monitoring: All of the carrier/combustion gas for each experiment was passed through collection devices, particulate traps, impingers, which utilized selective collecting medias depending on the analyses to be performed.

f. Results: The results were excellent as regards herbicide and TCDD destruction; the chlorine is released as essentially all hydrogen chloride as opposed to chlorine; particulate levels were significant; and the carbon was released essentially as carbon dioxide. No TCDD was indicated in any of the tests performed for TCDD. The phototoxicity experiments showed that hydrogen chloride is very phytotoxic (as expected) and that alkaline scrubbers are very efficient in entraining hydrogen chloride and any other phytotoxic gaseous compound in the combustion gas from Orange incineration.

g. Incomplete Combustion: Orange contains roughly three times as much carbon and oxygen; incomplete combustion could result in particulate matter and possibly carbon monoxide. In addition, roughly one-third of Orange herbicide is chlorine; therefore, certain chlorine compounds could result from the combustion Orange. The technical report lists the following theoretical compounds which could result from the complete/incomplete combustion of Orange: chlorine, chlorine monoxide, chlorine dioxide, chlorine hexoxide, chlorine heptoxide, chlorates, hydrogen chloride, hydrochloric acid, chlorinated water, hypochlorous acid, chlorous acid, chloric acid, perchloric acid, chlorine hydrate, and phosgene. All of these compounds are highly corrosive and toxic, about one-third are gases at normal temperature. The technical reports that "thermochemically speaking, however, hydrogen chloride and hydrochloric acid may be expected to be the chief, if not the only, chlorinated compounds released upon incineration of Orange herbicide." The experiments, as noted above, revealed the chlorine to be released as hydrogen chloride. In the experiments conducted for mass spectrograph analysis, the combustion gas was passed through a particulate trap (pyrex wool) and three impingers (benzene) in series. The analyses of the impinger samples for herbicide and TCDD was negative. The particulate matter traps were extracted with hexane and then with sodium hydroxide. The results are quoted from the technical report:

"Trace quantities (2.0-200 ppb) of 2,4-D and 2,4,5-T free acids were detected in the NaOH extracts of the particulate matter (Table 12). The 2,4-D n-butyl ester and 2,4,5-T isooctyl ester were, however, present in quantities ranging from 0.70 to 370 ppb in both the hexane and NaOH extracts of each particulate matter trap. The presence of 2,4,5-T isooctyl ester in the traps was unexpected as the 2,4,5-T component of Orange herbicide is the n-butyl ester. The origin of this compound cannot definitely be established on the basis of these investigations. It is, however, suspected to be an artifact, formed during combustion of the herbicide, which has an elution time coinciding with that of 2,4,5-T isooctyl ester and appears as such on the chromatogram. The gas chromatograms of the hexane extracts of the particulate matter traps indicated the presence of approximately 20 additional compounds which were not identified. Dioctylphthalate was identified as a contaminant by infrared spectroscopy. The results of this experiment have shown that at 1000°C traces of herbicides may be volatilized and be carried out of the burning range of the furnace. From a practical point of view, none of these materials would be expected to pass an alkaline scrubber where they would very likely be trapped and destroyed by the alkali."

h. Conclusions and Recommendations: The conclusions and recommendations are quoted from the technical report:

(1) Conclusions:

"a. A minimum temperature of 1000°C is necessary to insure complete combustion of pure dioxin (TCDD).

b. The bulk of the TCDD molecule (estimated 70%) is disintegrated at 850°C.

c. Both Orange and Orange II herbicides are completely combusted at 980°C, whereas normal butyl 2,4,5-T herbicide containing less than 0.1 ppm TCDD is combusted at 550°C.

d. More than 95% chlorine is recovered from burning orange herbicides at 800°C. The chlorine is released chiefly if not entirely as hydrogen chloride gas.

e. Dioxin (TCDD) was not detected in the incombustible residue (including the particulate matter) and the effluent scrubbing solutions following incineration of orange herbicides at 750, 800, and 850°C.

f. Incineration of herbicides under these experimental conditions does not produce carbon monoxide as none was detected in the effluent gas stream.

g. Oxygen supply during the incineration process appears to be less critical for dehalogenation than for cleavage of carbon-to-carbon bonds of herbicides.

h. Sodium hydroxide solutions of appropriate strength are for all practical purposes found to be the most efficient and desirable scrubbers for the effluent stream.

i. Unscrubbed effluent gases are found to be extremely toxic to young tomato plants. Hydrogen chloride in itself causes almost instantaneous kill.

j. One or more secondary burning chambers appear to be necessary for efficient incineration of orange herbicides."

(2) Recommendations:

"1. Even though the procedures used to obtain the preliminary data on thermal degradation of orange herbicides yielded important and very useful fundamental information, this information cannot be extrapolated and applied directly to a commercial incinerator.

2. A series of incineration runs with orange herbicides should be conducted within a short-term testing program in a research pilot incineration system.

3. The testing program should have as its chief objective the establishment in the shortest possible time of feasible parameters for the complete and safe incineration of Orange herbicides.

4. It is considered most urgent that the testing program should involve determination of the following:

   a. Temperature profile in the system

   b. Herbicide flow-rate (dwell time)

   c. Products of combustion by monitoring effluent gases, and

   d. Scrubber efficiency and composition of residues. Other factors may possibly also have to be considered but these could be established during the incineration tests.

5. Based on the tests currently being conducted by the investigators (with a pesticide pilot incineration system), it is estimated that a minimum of 90 days will be necessary to carry out the testing program and translate the laboratory research to a practical incineration system."

2. USAF ENVIRONMENTAL HEALTH LABORATORY, KELLY AFB TX

a. Report: Technical Report, Incineration of Orange Herbicide, July 1972, EHL(K) 72-7, USAF Environmental Health Laboratory, Kelly AFB TX. This report was prepared by Dr. R.A. Callahan.

b. Objectives: The scope of the laboratory work described in this report is to: 1) determine the feasibility of using Gas Liquid Chromatography (GLC) alone to analyze combustion gases and scrubbing blow-down water for the herbicide esters and TCDD, and 2) development of efficient methods of extracting the normal butyl esters and TCDD from gaseous and water discharges. In addition, the status of the Orange disposal via incineration including trip reports, impact statement comments, etc. was documented in this report.

c. Type of Incinerator: A small continuous burning flow through incinerator which approximated the fuel/air injection method, dwell time, air/fuel ratios and temperatures anticipated in commercial facilities was configured for the laboratory experiments. The incinerator chamber consisted of a Vycor-Pyrex tube with a length of 33 cm and a volume of 156 cc. This tube was placed in a Lindberg heavy duty furnace equipped with heating elements capable of operating at 1200°C. The system functioned as follows:

"Fuel (Orange Herbicide) was continuously delivered at a metered rate (via Hamilton 2.5 ml gas syringe mounted on a Sage Model 350M pump) to the tip of a blunted stainless steel 22 gauge needle. The tip of this needle was sealed in a stainless steel Luer Lock syringe fitting. Compressed air was metered into this fitting via a 0-1 ml/min rotometer. The Orange was continuously aerosoled from the tip of the fuel probe into the furnace tube. The air/fuel mixture was then deflected upwards by a dispersing cup. The combusting gases passed directly up and out of the furnace tube. The aerosol injection probe was a 20 gauge stainless steel pudental needle; the dispersing cup was also stainless steel."

d. Quantity of Orange Incinerated: Fourteen test runs are reported with a total of 14.12 ml of Orange incinerated. The run time for the experiments averaged 12 minutes with a minimum of 10 and a maximum of 30 minutes. The temperature of the combustion gases at the exit of the tube ranged from 740 to 950°C.

e. Monitoring: The entire combustion gas volume was passed through a sampling train consisting of midget impingers and a freeze trap. The apparatus was all glass and both tapered and fritted impingers were used. The impinger media was either distilled water or benzene. The sampling time was the same as the above mentioned run time; the air flow rate was usually 0.65 liters/min; therefore, the sample size was approximately 8.0 liters.

f. Results: Twelve runs were sampled, analyzed, and reported for herbicide; of these two were monitored, analyzed and reported for TCDD. The TCDD concentration in the Orange used for these two runs was 14 ppm while that of the remaining runs was <0.1 ppm. A summary of the results from the report is quoted:

"The destruction of the NB esters and TCDD in the model incinerator at 920°C, 2-3 second dwell times, and 150-180 percent stoichiometric air exceeded 99.999 percent for the esters and 93 percent for the TCDD. Total discharges of the combined esters ranged from 8.0-50.0 ppb (parts per billion) in the untreated gas discharges. The TCDD discharged when burning Orange containing high concentrations of TCDD were 3.0 and 18.0 ppb. Detailed data is presented in Appendix A, pg. 8."

g. Incomplete Combustion: The identification of incomplete combustion products or intermediate pyrolyzates was not within the scope of this project. Two chromatograms are shown in the technical report to depict the difference between a "clean" chromatogram - showing only residues of the herbicide esters and TCDD, and, a "less clean" chromatogram in which the peaks of five chlorinated pyrolyzates are present along with the peaks of herbicide esters and TCDD. The difference was attributed to temperature and excess air with the run having the higher temperature and greater excess air having the clean chromatogram.

h. Conclusions and Recommendations: Those conclusions and recommendations pertaining to the laboratory incineration test runs are quoted from the technical report.

(1) Conclusions:

"1. Monitoring the NB esters of 2,4-D and 2,3,5-T and TCDD in water and gas effluents resulting from commercial incineration appear feasible.

2. Limits of detection for each of the NB esters in effluent gas and water are 2.0 and 1.0 ppb respectively. The corresponding limits for TCDD are 3.0 and 1.0 ppb respectively.

3. Interference from other phyrolyzates will be negligible at temperatures of 1000°C, dwell times of 3 seconds and stoichiometric air/fuel ratios of 150%.

4. The very high water content of the gas samples taken from the incinerator stacks may interfere with the benzene charged fritted impinger extraction system. This condition is readily detectable. Substituting ethylene glycol for benzene in the first impinger should overcome this potential problem Other alternatives are available.

5. Emissions of the NB esters of 2,4-D and 2,4,5-T and TCDD when burned at 1000°C with 150% air and a dwell time averaging 3 seconds will be very low and safe to all forms of life. Incineration in tandem with the monitoring program developed above and outlined in detail in Appendix B of this report will offer negligible risks to the environment or human health from emissions of NB herbicide esters or from TCDD."

(2) Recommendations: "Identification of other pyrolyzates formed during the incineration of Orange herbicide should be accomplished as soon as possible. Pyrolysis of herbicide in such experiments should be accomplished in a continuously burning liquid injection incinerator as described herein to provide valid results."

3. THE MARQUARDT COMPANY, VAN NUYS, CA

a. Report: Report S-1224, "Report On The Feasibility of Destroying Herbicide Orange by Incineration Using the Marquardt SUE Burner," Ausust 1972,

the Marquardt Company, Van Nuys, CA. This report was prepared by Mr. R. Babbitt and Mr. J.L. Clure.

b. Objectives: The objective as described in the technical report was: "A test program was conducted to determine the feasibility of destroying herbicide Orange by means of combustion. Particular emphasis was placed on the ability to destroy the trace quantities of dioxin present in the herbicide. Attention was also placed on the ability to destroy the herbicide itself and to determine the nature and extent of the undesirable components in the exhaust gases and in the scrubbing liquid used to cool and scrub the exhaust gases."

c. Type of Incinerator: The incinerator system consists of a 12" diameter SUE Burner with a 48" air cooled combustion chamber and a 120" uncooled reaction tailpipe. The SUE stands for "sudden expansion" which describes the injection and combustion of fuel within the combustion chamber. The fuel injection sytem is at the entrance to the combustion chamber (a poppet value was used in these test runs) and an alkaline scrubber device (a venturi scrubber) is connected to the exit of the reaction tailpipe. The scrubber is connected to a gas/water separator and stack. The incinerator system is described fully in Appendix E.

d. Quantity of Orange Incinerated: A total of 56 test runs were made, 34 were in Phase I - Exploratory Testing, and 22 were in Phase II - Data Gathering Test Program. Of the 22 in Phase II, 11 were with the incineration of Orange only and no auxiliary fuel. The run time of the Phase II burns ranged from <1 to 5 minutes and the fuel flow rate and air flow rate ranged from 0.032 to .200 and 0.979 to 1.525 pounds per second, respectively. The temperature, measured about half way down the reaction tailpipe, ranged from 1730° to 2360°F. In all, approximately 37 gallons of Orange was incinerated in the Phase II testing.

e. Monitoring: During Phase II, samples of the combustion gases (near the exit of the reaction tailpipe), stack gas, and spent scrubber water were collected. Collection devices and techniques are described below; impinger trains were not used. The following is quoted from an Appendix of the report; the Appendix was prepared by the West Coast Technical Services Inc., Cerritos, CA, who performed the analytical analysis.

"APPENDIX A: The combustion products from the various test runs on the Marquardt Company SUE Burner have been analyzed by gas chromatography and mass spectroscopy. The gas analyses were performed by mass spectroscopy while the condensable materials were analyzed by gas chromatography and combined gas chromatography-mass spectroscopy.

I. SAMPLING PROCEDURES

A. Combustion Gases

An air-cooled probe was inserted into the center of the combustion tube immediately before the venturi scrubber. The entrance to the probe was restricted with an 0.015 in diameter orifice. The sample probe was then attached to a glass trap containing a built-in electrostatic precipitator. The outlet of the glass trap was attached to a

vacuum system equipped for flow measurement. The glass trap was cooled to 0°C in an ice bath and the electrostatic precipitator attached to a 3000 VDC. The samples were taken when the combustion system had reached equilibrium by opening the trap to the vacuum system. The flow rate and time were recorded. At the end of the desired sampling time the valves on the sample trap were closed.

The gases contained within the trap were analyzed by mass spectroscopy. The probe and glass traps were then washed with methylethylketone and chloroform. The washings were concentrated and analyzed by gas chromatography or combined gas chromatography-mass spectroscopy.

B. Grab Samples (Combustion Chamber Gases)

These samples were taken using the air-cooled sample probe described in "A" above. A standard glass sample bomb was used in place of the glass tray. The sample was taken by evacuating the bulb and purging the system with combustion gases. The bulb was allowed to fill with gas after which it was removed from the system. The gases were analyzed by mass spectroscopy.

C. Scrubber Exhaust Gases

The gases leaving the scrubber were purged through a glass sample tube. They were then analyzed by mass spectroscopy.

D. Scrubber Liquid

A sample liquid from the scrubber tank was removed. The sample was acidified with sulfuric acid and extracted with diethylether and carbontetrachloride. The extracts were dried over anhydrous sodium sulfate and removed by distillation. The concentration was treated with diazomethane in ether to convert the acidic compounds into their methyl esters or ethers. The methylated extracts were then analyzed by either gas chromatography or combined gas chromatography-mass spectroscopy."

f. Results: For ten runs analyzed for condensible products in the combustion gas, the results were less than the detectible limit for herbicide components (<20 ng) and TCDD (<15 ng). For one run, a total herbicide concentration of 19 ppm was detected in the combustion gases. During this run, the sample volume was increased 10 fold from the usual 14 liters to 140 liters. The results of analysis of scrubber gas is given for two runs, one of the runs being the same as the above mentioned run in which herbicide was measured in the combustion gases; both analyses revealed no herbicide or chlorinated compounds above the detection limit (.1 µg per liter of gas). Samples of spent scrubber water was analyzed from 6 test runs. All samples were below the detection limit for TCDD (.015 ppb) and the concentration of chlorinated compounds ranged from 0.4 to 17.0 ppb. Analyses of samples of spent scrubber water from two additional runs revealed total herbicide concentration of 172 ppb and 2,199 ppb. In addition, the combustion and scrubber exhaust gases were analyzed for the components: nitrogen, oxygen, argon, carbon dioxide, hydrocarbons as butane, hydrogen chloride, nitric oxide and phosgene. These were all within acceptable limits.

g. Incomplete Combustion: Eleven samples of combustion gas and 14 samples of scrubber exhaust gas were analyzed for phosgene, all results were reported as 0.0 mole percent. From a thermochemical standpoint, a computer program for the calculation of complex chemical equilibrium compositions was used to obtain theoretical combustion temperatures and products for Orange/natural gas/air ratios. The computer program is contained in NASA Report SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations by Sanford Gordon and Bonnie J. McBride," 1971. The computer output is presented in graph form in the technical report as a function of temperature and auxiliary fuel to air ratio. For a temperature of 2000°F and no auxiliary fuel, the predicted combustion products to a volume >99.9% are nitrogen, oxygen, water, carbon dioxide and hydrogen chloride.

h. Conclusions and Recommendations: The conclusions and recommendations are quoted from the technical report.

(1) Conclusions:

"1. Herbicide Orange can be effectively and safely destroyed by combustion.

2. The absence of raw herbicide, phosgene, hydrogen chloride and dioxin in the scrubber gases indicates that the impact on the atmospheric environment is not damaging. The impact on the ground and water environment is dependent on the type of scrubber material used and the ultimate disposition of the expended neutralizer.

3. Exotic type materials are not required. The 310 stainless steel material used for the combustion chamber and reaction tailpipe showed no evidence of deterioration due to the interaction of the hot exhaust gases with the metals. The durability of refractories for this application was not evaluated.

4. The incinerator must be gas tight up through the scrubber, otherwise hydrogen chloride vapors will be emitted and pose a serious problem.

5. A full scale incinerator system should have very large filter capacity with two parallel filter systems. This arrangement will permit cleaning one system while the other system is in use."

(2) Recommendations: "Additional design study and testing should be funded to determine the most feasible and economical type scrubbing system and scrubber material. The study should also include ways of disposing of the expended neutralizer."

4. THE MARQUARDT COMPANY, VAN NUYS CA AND THE USAF ENVIRONMENTAL HEALTH LABORATORIES, MCCLELLAN AND KELLY AFB.

a. Report: Report on the Destruction of Orange Herbicide by Incineration, 1974; this report was prepared by the Marquardt Company with inputs prepared by the USAF Environmental Health Laboratories. The Marquardt Company was primarily responsible for Orange handling and incineration operations; the Air Force conducted the majority of the

monitoring effort, and the West Coast Technical Services, Inc. performed, under contract to the Marquardt Co, most of the analytical chemistry. A FINAL DRAFT copy of this report is included as Appendix E to the Environmental Statement. The report was accomplished by Mr. R.J. Haas, Mr. R.P. Babbitt, and Mr. J.E. Hutson of the Marquardt Co. (TMC), with appendicies prepared by Captains C.W. Bullock and J.W. Jackson of the USAF Environmental Health Laboratories. The scope of the project reported on was to incinerate the contents of 28 drums of Orange herbicide, with complete operational and environmental monitoring, in test incineration runs of approximately 3 hours' duration. The objectives and conclusions are quoted below:

(1) Objectives

"Test Objectives: The objectives of the contract effort, as listed in tne Statement of Work, were as follows with agencies of prime responsibility noted:

a. Determine the capability of an incinerator system to destruct the "Orange" Herbicide over a range of selected incineration conditions (TMC and EHLs).

b. Obtain the necessary engineering data to adequately monitor, control, and document the incinerator operation during the project (TMC).

c. Evaluate the test burns' effects and project the long term effects of the combustion gases on the material of the incinerator unit (TMC).

d. Determine the combustion gas, scrubbed effluent gas, and "spent" scrubber water discharge mass rates of herbicide constituents and any other organic compounds which may be detected (EHLs).

e. Determine the presence of herbicidal pyrolyzates and hydrolozates, if any, in the combustion gases, scrubbed effluent gases, and "spent" scrubber water (EHLs and Analytical Chemistry Laboratory).

f. Determine the toxicity of "spent" scrubber water to several aquatic indicator organisms (EHL/K).

g. Evaluate the noise produced by an incineration system and assess its occupational hazard to operators (EHL/K).

h. Evaluate the effectiveness of a proposed drum cleaning procedure (EHL/K)."

(2) Conclusions

"14.0 CONCLUSIONS (Prepared by USAF EHL/K, EHL/M and TMC)

14.1 Destruction of "Orange" Herbicide by Incineration

"Orange" Herbicide was effectively and safely destroyed by incineration. No "Orange" Herbicide constituent was detected

in any system effluent when operating with the slot nozzles, and only in one spent scrubber water sample (Burn III) when operating with the poppet nozzle. Likewise, very favorable relative pyrolysis efficiencies were obtained, ranging from 99.98% to 99.999%. Also, no chlorinated phenolic compound was detected in any of the scrubbed effluent gas samples, and only in one combustion gas sample. The spent scrubber water from all burns contained monochlorophenol but at a level not exceeding $0.14 \times 10^{-6}$ grams /liter in the last five burns or $53 \times 10^{-6}$ grams/liter in all burns.

## 14.2 Engineering Data

Preheat of "Orange" Herbicide fuel prior to injection in the combustion chamber was an important combustion efficiency parameter. The RPE was improved significantly where the "Orange" Herbicide fuel was preheated to 175°F. Preheat of "Orange" Herbicide fuel to at least 90°F was required to accomplish acceptable fuel injection characteristics.

The method of fuel injection was an important combustion efficiency parameter. The radial slot nozzles produced a higher RPE (Appendix I) and only about 1/20 the mass of combustion chamber coke deposits produced when central poppet nozzles were used. In the incineration system utilized, the slot nozzles provided satisfactory results at higher fuel/air mass ratios and combustion temperatures and therefore permitted a higher destruction rate of the "Orange" Herbicide.

The basic flow control required for this incinerator was quite simple in that only fuel and air mass flow regulation was required once steady state was achieved. Transients were performed without incident due to the ease of ignition of "Orange" Herbicide into an established flame. The manual control systems were quite satisfactory in these regards and the only real flow control monitoring needed was to correct for minor changes in flow caused by changes in facility air storage pressure or changing fuel properties. It can be concluded that "Orange" flow regulation is no problem as long as temperature is maintained within a reasonable band as determined by system sizing and is properly filtered to prevent plugging of fuel nozzles. Basic incinerator control therefore consisted of fuel and air flow regulation with monitoring of the combustion gas temperature to verify the presence of combustion and provide a relative indication of combustion and consistency of operating parameters. Air and fuel mass flow depended on delivery system pressure. The burner system pressure provided an indication of combustion gas flow and downstream conditions. These control parameters were conventional and could be readily automated using existing process industry control components. Such systems quite routinely monitor and control flow and combustion processes and take appropriate corrective action in the event of system anomalies. From purely a combustion point of view, this incineration process was not much different than when using conventional fuels. However, the serious differences were in the structural integrity (safety) of the incinerator and the safety aspects of storage and delivery of the "Orange" Herbicide.

Scrubbing of the combustion gases and neutralization of acids was accomplished satisfactorily. Optimization of this system was not within the scope of this effort and it is recognized that other types of

scrubbers may be more desirable.

The on-line gas analyses equipment used was adequate for CO, $NO_x$, and HC monitoring of scrubbed effluent gas only. Gas analyses equipment incorporating additonal features would be suitable for sampling of combustion gas. However, the application of on-line sampling analysis to a production process would require additional study beyond the scope of this effort.

## 14.3 Effects on Incinerator Materials

Considering the absence of structural or sealing problems in the physical combustion chamber enclosures, the lack of evidence indicating physical deterioration in the materials utilized, the qualities of the materials used, and prior experience in similar systems, it can be concluded that the basic incinerator design would provide a unit of considerable longevity. There are design considerations that would be required, "external" to the basic combustion process, which could further ensure longevity and provide a reliable unit. Such design factors do not appear to be particularly unusual or exotic in nature. It can also be concluded that durability would be enhanced by long term continuous operations where start-stop transients are minimized.

## 14.4 Mass Discharge Rates of "Orange" Herbicide Constituents.

TCDD was detected in the spent scrubber water from Burn III at $0.25 \times 10^{-6}$ grams/liter. Otherwise, no "Orange" Herbicide constituent was detected in any scrubbed effluent gas sample or in any spent scrubber water sample. "Orange" Herbicide constituents were detected in the combustion chamber coke deposit from Burn III but these deposits were contained and the mass of the "Orange" Herbicide constituents in the coke was 64.4 mg.

Table 5 presents the maximum potentially undetected "Orange" Herbicide constituents that could have been discharged without being detected. The TCDD in the spent scrubber water from Burn III was included in the discharge. The average mass that could have been discharged in the scrubbed effluent gas during each burn was 9.3 mg ($\delta$ = 2.7 mg). The average mass that could have been discharged in the spent scrubber water was 3.4 mg ($\delta$ = 1.4 mg).

## 14.5 Spent Scrubber Water Quality

Spent scrubber water inorganic quality was directly related to applied caustic. Mineral content of spent scrubber waters would be minimized and acid gases effectively scrubbed if applied caustic were 2.0 ($\pm$ 0.1) times that required to neutralize the theoretically expected amount of HCl. Primary settling, and dechlorination, and adjustment of pH to about 9 may be required before discharging the spent scrubber water to natural waterways. For burns using the slot nozzles, the total average hydrocarbons were less than 20 µg/L and no hydrocarbons were detected in the water's suspended carbon particles. Of the 20 µg/L total hydrocarbons, less than 1.5 percent of them could have been undetectable compounds of the original herbicide feed.

## 14.6 Pyrolyzates and Hydrolyzates

All of the detected unchlorinated aliphatics, aromatics, and biphenyls were considered pyrolyzates. The total mass of these pyrolyzates in the scrubber water, combustor coke deposit, and scrubbed effluent gas averaged 1.32 gms as carbon per drum of herbicide incinerated in the less efficient burns (I, II, III) and was an order of magnitude less (0.42 gms as carbon per drum) in the high efficient burns (IV through VIII).

All of the detected monochlorophenol and dichlorobenzene were considered hydrolyzates. Since they were detected in only one effluent stream from the incinerator scrubber water, their total effluent mass averaged 0.86 grams as carbon per drum of herbicide incinerated in the less efficient burns (I, II, and III). These effluent masses of hydrolyzates decreased three orders of magnitude to an average of 0.006 grams as carbon per drum of herbicide incinerated during the more efficient burns.

## 14.7 Air Sampling

It was concluded that the data from the Beckman 109A hydrocarbon analyzer was not an indicator of RPE (Appendix I).

The formation of dichlorobenzene, dichlorophenol, and monochlorophenol by the reaction of nonchlorinated aromatic hydrocarbons with HCl, $Cl_2$ and Cl was indicated in locations of rapid combustion gas cooling. The quantity of these compounds that might be formed in other systems would not be expected to exceed the mass of aromatic hydrocarbons existing in the gas.

## 14.8 Bioassays

Conclusions about bioassay data will be published under separate cover by USAF EHL/K.

## 14.9 Noise Hazards

Unprotected personnel occupationally working within fifty feet of the incinerator(s) should be provided ear protection and be monitored via a hearing conservation program. The conventional masonry control room walls effectively protected the operators from the incinerator's hazardous noise levels and provided them an area quiet enough for reliable communication. Masonry walls around the incinerator pad would preclude ambient incinerator noises from interfering with any adjacent operations.

## 14.10 Drum Cleaning

Data of this study can be used to determine the volumetric rinses of used or contaminated JP-4 needed to meet any prescribed drum cleaning requirements. Under the following constraints, separate rinse procedures should be used to obtain maximal removal of the 450 ($\pm$ 25) grams of herbicide in the drained drums:

a. Some cleaning required but $\leq$5 gallons of clean or contaminated JP-4 available per drum. Use the five gallons in a single rinse

to obtain 70 percent herbicide removal.

b. Maximal cleaning required but ≦10 gallons of clean or contaminated JP-4 available per drum. Use two rinses of five gallons each to remove 79.1 percent of the herbicide.

c. Third rinses of less than five gallons of JP-4 did not improve overall herbicide removal by more than three percent.

Removing drum ends and spraying the rinse downward through the open drum would provide better rinse drainage. Depending on rinse volumes used, such a rinse application technique may improve herbicide removal efficiencies by 10 to 25 percent over the results of this study."

5. COMBUSTION POWER COMPANY INC., MENLO PARK, CA

a. Report: Technical Report TR 73-7, Progress Report of Determining the Feasibility of Disposing of Air Force Liquid Wastes in the LSW-500 Industrial Prototype, August 15, 1973, Contract No. F29601-73-C0128 for Air Force Weapons Laboratory (AFSC), Kirtland AFB NM 87117, by Combustion Power Inc, Menlo Park CA. This report is not a final report but is a progress report, the last revision was incorporated as of 18 Jan 74.

b. Objectives: To determine the feasibility of disposal of selected Air Force liquid waste including paint stripping waste, petroleum based wastes, wash rack wastes, and Orange herbicide via fluidized bed incineration.

c. Type of Incineration: The incinerator unit used is the LSW-500 Industrial Prototype. The combustion zone is 3 feet in diameter and the bed material is normally sand. Air is used to fluidize the bed and the velocities through the unit have been usually 4 to 6 feet per second. For acid gas control, dolomite or limestone is placed into the unit as part of the bed material. The acid gas produced by the incineration is then absorbed chemically within the fluidized bed. As the limestone is used up, it has to be removed and replaced with fresh limestone. This method eliminates the need for a liquid scrubber for acidic combustion gases. The combustion gases are presently passed through three separators for particulate removal and sand recovery. Prior to incineration of Orange, tests were conducted with dichloro-benzene to determine the efficiency of dolomite in hydrogen chloride absorption.

d. Quantity of Orange Incinerated: Five test runs of Orange have been conducted; the total volume of Orange incinerated, in a chronological order per run, was 3.10, 2.18, 5.5, 10 and 18.3 gallons respectively. The feed rates for these runs were 0.505, 0.705, 2.36, 2.79 and 3.25 pounds per minute. In the first two runs the bed material was all dolomite, the bed temperature was 1500°F and the superficial velocity was 4 and 6 feet per second respectively. For the third run the bed material was 50 percent dolomite and 50 percent sand, the bed temperature was 1490°F and the freeboard temperature was 1150°F, and the superficial velocity was 4.0 feet per second. The bed material for test 4 and 5 was a combination of s ıd and limestone and the average bed temperature was 1530°F and 1510°F respectively.

e. Monitoring: The exhaust gas of each run was sampled for subsequent herbicide and TCDD analyses by Combustion Power Co personnel using an impinger train with benzene as collecting media. In addition, monitoring was accomplished

for oxygen, carbon dioxide, carbon monoxide, hydrocarbons, sulfur dioxide, and oxide of nitrogen. The analyses of herbicide components and TCDD is to be accomplished by Stoner Laboratories, Inc, Santa Clara CA. At present, the results have been documented for the first three runs for the herbicide components and no results have been attained for TCDD. The TCDD analyses has been delayed due to problem associated with obtaining a laboratory standard; however, action has been taken to be sure that the TCDD samples will be analyzed.

f. Results: The concentrations of herbicide components in the exhaust gases, corrected to 10% $O_2$, were as follows: Run 1: 4.068 ppb nb 2,4-D, 10.96 ppb nb 2,4,5-T, 0.2913 ppb 2,4-D acid and 0.5044 ppb 2,4,5-T acid; Run 2: 0.3196 ppb nb 2,4-D, 2.370 ppm nb 2,4,5-T, and none detected (ND) for either acid, and Run 3: 0.5221 ppb nb 2,4-D, 0.5418 nb 2,4,5-T, and ND for either acid. The ranges of the other constituents were all within acceptable limits.

g. Conclusions: This report being reviewed is a progress report whose function is primarily to report data. A discussion of date and conclusion will be contained in the final technical report to be prepared by Combustion Power Co. It is apparent that practically all of the ester components herbicide are being destroyed by the incineration process.

C. SUMMARY AND CONCLUSION: The results of two laboratory, two full scale, and one industrial prototype scale Orange incineration projects have been reviewed. The methods of incineration have included heating, flame, and fluidized bed. The data and conclusions of the investigations have revealed incineration an efficient method of large scale destruction of Orange herbicide. The essentially complete destruction of the herbicidal components of Orange as reported in all of the projects, dictates that the herbicidal effect of combustion gases will be minimal to non-existent. Therefore, such gases could be discharged into a remote, non-vegetative environment. The hydrogen chloride generated by the incineration process is phytotoxic; the removal of hydrogen chloride via alkaline scrubbing is extremely efficient and is also positive as regards removal of particulates from the combustion gas. The data shows that the discharge of alkaline scrubbed combustion gases via a stack would be acceptable to practically any environment. The discharge of spent scrubber water will require consideration for its impact on the receiving water. The TCDD situation requires placement into proper perspective. The total amount of TCDD in the entire Orange stock is approximately 50 pounds. All the reviewed projects revealed the TCDD concentration in the exhaust streams to be non-detectable or extremely small. Under high temperature incineration, the data indicated that essentially all of the TCDD will be destroyed. Orange destruction efficiencies of 99.9 to 99.999 percent appear feasible for the large scale incineration project. This will respectively result in a total discharge of 0.05 to 0.0005 pounds of TCDD via the exhaust streams over the duration of the project. The exhaust streams would, in turn, be diluted in the environment into which they are discharged. When judged against certain alternatives, for example, storage under conditions where a catastrophic event could result in gross detrimental environmental impact, the incineration of Orange, with due considerations for the extreme toxicity of TCDD, is an acceptable method of disposal. In addition, USDA (1970) reports that some 9.0 million pounds of 2,4,5-T were being applied annually in the United States when in April 1970, restrictions were placed on its use. If these nine million were assumed to have 2 mg/kg of TCDD, the same as that of the Orange stock, then the TCDD released to environment annually during application was about 18 pounds. The possible incineration effluent discharge noted above, 0.05 to 0.0005, re-

presents only 0.27 to 0.0027 percent of the estimated release which had occurred during one year of application of 2,4,5-T. The situation as regards pyrolyzates and hydrolyzates of Orange herbicide incineration has been addressed in this review. Existing data, together with theoretical considerations and applied thermochemistry, show that such products are minimized with efficient, high temperature incineration. The data also indicate that if such products were present their concentrations would be extremely small and environmentally insignificant. In view of the above, it is concluded that incineration, with proper concern for the environment in which such incineration will take place, is an environmentally safe method for disposal of Orange herbicide.

APPENDIX E

FINAL REPORT

REPORT ON THE DESTRUCTION OF

"ORANGE" HERBICIDE BY INCINERATION

A

FINAL REPORT

# REPORT ON THE DESTRUCTION OF "ORANGE" HERBICIDE BY INCINERATION


Prepared by:

J. E. Hutson, P.E.
Project Engineer

Approved by:

R. P. Babbitt, P.E.,
Manager, Environmental
Process Systems

R. J. Haas, General Manager
CCI Environmental Systems
Division



April, 1974

THE MARQUARDT COMPANY
16555 Saticoy Street
Van Nuys, California

Prepared for:

UNITED STATES AIR FORCE
ENVIRONMENTAL HEALTH LABORATORY
Kelly Air Force Base, Texas

CONTRACT NO. F41608-74-C-1482

ACKNOWLEDGEMENTS

During this project, personnel from the USAF Environmental Health Laboratories performed the gas sampling, scrubber water sampling, biomonitoring, noise testing, and analyses of data for certain portions of this report. Team members from the USAF Environmental Health Laboratory Kelly AFB TX (EHL/K) were Majors Carlton R. Williams and Roger C. Inman, Capt Charles W. Bullock, TSgt Jerrold C. Akey, SSgt John J. DiLorenzo, A1C Gregory S. Knerl and Mr. Leopoldo L. Rodriguez; and team members from the McClellan AFB, CA (EHL/M) laboratory were Maj John J. Gokelman, Captains Jerry W. Jackson, Marlin L. Swegart and Kenneth E. Hundley, and Staff Sergeants Fred Ward and Henry F. Pauley.

Capt Charles Bullock (EHL/K) prepared Appendices C, Sample Code Designations; E, Scrubber Water Monitoring; F, Drum Cleaning, Disposal, and Analyses of Drum Rinse Samples; and J, Noise Monitoring. Capt Jerry Jackson (EHL/M) prepared Appendix D, Combustion and Scrubbed Effluent Gas Monitoring. Both Captains Bullock and Jackson prepared Appendix I, Evaluation and Discussion of Organic Analyses of Blended Herbicide, Scrubber Water, Combustion Gas, Scrubbed Effluent Gas, and Residues.

D

# FOREWORD

The work reported herein is submitted in fulfillment of Contract No. F41608-74-C-1482, let by USAF, AFLC, San Antonio Air Materiel Area (SAAMA), Procurement Directorate, Kelly Air Force Base, Texas. The project was monitored by USAF Environmental Health Laboratory, Kelly Air Force Base, Texas, in coordination with SAAMA Procurement.

This report was written and concluded jointly by The Marquardt Company, Van Nuys, California; USAF Environmental Health Laboratory, Kelly Air Force Base, Texas (USAF EHL/K); and USAF Environmental Health Laboratory, McClellan Air Force Base, California (USAF EHL/M).

The work was accomplished between 8 October 1973 and 21 December 1973 at the Air Force-Marquardt Jet Laboratory (AF-MJL) at Van Nuys, California. Activities were conducted and monitored by a team consisting of The Marquardt Company, the USAF EHL/K, and the USAF EHL/M. Organic analyses of samples from test burns were performed by West Coast Technical Service, Inc. (WCTS) of Cerritos, California. Inorganic analyses of test burn and drum cleaning samples were performed by the EHL's.

The Marquardt Company has no proprietary interests or restrictions on this report.

## ABSTRACT

A test program was conducted to evaluate the incineration of "Orange" Herbicide in a commercial incinerator over a range of selected incineration conditions. Particular emphasis was placed on the ability to destroy the parts per million quantities (11-16 mg/kg) of 2,3,7,8-tetrachlorodibenzo-p-dioxin present in the herbicide. Extensive sampling was conducted to evaluate the unscrubbed combustion gases, the scrubbing liquid used to cool and scrub the combustion gases, scrubbed effluent gases and any solid residues deposited in the system. Additional objectives were: to obtain engineering data relative to controlling and monitoring the incineration process, to evaluate noise produced by the incineration system, to evaluate long term effects of herbicide combustion on incinerator materials, to evaluate the effectiveness of a proposed drum cleaning procedure, to assess the toxicity of discharged scrubber water to several aquatic organisms, and to assess the effects of scrubbed effluent gas on tomato plants.

The program was conducted using a Marquardt incinerator system. Samples were analyzed by mass spectroscopy, flame ionization gas chromatography, and atomic absorption.

A total of 30.5 hours of burn time on undiluted "Orange" Herbicide fuel was accumulated during eight record burn periods. Test data demonstrated that the incineration system operated very satisfactorily using undiluted "Orange" Herbicide as a fuel and that the herbicide was effectively and safely destroyed in the combustion process; i.e., gaseous and spent scrubber water effluents, within the analytical limits of detection, did not contain any of the compounds identified in the herbicide feed. Criteria were also established regarding effluent biological impact, incinerator noise generation, drum cleaning procedures, and incinerator process system functions.

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DEPARTMENT OF THE AIR FORCE
OL AA, USAF OCCUPATIONAL AND ENVIRONMENTAL HEALTH LABORATORY (AFSC)
KELLY AIR FORCE BASE, TEXAS 78241

REPLY TO ATTN OF CC

OCT 22 1976

SUBJECT Transmittal Letter - Amendment to USAF Final Environmental Statement, "Disposition of Orange Herbicide by Incineration," November 1974

TO SAF/ILE (Major Charles Bullock)
Pentagon
Room 4C885
Washington DC 20330

Request you use the indorsement below to acknowledge receipt of attached statement(s). For your convenience, a self-addressed envelope is inclosed.

FOR THE COMMANDER

Walter W. Melvin, Jr.
WALTER W. MELVIN, JR., Col, USAF, MC
Chief, OL AA, OEHL

1 Atch
SAF/ILE Letter w/1 atch

1st Indorsement

TO: OL AA; USAF Occupational & Environmental Health Lab, Kelly AFB TX 78241

Receipt acknowledged. Copy number 810 135-144

Date _____

Signature _____

DEPARTMENT OF THE AIR FORCE
WASHINGTON, D.C. 20330

OFFICE OF THE ASSISTANT SECRETARY

OCT 22 1976

SAF/ILE (Major Charles Bullock)
Pentagon
Room 4C885
Washington DC 20330

In accordance with the Guidelines of the Council on Environmental Quality, a copy of the Amendment to the Final Environmental Statement (FES) for the Disposition of Orange Herbicide is forwarded for your information.

This Amendment is an update of the November 1974 Orange Herbicide Final Environmental Statement. Based upon comments raised during deliberations regarding ocean incineration, the option for herbicide reprocessing and use was further explored. Pilot plant studies indicate that charcoal treatment of the herbicide is a feasible means of removing the dioxin contaminant to levels currently considered acceptable by the Environmental Protection Agency. This Amendment, therefore, proposes herbicide reclamation rather than destruction. This proposal is considered desirable and consistent with previous disposition efforts documented in the Final Environmental Statement.

Should you have any comments, please furnish them to the undersigned by November 22, 1976.

Sincerely,

BILLY E. WELCH, Ph.D.
Special Assistant for
Environmental Quality

Attachment-
Amendment to FES

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# GLOSSARY OF TERMS AND SYMBOLS

Unless otherwise stated, all terms and symbols used in this report are as defined below.

Chemical symbols other than those listed below are defined in standard chemical texts.

ALPHABETIC

| | |
|---|---|
| AFB | Air Force Base |
| AFLC | Air Force Logistics Command. |
| AF-MJL | Air Force-Marquardt Jet Laboratory |
| ATL | Aero Thermo Laboratory |
| Cal | calories |
| cc | cubic centimeters |
| (Cl) | monatomic chlorine |
| cm | centimeter |
| dbA | decibels - "A", weighted octave band |
| dbC | decibels - "C", weighted octave band |
| DGF | dry gas fraction |
| EHL(K) | USAF Environmental Health Laboratory, Kelly AFB |
| EHL(M) | USAF Environmental Health Laboratory, McClellan AFB |
| EPA | Environmental Protection Agency |
| F/A | fuel/air mass ratio |
| FSN | Federal Stock Number |
| ft/sec | feet per second |
| gal | gallon |
| gm | gram |
| $GN_2$ | gaseous nitrogen |
| gpm | gallons per minute |
| gr/scf | grains per standard cubic foot corrected to 12% carbon dioxide |
| HC | hydrocarbons |
| Hg | mercury |
| hp | horsepower |
| ID | inside diameter |
| JP-4 | jet engine fuel grade |
| Kg | kilogram |
| l | liter |
| lbs | pounds |
| m | meter |
| mg | milligram |
| mg/kg | milligram per kilogram |
| mg/l | milligrams per liter |
| min | minute |
| ml | milliliters |
| mm | millimeters |
| mph | miles per hour |
| MSA | Mine Safety Appliances |

| | |
|---|---|
| mw | molecular weight |
| NA | not applicable |
| NaOH | sodium hydroxide |
| nb | normal butyl |
| ND | none detected |
| NE | not evaluated |
| no | number |
| $NO_x$ | nitrogen oxides (NO and $NO_2$) |
| $\frac{N_U}{N_T}$ | ratio of applied NaOH to theoretical amount of NaOH required |
| "Orange" Herbicide | A chlorinated-phenoxy hydrocarbon herbicide procured by the USAF to contain, by volume, 50% (± 1.5%) 2,4-D and 50% (± 1.5%) 2,4,5-T |
| P/N | part number |
| ppm | parts per million by volume in gases, parts per million by weight in liquids |
| pps | pounds per second |
| psid | pressure differential, pounds per square inch delta |
| psig | pounds per square inch gauge |
| RPE | relative pyrolysis efficiency |
| s or $s$ | standard deviation of sample population |
| SAAMA | San Antonio Air Materiel Area |
| sample codes | See Appendix C |
| SSW | spent scrubber water |
| STP | standard temperature (70°F) and pressure (29.92 inches Hg) |
| SUE® | "Sudden Expansion" Burner, Registered Trade Mark, The Marquardt Company |
| TBC | total burn composite |
| TC | thermocouple - subscript number denotes location |
| $TC_{AVG}$ | average of theoretical combustion temperature ($TC_{THEO}$) and reading of $TC_7$ |
| TCDD | 2,3,7,8-tetrachlorodibenzo-p-dioxin |
| $TC_{THEO}$ | theoretical temperature of combustion |
| TMC | The Marquardt Company |
| USAF | United States Air Force |
| vs | versus |
| W | mass flow rate in pounds per second |
| WCTS | West Coast Technical Service, Inc. of Cerritos, California |
| $\bar{x}$ | mean or average value of samples |

NUMERIC

| | |
|---|---|
| 2,4-D | normal butyl 2,4-dichlorophenoxyacetate |
| 2,4,5-T | normal butyl 2,4,5- trichlorophenoxyacetate |
| 40 CFR 76 | Code of Federal Regulations, Title 40, Part 76 |

GREEK

| | |
|---|---|
| $\Delta P$ | pressure differential in pounds per square inch |
| $\mu$ | micro or micron |
| $\mu g$ | microgram |
| $\mu g/l$ | microgram per liter |
| $\mu l$ | microliter |
| $\mu l/l$ | microliter per liter |
| $\mu mho/cm$ | micro mho/centimeter |

SYMBOLS

| | |
|---|---|
| $^oC$ | degrees Centigrade |
| $^oF$ | degrees Fahrenheit |
| $^oR$ | degrees Rankine |
| $<$ | less than |
| $\leq$ | less or equal to |
| $>$ | greater than |
| $\geq$ | greater or equal to |
| # | pounds |
| " | inches |
| $\sim$ | approximately equal to |
| % | percent |

SUBSCRIPTS

| | |
|---|---|
| a | air |
| f | fuel |
| c | caustic solution |
| w | water |

## 1.0 SUMMARY

This report describes a program conducted jointly by the United States Air Force and The Marquardt Company to investigate the destruction of "Orange" Herbicide by incineration in a commercial incineration system. Particular emphasis was placed on the destruction of ppm quantities (11-16 mg/kg) of 2,3,7,8-tetrachlorodibenzo-p-dioxin present in the herbicide. Other objectives were to obtain engineering data relative to controlling and monitoring the incineration process, to evaluate noise produced by the incineration system, to evaluate long term effects of "Orange" Herbicide combustion on incinerator materials, to evaluate the effectiveness of proposed drum cleaning operations, and to access the toxicity of scrubber water and scrubbed gas effluents to several aquatic organisms and plants, respectively.

The program was conducted at the Air Force-Marquardt Jet Laboratory, Van Nuys, California between 8 October 1973 and 21 December 1973 utilizing a Marquardt incineration system. A total of 30.5 hours of burn time on undiluted "Orange" Herbicide fuel was accumulated during eight record burn periods. Average combustion temperatures varied from 2273°F to 2772°F, "Orange" Herbicide destruction rates ranged from 0.123 to 0.185 pps, and excess air ranged from 34 to 89%. In addition, 7.1 hours of burn time was accumulated during which drum rinse solutions of "Orange" Herbicide and JP-4 were incinerated.

Extensive sampling and analyses were conducted to quantitate the constituents of the unscrubbed combustion gases, the liquid used to cool and scrub the combustion gases, scrubbed effluent gases, drum cleaning samples, and any solid residues deposited in the system. Samples were analyzed by mass spectroscopy, flame ionization gas chromatography, and atomic absorption. Process system parameters and noise data were observed and recorded.

No significant problems were encountered in the storage, transfer, steady state or transient combustion of "Orange" Herbicide. Likewise, no significant problems were encountered in the structural integrity (safety) or deterioration of the incinerator or related process flow systems. Problems due to high viscosity of the "Orange" Herbicide were remedied by preheating to 95°F (± 5).

Test data demonstrated that the "Orange" Herbicide was effectively and safely destroyed by incineration; no herbicide feed compounds were found (within the limits of detectability) in any combustion gas, scrubbed effluent gas, spent scrubber water or combustion chamber deposit sample resulting from incinerator operation (four test burns) while using slot type fuel injection nozzles. Likewise, no herbicide feed compounds were found in samples resulting from incineration operations (four test burns) while using a central poppet type fuel nozzle except for one combustion chamber

deposit sample and one spent scrubber water sample. This anomaly was attributed to the characteristics of poppet nozzle fuel injection. From sample analyses data, conclusions were made regarding possible undetectable discharge mass rates of herbicide constituents, effluent biological impact, formation of pyrolyzates and hydrolyzates, and possible criteria for drum cleaning operations. Criteria were also established regarding incinerator noise generation and incinerator process system functions.

## 2.0 INTRODUCTION

### 2.1 Program History

The United States Air Force is investigating the disposal of excess "Orange" Herbicide by incineration. Two bench scale incineration studies and a previous Marquardt small scale pilot study have provided basic understandings of the "Orange" Herbicide incineration process and have shown incineration to be a feasible disposal method.[1][2][3] The current program was initiated to obtain data on the herbicide's destruction in a commercial incinerator as required for evaluation and use in an environmental statement.

### 2.2 Description of "Orange" Herbicide

"Orange" Herbicide is a chlorinated phenoxy hydrocarbon compound procured under specifications to contain 50% (± 1.5%) by volume of normal butyl 2,4-dichlorophenoxyacetate (2,4-D) and 50% (± 1.5%) by volume of normal butyl 2,4,5-trichlorophenoxyacetate (2,4,5-T). The herbicide "Orange II" was procured under the same specifications except that iso-octyl 2,4,5-trichlorophenoxyacetate (IO 2,4,5-T) was substituted for normal butyl 2,4,5-T. The subject program was conducted exclusively with "Orange" Herbicide.

Both "Orange" and "Orange II" Herbicides contain trace amounts of a toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The Air Force has analyzed its "Orange" Herbicide stocks and found TCDD concentrations ranging from <0.05 to 47.0 mg/kg. Statistical evaluation of these data indicated that pooled stocks would have an estimated average TCDD concentration of 1.9 mg/kg (± 0.7 mg/kg) at a 95% confidence level.

### 2.3 Test Objectives

The objectives of the contract effort, as listed in the Statement of Work, were as follows with agencies of prime responsibility noted:

a. Determine the capability of an incinerator system to destruct the "Orange" Herbicide over a range of selected incineration conditions (TMC and EHLs).

b. Obtain the necessary engineering data to adequately monitor, control, and document the incinerator operation during the project (TMC).

c. Evaluate the test burns' effects and project the long term effects of the combustion gases on the material of the incinerator unit (TMC).

d. Determine the combustion gas, scrubbed effluent gas, and "spent" scrubber water discharge mass rates of herbicide constituents and any other organic compounds which may be detected (EHLs)

e. Determine the presence of herbicidal pyrolyzates and hydrolozates, if any, in the combustion gases, scrubbed effluent gases, and "spent" scrubber water (EHLs and Analytical Chemistry Laboratory).

f. Determine the toxicity of "spent" scrubber water to several aquatic indicator organisms (EHL/K).

g. Evaluate the noise produced by an incineration system and assess its occupational hazard to operators (EHL/K).

h. Evaluate the effectiveness of a proposed drum cleaning procedure (EHL/K).

## 2.4 Program Scope

Twenty-eight 55-gallon drums (1540 gallons) of "Orange" Herbicide were supplied by the Air Force for use in conducting this program. Program scope was defined as follows:

a. Take all appropriate measures to ensure safe storage, handling, transfer and combustion of the "Orange" Herbicide.

b. Conduct a minimum of six documented incinerator test burns of at least 3 to 4 hours duration each.

c. Conduct and duplicate the test burns at theoretical combustion temperatures of 2100°F, 2500°F and 2900°F burning undiluted "Orange" Herbicide with a minimum of 30% excess air.

d. Control within $\pm$ 5%, measure and record all system operating parameters.

e. Collect gas and particulate samples from combustion gases and scrubbed effluent gases and collect spent scrubber water from each burn period for analyses of chemical quality and toxicity.

f. Utilize on-line gas analyses equipment for monitoring combustion gas and scrubbed effluent gas quality during testing.

g. Retain spent scrubber water in holding tanks to measure toxicity before disposal.

h. Record noise intensities around the incinerator system and in the control room during test burns.

i. Rinse emptied "Orange" Herbicide drums in a specified manner with JP-4 and analyze the rinse samples.

j. Perform a final rinse of the entire system and incinerate all collected rinses and spillage at conditions similar to those used during test burns of "Orange" Herbicide.

## 2.5 Program Task Organization

The efforts described herein were conducted in the Aero Thermo Laboratory (ATL) of the Air Force-Marquardt Jet Laboratory at Van Nuys, California. Test activities were conducted, monitored, and evaluated by a team consisting of The Marquardt Company; the USAF Environmental Health Laboratory, Kelly AFB (EHL/K); and the USAF Environmental Health Laboratory, McClellan AFB (EHL/M). EHL/K monitored the project, provided liaison of all military activities, performed scrubber water sampling and inorganic analyses of these samples, conducted the bioassays, and collected noise measurements. EHL/M collected the gas and particulate samples from the combustion and scrubbed effluent gases and performed inorganic analyses of these samples. West Coast Technical Service (WCTS) of Cerritos, California, under subcontract to The Marquardt Company, performed organic analyses of all EHL test burn samples. The test burn schedule was arranged so that WCTS analyses of samples could commence on the day following sample collection.

## 2.6 Theoretical Combustion Data

Computer analysis of the combustion process was performed as detailed in Appendix A. Theoretically expected combustion products included CO, $N_2$, $CO_2$, $H_2O$, HCl, $O_2$, NO and monatomic chlorine. Figure A-1 presents theoretical combustion temperatures as a function of "Orange" Herbicide/air mass ratios assuming inlet air at 537°R and 1000°R. The equilibrium composition of these combustion products are presented in Figure A-2 as a function of "Orange" Herbicide combustion temperatures in air. The theoretical prediction of HCl and monatomic chlorine in the combustion gases indicated a need for caustic scrubbing for the neutralization and removal of these elements from the combustion gases.

Theoretical computer analysis was also conducted to predict the effects of incomplete combustion or pyrolysis in the event of incinerator failure, particularly regarding the formation of phosgene. Gases were analyzed for "Orange" Herbicide/air mass ratios up to 1.5 times stoichiometric. See Figure A-3 and A-4. Although these studies did not indicate the formation of phosgene or any other gaseous products of incomplete pyrolysis, precautions were nevertheless taken during test operations as described in paragraph 5.

## 3.0 TEST FACILITIES

A schematic diagram of the test system is presented in Figure 1. A pictorial of the installed system components is shown in Figure 2. The major components of the system consisted of a SUE® Burner incinerator and reaction tailpipe, venturi scrubber, scrubber collection tank, natural gas and "Orange" Herbicide fuel supply systems, air supply system, caustic solution supply system, scrubber water collection system, and scrubbed effluent stack and sampling platform. Operating personnel, controls, and instrumentation were housed in a concrete block control room which was adjacent to the test setup and provided visibility of the test cell. A detailed description of the test setup and control system is described in Appendix B. The following paragraphs present a brief description of the system components and facilities utilized.

### 3.1 Incinerator and Reaction Tailpipe

The basic air-cooled SUE® incinerator and uncooled reaction tailpipe are shown in Figure 3. Natural gas was used for system ignition and temperature stabilization. "Orange" Herbicide was injected either via slot nozzles (configuration shown) or with a single central poppet type nozzle. The incinerator/reaction tailpipe was 12 inches in diameter with a combined length of 19 feet.

### 3.2 Venturi Scrubber and Scrubber Tank

Combustion gas leaving the reaction tailpipe passed through the venturi scrubber and into the scrubber tank. Scrubbing water or a caustic solution (NaOH/water) was injected at the venturi inlet and mixed with the combustion gas at velocities up to 400 ft/sec. in the venturi throat. Spent scrubber water was pumped from the scrubber tank to holding tanks for disposal. The water saturated, scrubbed effluent gases were discharged through the scrubber stack. See Figures 6 and 16.

### 3.3 Air Supply System

Combustion air was supplied from the facility air storage system via a remotely operated control valve and a choked venturi meter. See Figure 3.

### 3.4 Natural Gas System

Natural gas was used to preheat the incinerator system to an equilibrium temperature (approximately 800°F) prior to introduction of the herbicide. Upon ignition of the herbicide, the natural gas was turned off and a small air flow was supplied through the natural gas system to cool the gas injection nozzles during sustained herbicide combustion. Both natural gas and cooling air mass flow were measured with a choked venturi meter. Cooling air

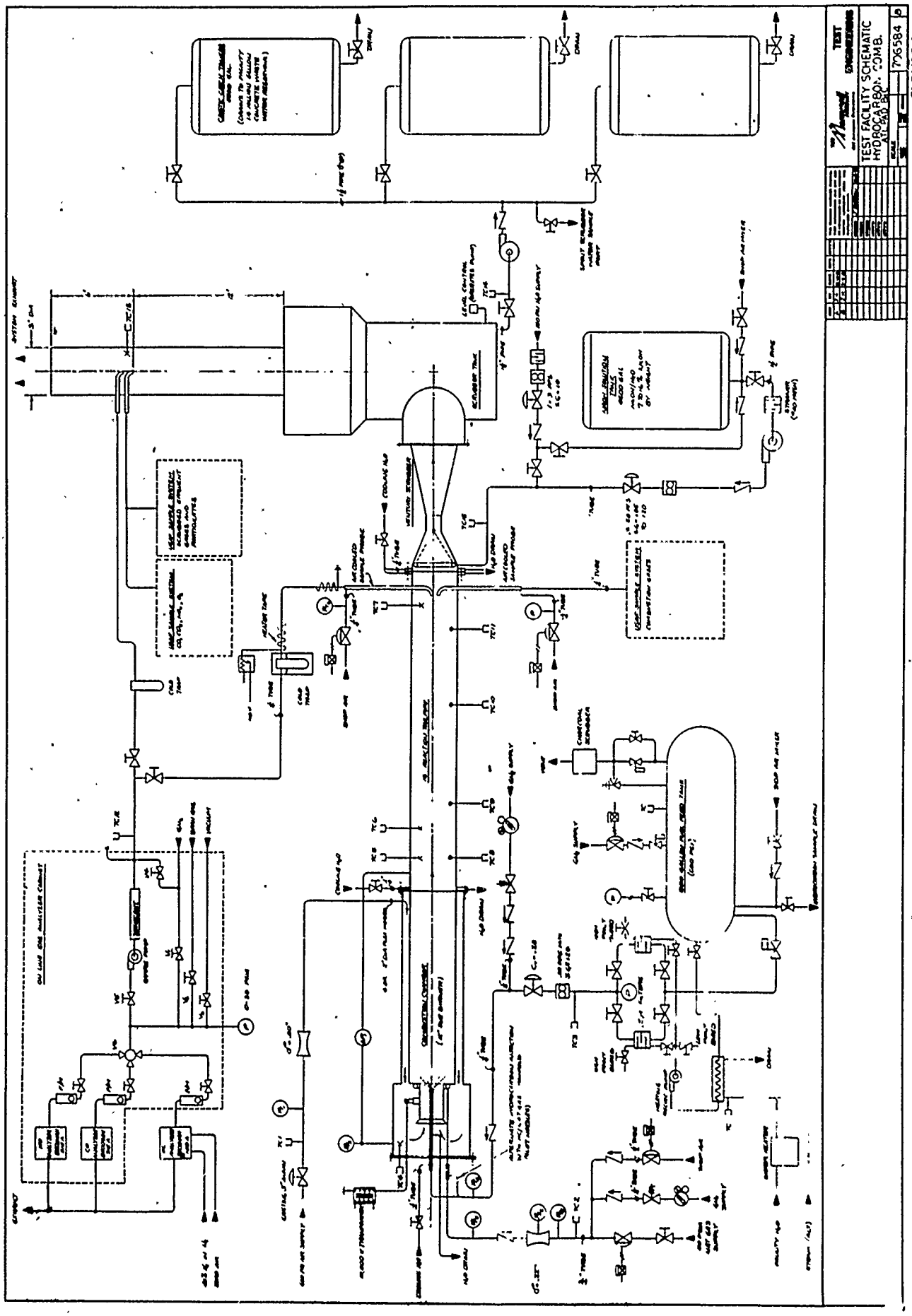
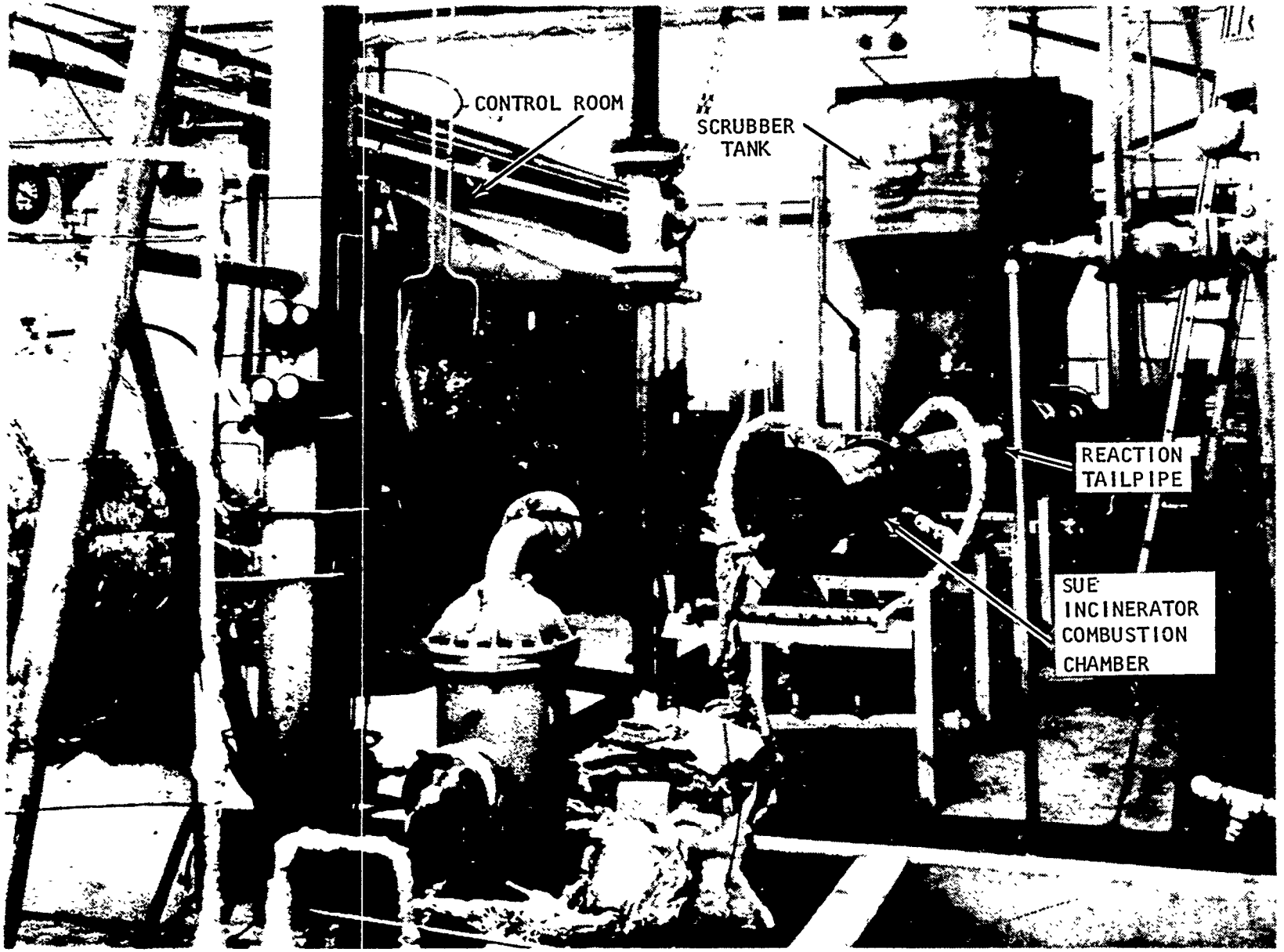

TEST ENGINEERING
TEST FACILITY SCHEMATIC
HYDROCARBON COMB.
ATP-PAD 80
7X6584 D

FIGURE 1

# GENERAL TEST SET-UP - ATL PAD B



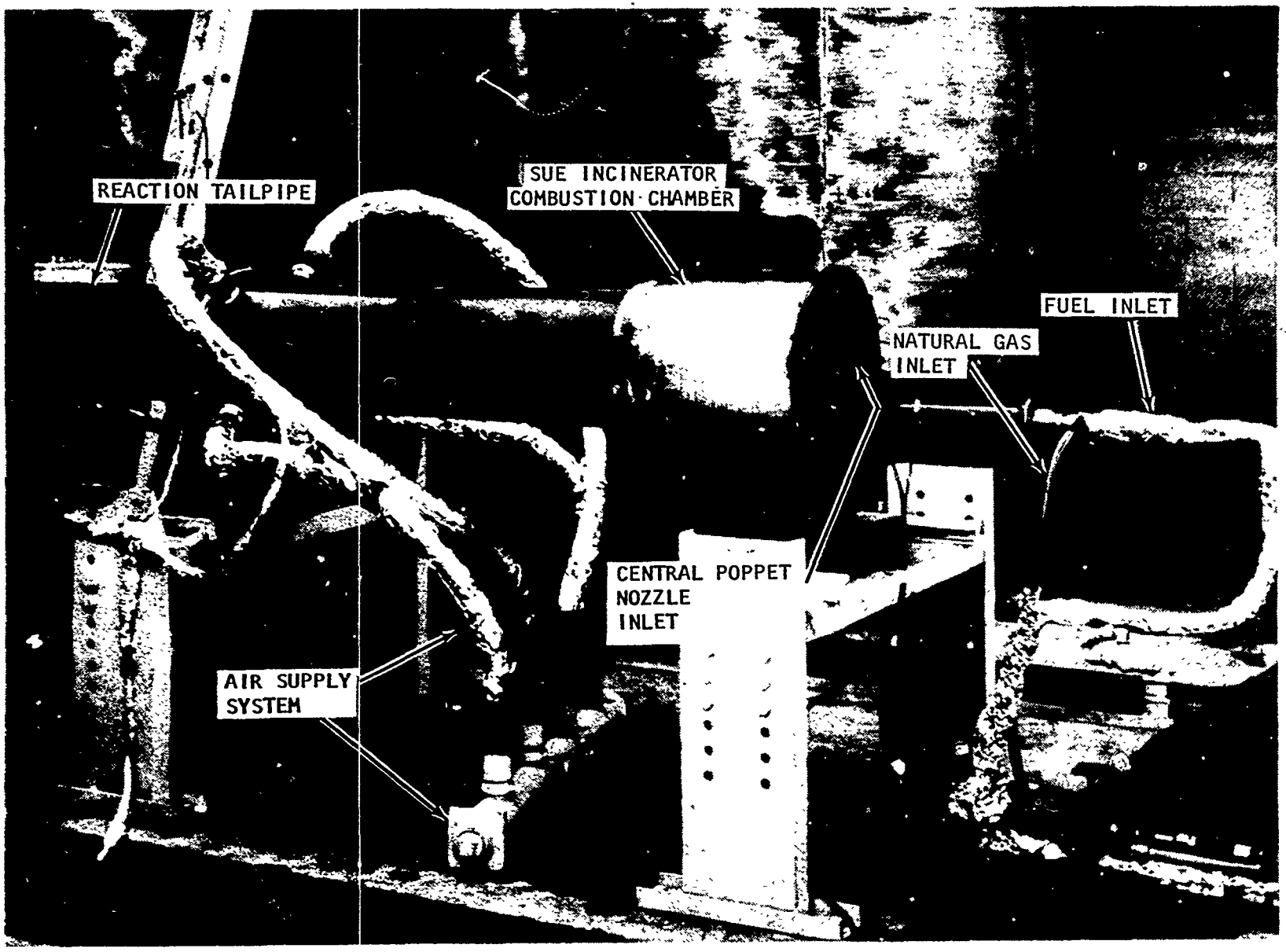

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FIGURE 2.

# SUE INCINERATOR UNIT

## (SLOT NOZZLE MANIFOLD SET-UP)




NEG 72-256-21

A73-12-565-11

FIGURE 3

flow was added to primary air flow in calculating total incinerator mass flow and fuel/air ratio. Flow was regulated by a remotely operated control regulator. A gaseous nitrogen ($GN_2$) purge system was included to clean the system during shutdowns.

### 3.5 Primary Fuel ("Orange" Herbicide or JP-4) System

Fuel was supplied from a 300 gallon, 500 psig feed tank through either of two parallel 5 micron filter pots, a remotely operated control valve, and a turbine type flowmeter. This system is shown in Figure 4. The feed tank was pressurized with nitrogen which was vented to atmosphere through a charcoal bed. A herbicide fuel tank preheater was used to permit heating of the "Orange" Herbicide to 90 to 180°F prior to incineration. The fuel line to the incinerator was purged with a $GN_2$ system. Fuel injection in the incinerator was either by a single central poppet type nozzle or a series of radial injection slot nozzles as discussed in Appendix B. A shop air bubbler was used to mix the fuel tank contents prior to test.

### 3.6 Caustic Solution and Water Supply Systems

A solution of NaOH and water was injected into the system at the venturi scrubber inlet to neutralize the HCl and $Cl_2$ resulting from combustion of "Orange" Herbicide. The solution was approximately 12% by weight of NaOH and was injected at a rate to provide 1.1 to 3.1 times the amount required to neutralize the theoretically expected amounts of HCl. Fresh water was also injected at the same location to cool the combustion gases to saturation temperature, and to provide a total liquid flow of approximately 5 gpm per 1000 cubic feet of gas flow. The caustic solution was stored in a 4500 gallon tank and supplied to the control valve by a pump. See Figure 5. Caustic solution (50% by weight of NaOH) was loaded from drums into the caustic supply tank and tap water added to obtain the desired strength solution. Provisions were included to bubble shop air through the solution to ensure thorough mixing. Fresh water was supplied from the 140 psig facility system. Both flows were controlled by remotely operated control valves and metered with turbine type flowmeters. See Figure 14 foreground.

### 3.7 Scrubber Liquid Collection System

Spent scrubber water was collected in the scrubber tank and periodically pumped, by a float actuated switch, from the scrubber tank to one of three 5500 gallon holding tanks. See Figure 6. All spent scrubber water from an entire burn was thus collected and held until the results of the Air Force bioassay testing for that burn indicated that the water could be safely drained into the facility's 1.4 million gallon concrete waste water tank (also referred to as a holding pond). The system included a sample tap for the collection of spent scrubber water samples for chemical analyses and bioassay testing. Scrubber water samples were also drawn from the bottoms and sides of the holding tanks.

A73-12-565-10

# FUEL STORAGE AND SUPPLY SYSTEM

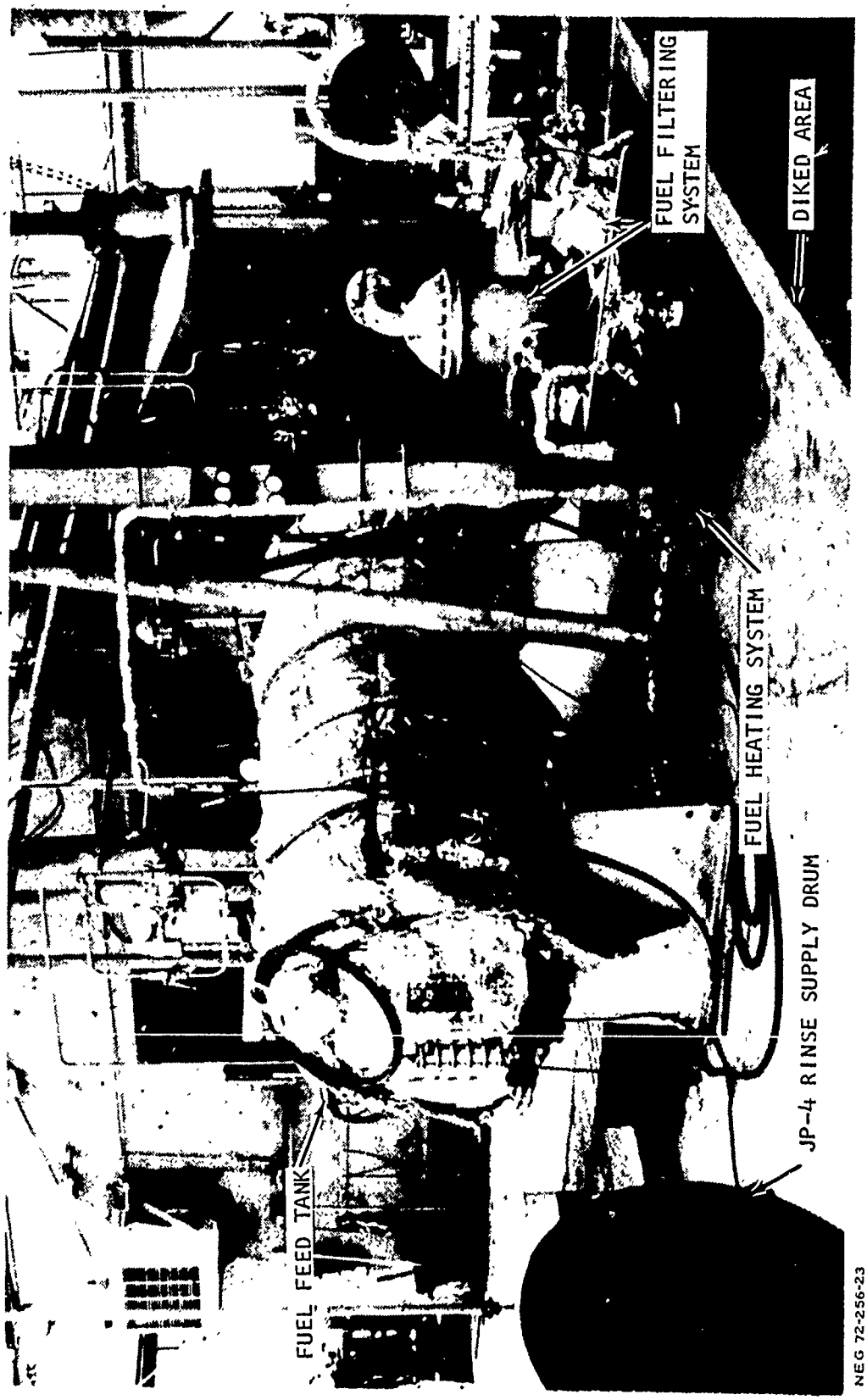



FIGURE 4

# CAUSTIC SOLUTION SUPPLY SYSTEM

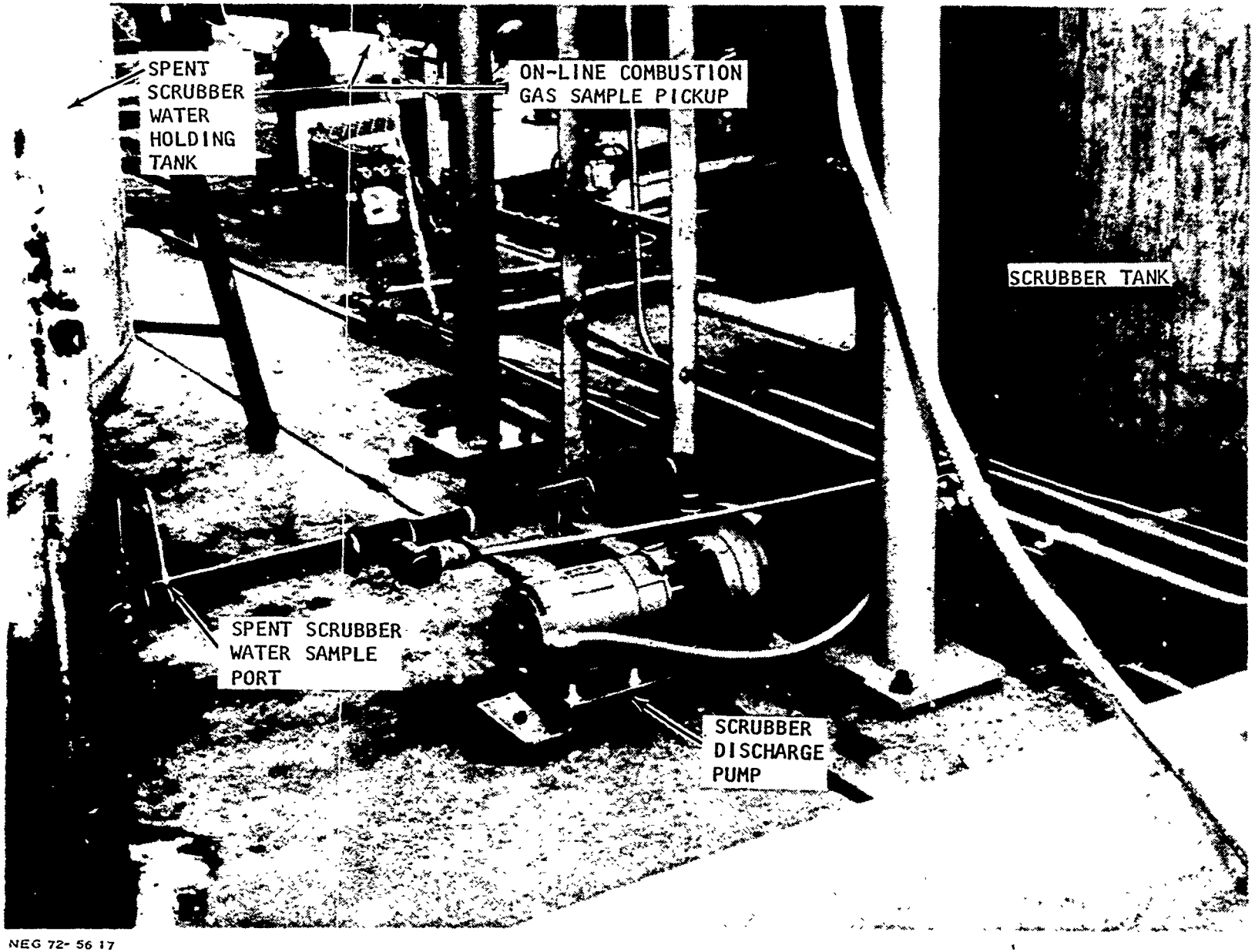



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A73-12-565-3

FIGURE 5

# SCRUBBER DISCHARGE SYSTEM




NEG 72-56 17

A73-12-565-2

FIGURE 9

### 3.8 Control Room

System controls were provided from the control room console. See Figure 7. Direct reading instrumentation was mounted outside the control room window. Remote reading instrumentation was located in the control room as shown in Figure 8. A complete listing of all measured parameters is included in Appendix B. All instrumentation was calibrated and certified by the Marquardt Standards Lab prior to use.

### 3.9 Test Cell

The Aero Thermo Lab, Pad B, is shown in Figure 2. This area was modified for the program by adding curbs around the cell pad, and by plugging the trench drains, to contain any possible herbicide spillage.

### 3.10 Herbicide Storage and Drum Rinsing

All "Orange" Herbicide drums, full or empty, were received and stored in a partially enclosed area north of Building 57 (about 50 yards from the test cell). See Figure 9. This area was prepared for drum storage with a resurfaced, sloping floor and completely curbed to contain a total herbicide spill. Additional protection was supplied by an existing water deluge system. The drums were transported individually to the fuel run tank area for transfer to the run tank and immediately returned to the storage area. All drum rinsing and rinse sampling was done within this diked drum storage area. A supply of JP-4 was maintained in the area for possible rinsing of herbicide spillage. All drums were kept covered with plastic sheeting as shown in Figure 9.

### 3.11 Bioassay/Inorganic Chemistry Test Area

An area was provided in Building 65 for use by EHL/K for conducting bioassays and inorganic chemical testing of the spent scrubber water. Part of the bioassay test setup is shown in Figure 10. The results and discussion of the bioassay portion of the program will be published by EHL/K at a later date under separate cover.

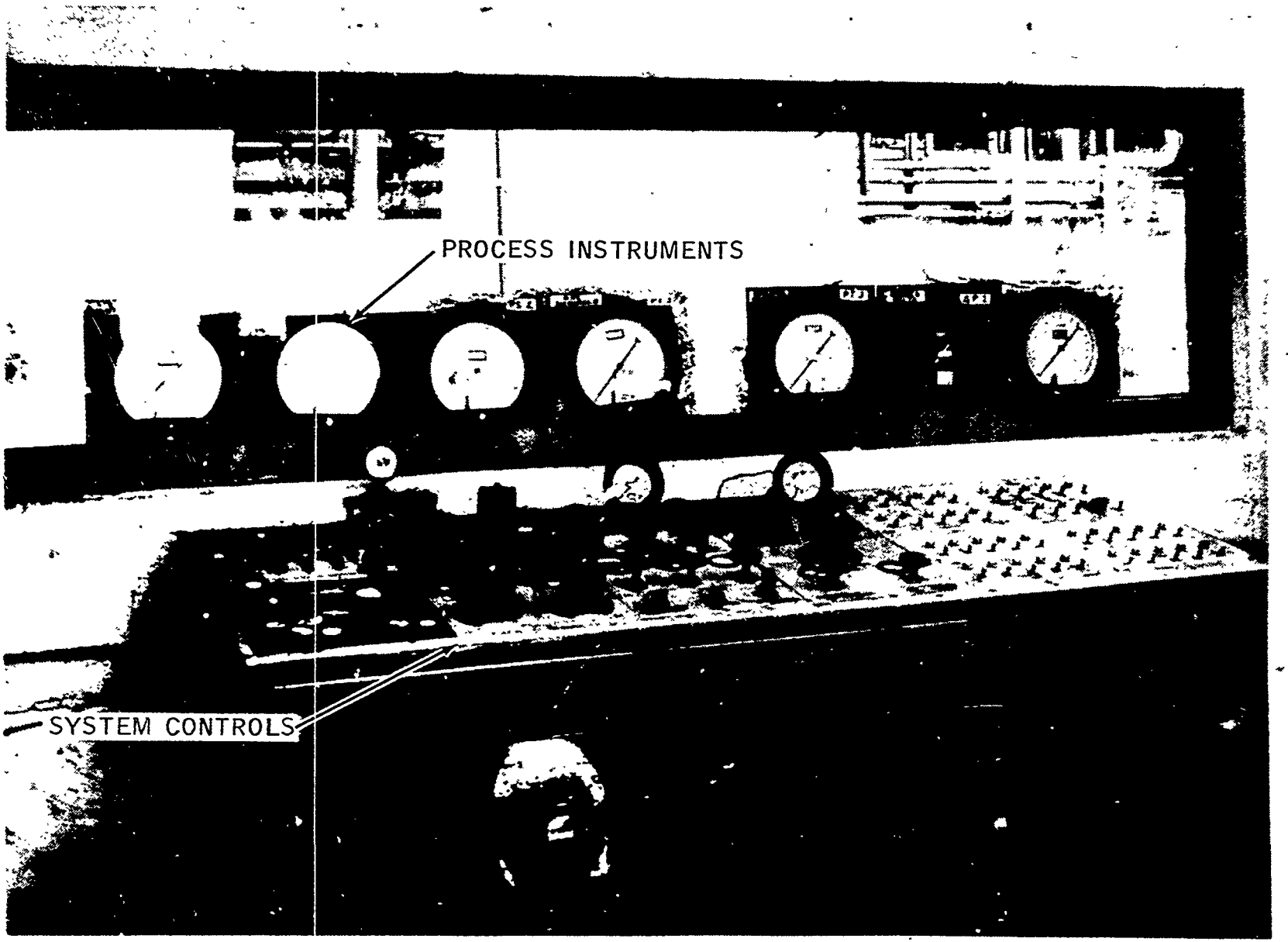
### 3.12 Air Sample Preparation Area

An area was provided in Building 84 for use by EHL/M in preparing the air sampling apparatus for testing. Part of this area is shown in Figure 11.

### 3.13 Other Facilities

Office space was provided for Air Force personnel in Building 26 (Engineering Building). Other facilities were used in support of testing activities, particularly the Standards Lab for weighing of residue samples.

# CONTROL CONSOLE AND DIRECT INSTRUMENTATION



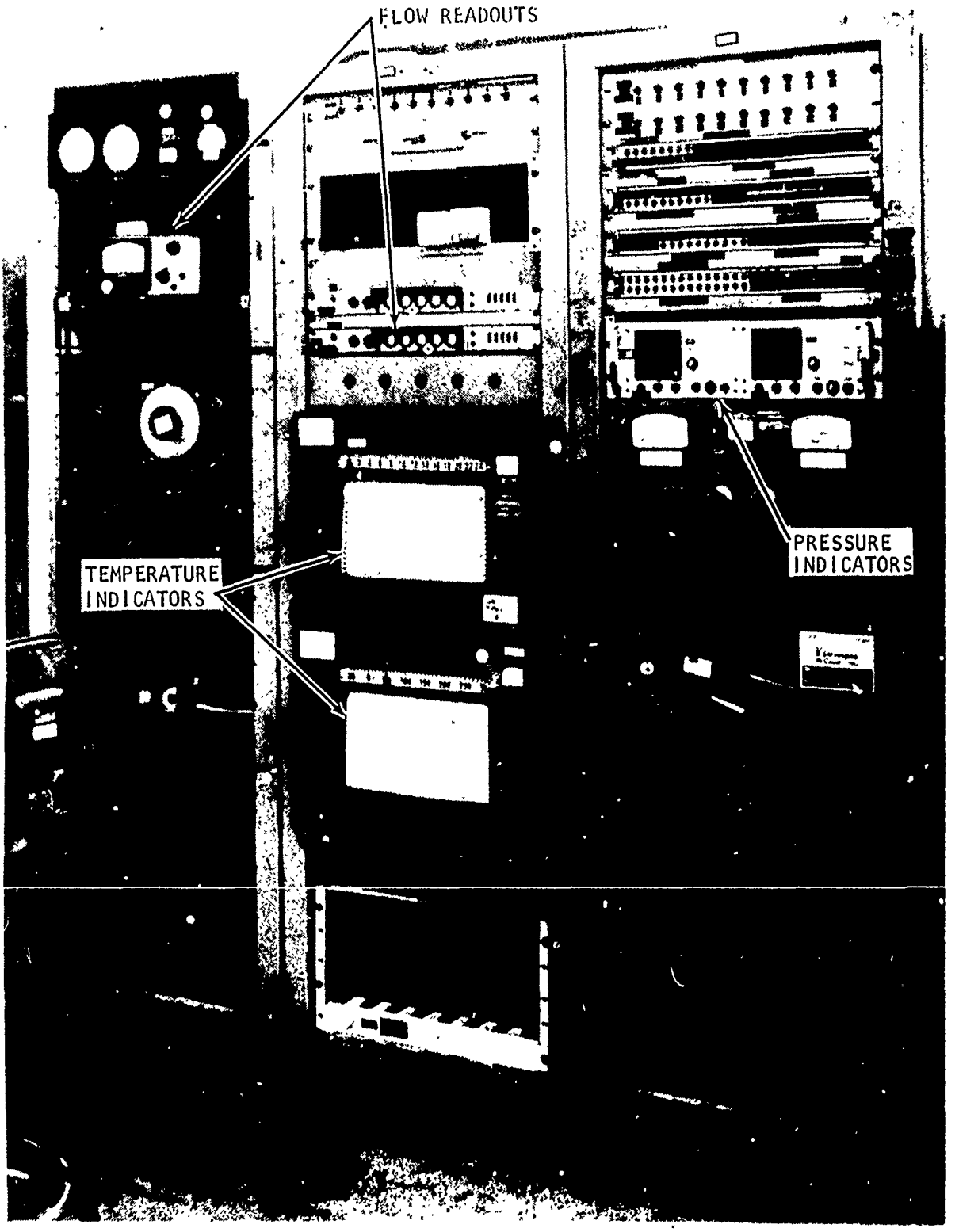

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FIGURE 7



A73-12-565-15

# REMOTE INSTRUMENTATION AND RECORDERS




NEG 72-256-15

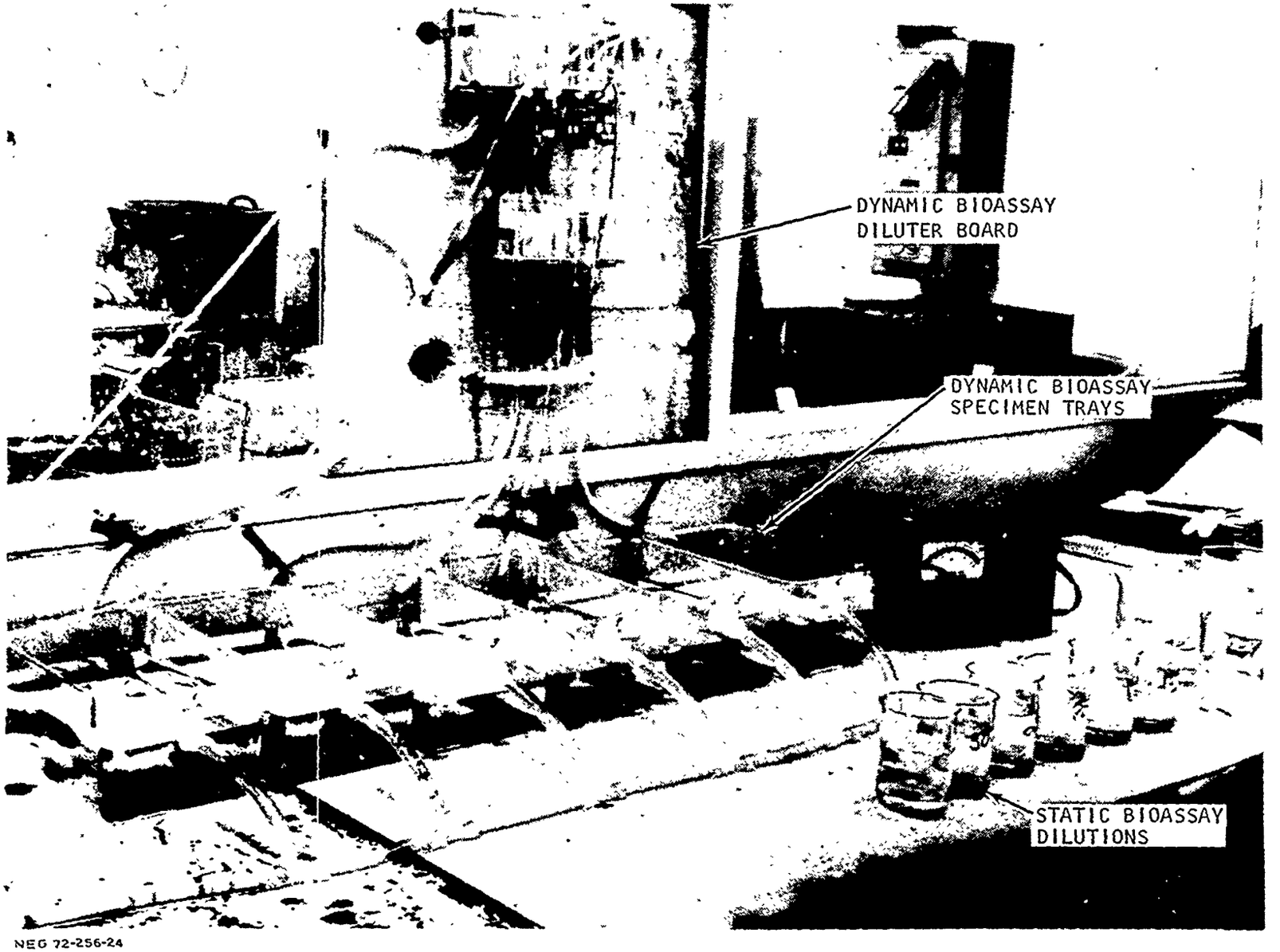
FIGURE 8

A73-12-565-6




FIGURE 9

# BIO ASSAY TEST APPARATUS - BLDG. 65




NEG 72-256-24

A73-12-565-4

FIGURE 10

A73-12-565-7

GAS SAMPLING PREPARATION AREA - BLDG. 84



NEG 72-25628

FIGURE 11

## 4.0 GAS AND LIQUID SAMPLING SYSTEMS

Analyses of combustion gas, scrubbed effluent gas, spent scrubber water, and system residue was of prime importance in this program. A considerable portion of pre-test effort was devoted to preparation of these systems by EHL/K, EHL/M, and The Marquardt Company. A pre-test meeting was held on 9 November 1973 between these parties and Dr. Fisher of West Coast Technical Service, Inc. to finalize plans for sample analyses and to establish procedures for Air Force monitoring of sample analyses, sample deliveries and data feedback. A detailed description of the sample collection and analyses procedures is presented in Appendices C through G and I. The following paragraphs provide a brief description of sampling system elements.

### 4.1 On-Line Equipment

An on-line system using Beckman gas analyzers was used during testing for quick determination of CO, NO, and hydrocarbon (HC) concentrations produced. This system permitted determination of the effects of variations to test parameters and a relative indication of combustion efficiency. The system was used to sample combustion or scrubbed effluent gases. This equipment was located in the control room and is shown pictorially in Figure 12. Combustion gases were extracted from the reaction tailpipe with an air cooled probe. See Figure 13. This probe, with a 1/8 inch inner gas tube, extended into the gas stream about 5 inches and faced upstream. Combustion gases extracted through the probe were maintained at approximately 300°F in heated tubing before passage through a cold trap and into the analyzer system. Scrubbed effluent gases were extracted with a plain tube probe and passed through unheated tubing and a cold trap before entry into the analyzer system.

Calibrations were performed on the Beckmans before each test and sometimes during or after testing. Pertinent analyzer data were:

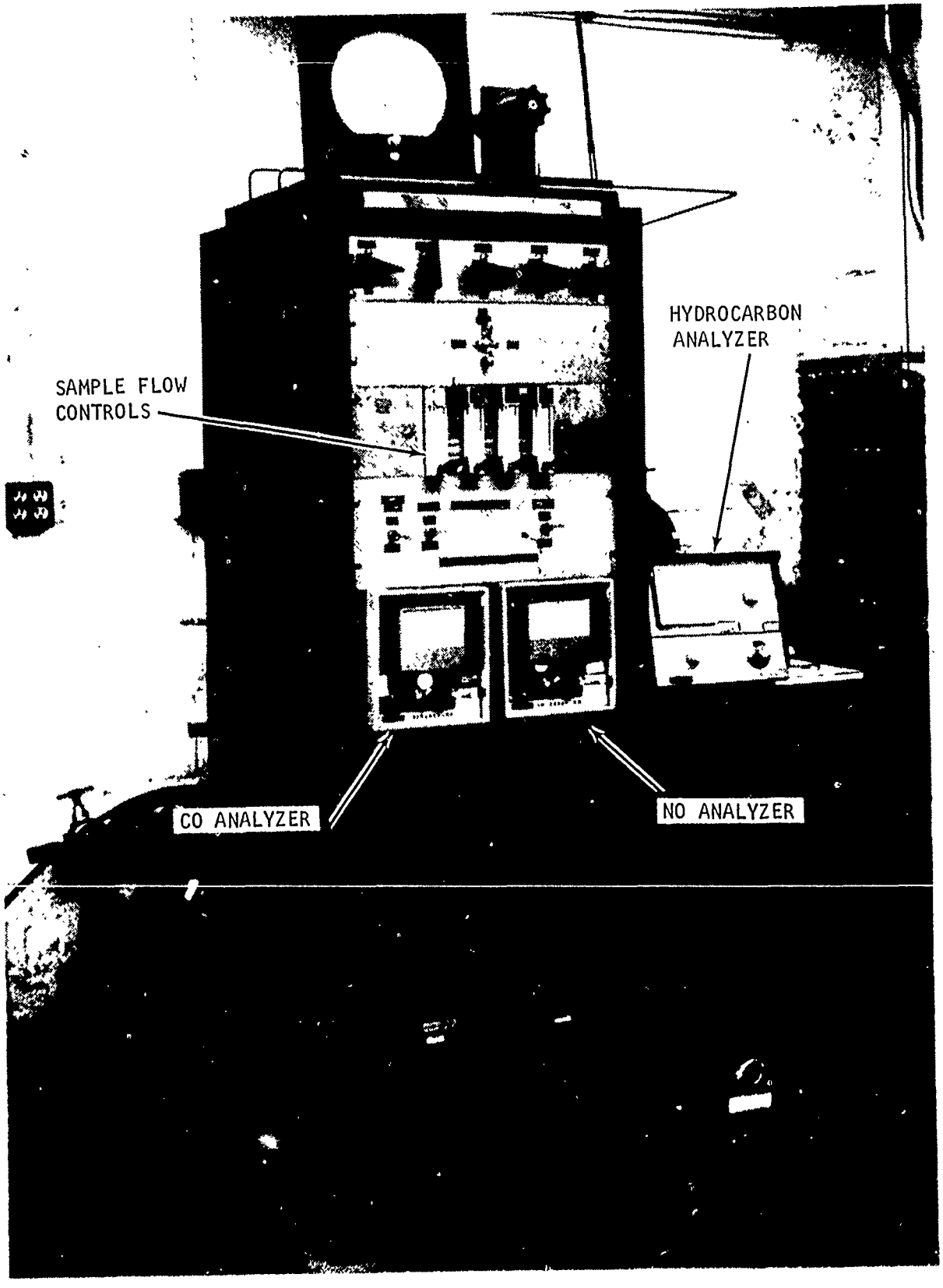
- The NO analyzer was a Beckman Model 315A infrared analyzer, span 0 to 2000 ppm. Nitrogen was used as a "zero" calibration gas. A 205 ppm NO/balance $N_2$ gas was used for "span" calibration.

- The CO analyzer was a Beckman Model 315A infrared analyzer, span 0 to 5000 ppm. Nitrogen was used as a "zero" calibration gas. A 415 ppm CO/balance $N_2$ gas was used for "span" calibration.

- The HC analyzer was a Beckman Model 109A hydrocarbon analyzer which used the flame ionization method of detection. Process gases were 40% $H_2$ in $N_2$ and "zero" air. The "zero" air was also used as a "zero" calibration gas. A 390 ppm $C_3H_8$/balance $N_2$ gas was used for "span" calibration.

# ON-LINE GAS ANALYSES EQUIPMENT

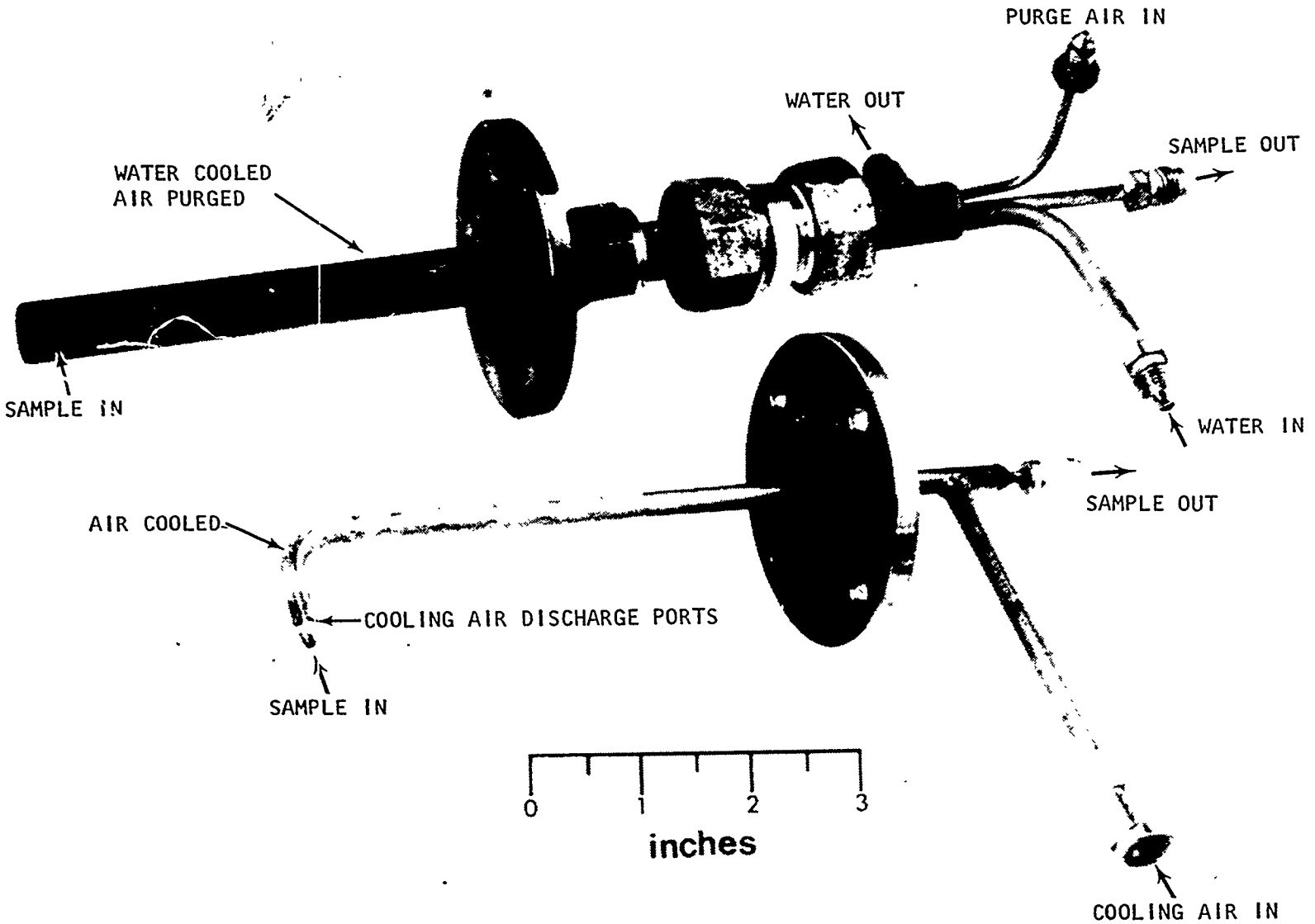
A73-12-565-13




NEG 72-256-13

FIGURE 12

# COMBUSTION GAS SAMPLING PROBES




NEG 72-256-29

FIGURE 15

A73-12-565-17

### 4.2 Combustion Gas Sampling

The combustion gas sampling apparatus was supplied and operated by EHL/M. The combustion sampling train setup is shown in position at the exit of the reaction tailpipe in Figure 14. This apparatus was connected by the umbilical to the remotely stationed flow control apparatus shown in Figure 15. The sampling train extracted gas through either an air cooled probe identical to that described in paragraph 4.1, or from the water cooled probe shown in Figure 13. The water cooled probe incorporated a purge air bleed feature to keep combustion gas out of the probe until sampling was initiated. A detailed description of the combustion gas sampling equipment and procedures is presented in Appendix D.

### 4.3 Scrubbed Effluent Gas Sampling

Scrubbed effluent gas and particulate sampling was also performed by EHL/M. The sampling equipment with integral probes were operated from a platform and withdrew gases 6 feet below the top of the stack exit. The setup is shown in Figure 16. Figure 17 depicts the apparatus in use during actual testing. A remotely stationed flow control station was also used in this system (Figure 15). See Appendix D for details of this equipment.

### 4.4 Spent Scrubber Water Sampling

Spent scrubber water samples were collected during the scrubber water pumping cycles of each test burn. These samples were composited for chemical analyses and bioassay tests. The sample tap was located just downstream of the discharge pump as shown in Figure 6. A detailed description of scrubber water sampling is included in Appendix E.

### 4.5 Herbicide Sampling

Samples of undiluted herbicide were drawn from the mixed fuel supply tank prior to each test burn. Sample analyses provided characterization of the composite herbicide mix from the various drums used to load the tank.

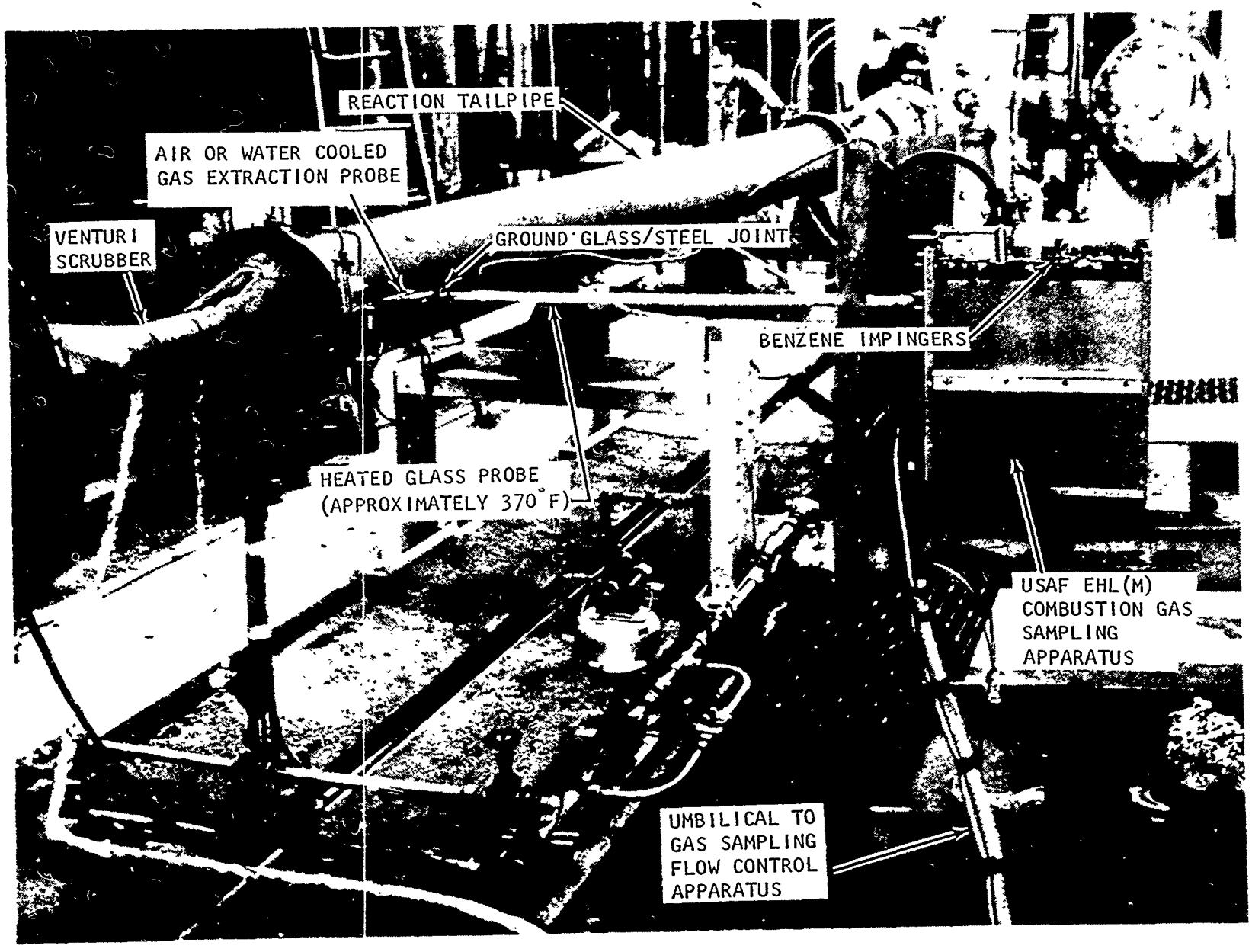
### 4.6 Drum Rinse Sampling

Each supplied "Orange" Herbicide drum was allowed to free drain until empty and then rinsed three times with specified quantities of JP-4. These rinse solutions were sampled and analyzed by EHL/K to determine the effectiveness of rinse operations. See Appendix F for detailed description of drum cleaning procedures.

### 4.7 System Residue Sampling

Residue samples were manually collected from the combustion chamber at various times between test burns. These samples were placed in new aluminum foil and given to EHL/K to weigh and forward to WCTS for organic analyses.

# USAF EHL/M COMBUSTION GAS SAMPLING APPARATUS




NEG 72-256-18

FIGURE 14

A73-12-565-9

# USAF EHL(M) GAS SAMPLE FLOW CONTROL APPARATUS

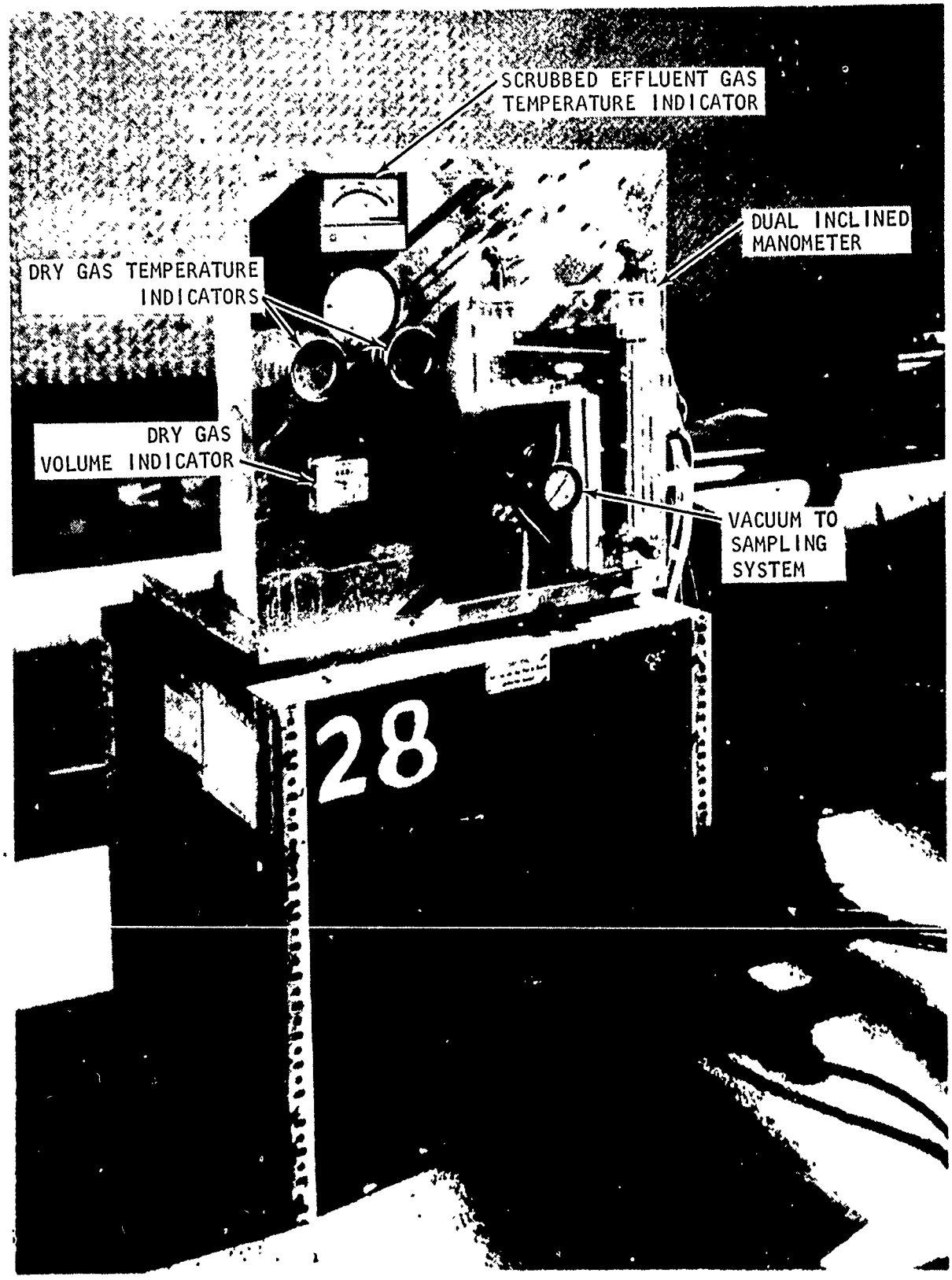



FIGURE 15

# GAS EFFLUENT STACK

A73-12-565-8

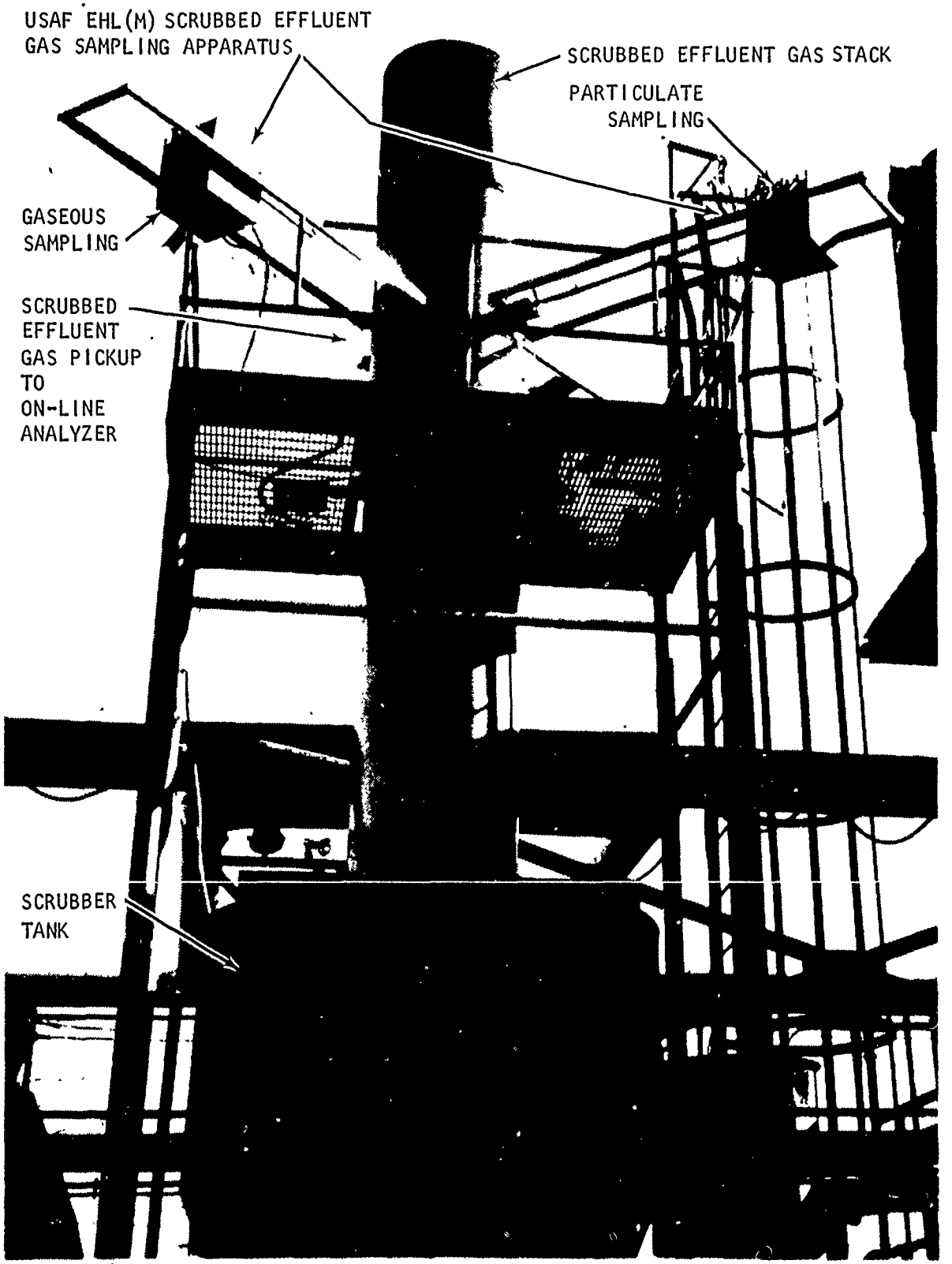
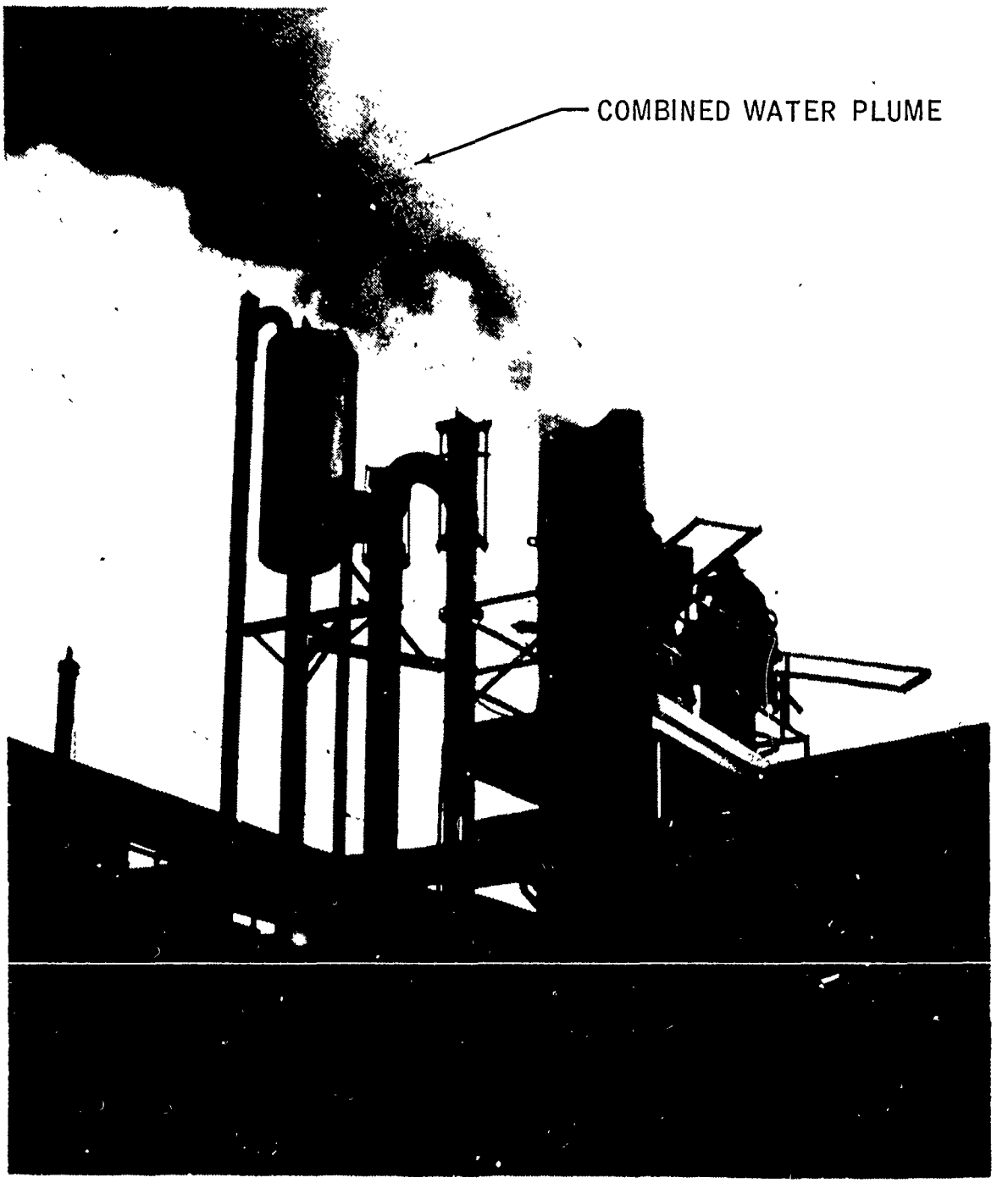



FIGURE 16

# SCRUBBED EFFLUENT SAMPLING DURING TEST




NEG 72-256-11

FIGURE 17

## 5.0 SAFETY AND HANDLING

Due to the potential hazards of this program, certain facilities and operations were established to ensure safe storage, handling and disposition of "Orange" Herbicide. In addition, requirements were established regarding monitoring inspection, personnel physical examinations, special equipment usage, herbicide handling, and general procedures which are discussed in detail in Appendix H. Since The Marquardt Company has a long history of activities involved in use of toxic propellants, safety considerations were guided by established procedures regarding such materials. Other comments relative to the handling of "Orange" Herbicide during this program have been incorporated into Sections 7 and 13.

## 6.0 INCINERATOR TEST BURN PROCEDURES

This section outlines the general preparations and procedures used throughout the program.

### 6.1 Systems Preparation

The test system was assembled as shown in Figure 1 and as discussed in Section 3.0 and in Appendix B. Some modifications were made to the system during the program as operating experience developed. These changes are discussed later. Considerable effort was expended to ensure the operational reliability of this system, such as:

- All flow systems, particularly fuel, were thoroughly flushed and cleaned.
- Most system elements (valves) were overhauled. Seals and wearable components were replaced.
- Completed systems were pressure and flow checked.

These efforts were dictated by the nature of the herbicide and by the contract test schedule. Also, these efforts paid off in that no significant systems problems were encountered throughout the test sequence.

### 6.2 Preliminary Testing

Preliminary tests were conducted using JP-4 as the primary fuel to check out the entire system and obtain operating experience. Test and operating conditions expected to be used for herbicide combustion were simulated and the system was found to operate satisfactorily.

## 6.3 Herbicide Loading and Preheating

Herbicide was loaded prior to each test as required to give a full fuel feed tank for each burn. "Orange" Herbicide drums were picked at random. Once loaded, the tank's contents were agitated with shop air to ensure complete mixing. A sample was then withdrawn for WCTS organic analysis of the blended herbicide feed. After the first test burn with "Orange" Herbicide (Test Number 4), it was concluded that preheating of the blended herbicide was required to obtain the fluid properties necessary to achieve rated fuel mass flow rates. For all subsequent tests, the "Orange" Herbicide was preheated utilizing a hot water heat exchanger. Fluid temperatures were elevated to approximately 90 to 110°F except for a single test where preheat to approximately 180°F was utilized.

## 6.4 Typical Burn Sequence of Events

A detailed incinerator burn procedure was generated to prescribe the steps required to place the system in operation, to conduct the test, to shut down, and to provide safety verifications. A generalized burn consisted of the following sequential steps:

a. Prepare all systems for incinerator testing.

b. Establish pad area isolation and personnel accountability.

c. Establish the desired air mass flow rate through the incinerator.

d. Turn on the tap water to the desired flow rate for combustion gas cooling and scrubbing and to adjust the caustic to the desired strength.

e. Turn on natural gas, ignite it, and allow the incinerator to stabilize at 800 - 1000°F (10 - 20 minutes).

f. Turn on caustic solution flow to the desired flow rate.

g. Introduce herbicide and establish combustion. Turn off natural gas.

h. Adjust herbicide flow to the rate desired to produce the required average theoretical combustion temperature.

i. Initiate phosgene gas monitoring in the pad area.

j. Record data parameters periodically.

k. Establish scrubber water sampling routine.

l. Establish noise data collection.

m. Initiate combustion and scrubbed effluent gas sampling after about one hour of burning on condition.

n. Continue test burn until fuel feed tank empties or a desired total burn time has elapsed.

o. Reestablish natural gas flow and combustion.

p. Terminate herbicide flow and purge line with $GN_2$.

q. Terminate caustic solution flow.

r. After system stabilization, terminate natural gas flow, scrubber cooling tap water flow, and air cool the system.

s. Terminate air flow.

t. Secure all systems.

## 7.0 INCINERATOR TEST PROGRAM

### 7.1 General

A total of 16 test runs were made during the program as summarized on Table 1. Tests were grouped as follows:

- Tests 1, 2, 3 - Preliminary tests on JP-4
- Tests 4, 5 - Preliminary tests on "Orange" Herbicide
- Tests 6 through 13 (AF Record Burns I through VIII) - Record tests on "Orange" Herbicide
- Tests 14, 15 - Incineration of JP-4/"Orange" Herbicide rinsings
- Test 16 - Final system flush with JP-4

Table 1 also summarizes loading of "Orange" drums in time sequence of the program. All "Orange" Herbicide supplied by the Air Force was destroyed (1540 gallons).

### 7.2 Combustion Temperatures

The contract specified that a minimum of two record burns be made at each of three different theoretical combustion temperatures: specifically, 2100°F, 2500°F, and 2900°F. Because the temperature in the combustion chamber could not be measured

TABLE 1

GENERAL TEST PROGRAM EVENT SUMMARY -- "ORANGE" HERBICIDE INCINERATION

| Date (1973) | Drums Loaded (EHL/K No.) | Test No. | | Start Time | Duration (Min.) | Fuel | Orange Used (Gal.) | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | TMC | AF Burn No. | | | | | |
| 11-1 | | 1 | - | 14:20 | 60 | JP-4 | - | Initial systems checkout. 1.5 pps air, exit temp to 2200°F. Poppet nozzle. |
| 11-2 | | 2 | - | 13:15 | 135 | JP-4 | - | Systems check. 1.5 pps air, $TC_{AVG}$ of 2100, 2500, 2900°F |
| 11-8 | | 3 | - | 15:15 | 60 | JP-4 | - | Systems check. AF sampling. 1.5 pps, $TC_{AVG}$ to 2900°F |
| 11-10 | 62,63 64,65 | | | | | | | No transfer problems |
| 11-12 | | 4 | - | 11:45 | 15 | Orange | 6 | Initial Orange combustion. System mods required. |
| 11-13 | | 5 | - | 11:44 | 15 | Orange | 14 | Satisfactory systems check. |
| 11-13 | | 6 | I | 14:01 | 191 | Orange | 143 | Satisfactory low temp burn. 1.5 pps air. Poppet nozzle. |
| 11-15 | 76,77, 91 | | | | | | | No transfer problems. |
| 11-16 | | 7 | II | 15:05 | 218 | Orange | 165 | Satisfactory low temp burn. 1.5 pps air. Poppet nozzle. |
| 11-17 | 78,80 89,92 | | | | | | | No transfer problems. |
| 11-19 | 86,87, 90 | 8 | III | 13:41 | 235 | Orange | 216 | Satisfactory med temp burn. 1.5 pps air. Poppet nozzle. |

TABLE 1 (Cont'd)

| Date (1973) | Drums Loaded (EHL/K No.) | Test No. | | Start Time | Duration (Min.) | Fuel | Orange Used (Gal.) | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | TMC | AF Burn No. | | | | | |
| 11-20 | | 9 | IV | 13:10 | 236 | Orange | 216 | Satisfactory med temp burn. 1.5 pps air. Poppet nozzle. |
| 11-26 | 71,81, 82,84 | | | | | | | No transfer problems. |
| 11-27 | | 10 | V | 12:45 | 213 | Orange | 221 | Satisfactory high temp burn. 1.5 pps air. Slot nozzles. |
| 11-28 | 69,73, 66,83, 85,88 | 11 | VI | 10:32 | 136 | Orange | 124 | Short medium temp burn. 1.5 pps air. Slot nozzles. |
| 11-29 | 68,70, 74,75 | 12 | VII | 9:13 | 213 | Orange | 222 | Satisfactory high temp burn. 1.5 pps air. Slot nozzles. |
| 11-30 | | 13 | VIII | 8:56 | 356 | Orange | 245 | Satisfactory high temp burn. 1.0 pps air. Slot nozzles. All Orange burned. |
| 12-5 | | 14 | - | 11:00 | 296 | JP-4 Orange | ~17 | Rinse solution burn. |
| 12-6 | | 15 | - | 13:30 | 130 | JP-4 Orange | ~4 | Final rinse solution burn. |
| 12-7 | | 16 | - | 13:54 | 127 | JP-4 | - | Final system rinse burn. All program burns completed. |

directly and this temperature was not representative of the gas temperature throughout the incinerator, the contractually specified combustion temperature was defined as the "average theoretical combustion gas temperature" ($TC_{AVE}$). This value was calculated as the average of the "theoretical temperature of combustion" ($TC_{THEO}$) as determined by computer analysis, and the measured combustion gas temperature at the reaction tailpipe exit ($TC_7$). The computer program calculations were based on least entropy considerations to predict the equilibrium chemical products of combustion, the theoretical combustion temperature ($TC_{THEO}$), and the thermodynamic properties of the combustion gas. The computer program inputs included "Orange" Herbicide/air mass ratios, ambient "Orange" Herbicide and air temperatures, and combustion chamber pressure. See Appendix A. The predicted $TC_{THEO}$ values were considered to be the temperatures achieved within the combustion chamber at a point half way between the "flameholder" and the entry into the reaction tailpipe.

Prior to the initiation of "Orange" Herbicide testing, a range of possible incinerator conditions was analyzed by the computer program. From this data the selection of "Orange" Herbicide/air mass ratios was made prior to each burn which would achieve the desired $TC_{AVE}$. Upon testing completion, computer analysis was performed using actual recorded data for each burn condition to determine $TC_{THEO}$, and therefore $TC_{AVE}$, for each burn.

Achieved actual $TC_{AVE}$ values were about 180° above the target of 2100°F, within about 70° of the target of 2500°F, and about 145°F below the target of 2900°F. The differences at the high and low target conditions were attributed to:

- The selection of a nearly constant air mass flow rate (1.55 pps) for all burns except Burn VIII.
- The contract requirement that excess combustion air be greater than 30%.
- Increased radiation heat losses from the reaction tailpipe as combustion gas temperatures increased.

The increased reaction tailpipe skin temperatures supported the contention of increased radiation heat losses. These radiation losses kept $TC_7$ temperature at near constant values for all burns and this produced lower calculated $TC_{AVE}$ values than were targeted for the higher temperature burns.

### 7.3 Summary of Incinerator Functioning

The functioning of the incinerator and systems was very satisfactory and is summarized as follows:

- There were no structural failures or leaks of the incinerator system.
- There were no leaks, plugging, or filter flow problems in the herbicide supply system.
- There were no problems in supply or collection of caustic solution and spent scrubber water except for a plugged screen in the spent scrubber water discharge line which was cleaned.
- Transition to combustion of "Orange" Herbicide was very smooth and the herbicide burned smoothly over all the tested temperature ranges without visible (smoke or odor) or audible evidence of poor combustion.
- No blowouts were experienced when burning the undiluted herbicide.
- No emergency shutdowns were required and normal transition back to natural gas was accomplished without difficulties.
- There were no modifications made to the basic configuration except that slot nozzles were used on Test No. 10 (Record Burn V) and subsequent tests in place of the central poppet nozzle.

### 7.4 Test Descriptions and Data

A summary of test data for the eight record burns is presented in Table 2. Process flow rates, pressures, and temperatures were recorded periodically throughout each test and the average or high/low values presented in Table 2. Calculated process parameters are presented and the basis for these calculations shown at the bottom of the table. The following items are noted:

- $TC_{THEO}$ and $TC_{AVE}$ were calculated using the computer program as discussed in paragraph 7.2.
- The stoichiometric "Orange" Herbicide/air mass ratio was 0.162 from chemical equilibrium of a 50/50 by volume mixture of 2,4-D and 2,4,5-T in air.
- The required theoretical amount of NaOH was the product of 0.31 pound HCl generated per one pound of "Orange" Herbicide burned times 1.1 pounds NaOH to neutralize one pound of HCl.
- Excess air was defined as the weight of air not reacted divided by the weight of air actually reacted.
- "Orange" Herbicide mass flow (pps) recorded during test was corrected for actual viscosity and specific gravity as determined by the fluid temperature at the flowmeter.

TABLE 2

COMBUSTION SYSTEM PARAMETERS DATA SUMMARY (RECORD BURNS ONLY)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PROCESS FLOW RATES | | | | PRESSURES | | TEMPERATURES | | | | | CALCULATED PROCESS PARAMETERS | | | | | | | | | BECKMAN DATA | | | | |
| RECORD BURN NO. | Duration Min | Air $W_a$ Avg pps | Orange $W_f$ Avg pps | Caustic $W_c$ Avg pps | Tap $H_2O$ $W_w$ Avg pps | Burner $P_{T_3}$ Hi/Lo psia | Burner $\Delta P$ $\Delta P_1$ Hi/Lo in.$H_2O$ | Fuel $TC_3$ Hi/Lo °F | Pre-Heat $TC_4$ Avg °F | Burn Gas $TC_{5/6}$ Avg °F | Exit Gas $TC_7$ Avg °F | Scrub Exit $TC_{13}$ °F | Fuel/Air $W_f/W_a$ - | $TC_{THEO}$ °F | $TC_{AVG}$ °F | $T_{SKIN}$ Avg °F | Chbr. Vel. Avg Ft/Sec | Stay Time Sec | Applied Avg NaOH pps | $\frac{N_U}{N_T}$ Avg | Total Orange Burned # | HC Hi/Lo ppm | CO Hi/Lo ppm | NO Hi/Lo ppm | Excess Air % | Nozzle Type |
| I | 191 | 1.55 | .134 | 1.88 | 1.28 | 4.5/3.2 | 6.5/6.0 | 66/63 | 578 | 1820 | 1900 | 165 | .086 | 2647 | 2273 | 1382 | 118 | .16 | 0.139 | 3.05 | 1536 | 8/1 | 180/50 | - | 89 | P |
| II | 218 | 1.57 | .135 | 1.87 | 1.28 | 3.2/2.9 | 6.5/5.5 | 98/96 | 540 | 1759 | 1850 | 165 | .086 | 2722 | 2286 | 1253 | 125 | .15 | 0.146 | 3.18 | 1766 | 24/12 | 240/190 | 18/8 | 89 | P |
| III | 235 | 1.55 | .164 | 0.84 | 2.32 | 5.9/5.6 | 3.6/3.1 | 92/90 | 598 | 1900 | 1973 | 168 | .106 | 3162 | 2567 | 1372 | 118 | .16 | 0.115 | 2.06 | 2312 | 395/98 | 240/180 | 36/14 | 52 | P |
| IV | 236 | 1.55 | .163 | 0.85 | 2.32 | 3.7/2.8 | 9.7/5.7 | 179/175 | 668 | 1786 | 1838 | 165 | .105 | 3181 | 2508 | 1295 | 132 | .14 | 0.120 | 2.16 | 2308 | - | 350/220 | 34/30 | 53 | P |
| V | 213 | 1.55 | .185 | 0.91 | 2.30 | 4.8/3.9 | 5.9/5.6 | 103/95 | 519 | 2049 | 2135 | 171 | .120 | 3333 | 2734 | 1418 | 135 | .14 | 0.124 | 2.23 | 2364 | 87/72 | 250/230 | 86/64 | 34 | S |
| VI | 136 | 1.55 | .163 | .62/.83 | 2.54/2.17 | 6.2/2.6 | 5.9/4.5 | 106/102 | 490 | 2100 | 1850 | 167 | .106 | 3057 | 2454 | 1295 | 122 | .16 | 0.117 | 2.11 | 1330 | 175/130 | 190/170 | 64/62 | 52 | S |
| VII | 213 | 1.55 | .186 | 0.92 | 2.26 | 7.7/3.9 | 5.8/5.2 | 110/100 | 553 | 2053 | 2225 | 171 | .120 | 3318 | 2772 | 1410 | 128 | .15 | 0.143 | 2.26 | 2377 | 115/50 | 230/210 | 196/140 | 34 | S |
| VIII | 356 | 1.05 | .123 | .57/.70 | 1.52 | 1.9/1.6 | 5.3/4.4 | 98/90 | 601 | 2210 | 2155 | 170 | .118 | 3363 | 2759 | 1225 | 107 | .18 | 0.054 | 1.29 | 2627 | 62/25 | 210/190 | 180/168 | 37 | S |



NOTES: See Figure 1 for instrumentation designation and locations.

Column No.

15 $TC_{THEO}$ = Theoretical max. combustion temperature based on fuel/air ratio, $TC_4$, and average $P_{T_3}$

16 $TC_{AVG}$ Defined = Average of $TC_{THEO}$ and $TC_7$

17 $T_{SKIN}$ Avg = Average of reaction tailpipe skin temperatures $TC_8$ and $TC_{11}$

18 Combustion Chamber Velocity based on $TC_{AVG}$, $P_{T_3}$ avg, total mass flow, and theoretical gas composition

19 Stay Time = Length/burn velocity for length = 19'

20 Applied Avg NaOH = $W_c$ x weight fraction of NaOH in caustic solution

21 $$\frac{N_U}{N_T} = \frac{\text{Applied avg NaOH}}{\text{NaOH theoretically required}} = \frac{\text{Applied avg NaOH}}{W_f \times .34}$$

26 Excess Air = $100\left(\frac{1}{\phi} - 1\right)$ where $\phi = \frac{(F/A)_{actual}}{(F/A)_{stoic}} = \frac{(F/A)_{actual}}{.162}$

27 Nozzle Type Code: P – Central poppet nozzle

S – Slot nozzles

## 7.5 Summary of Each Test and Record Burn

- Test 1. Initial test on JP-4. Satisfactory ignition on natural gas and transition to JP-4 using the central poppet nozzle. Held air flow to 1.0 pps at a burner exit temperature ($TC_5$) of 2200°F.

- Test 2. Systems checkout on JP-4 at air flow to 1.5 pps and simulated $TC_{AVE}$ of 2100, 2500 and 2900°F per contract requirements.

  - Minor system corrections made. System ready for "Orange" Herbicide testing but modifications and additions required for Air Force gas sampling trains.

- Test 3. Systems checkout on JP-4 with Air Force sampling systems installed. Air flow to 1.5 pps and $TC_{AVE}$ of 2900°F.

  - Fuel system drained of JP-4 and loaded with four drums of "Orange" Herbicide. Loading was noticeably slower as ambient temperature decreased during the loadings.

- Test 4. This was intended as the first record burn. Combustion was initiated satisfactorily on undiluted "Orange" Herbicide but fuel system pressure losses were so excessive that the desired fuel mass flow rate could not be obtained.

  - It was obvious that the "Orange" Herbicide could not be injected into the combustion chamber at the desired mass flow rate at lower temperatures (60°F) due to its very steep viscosity/temperature characteristic. (See Figure B-7.) A temporary hot water heat exchanger was added to the fuel line and the trim was changed in the fuel control valve. The Beckman system was modified to include a cold trap about 5 feet from the sample probe and sample line heating between the cold trap and the analyzer was removed. The backup (Air Force) HC analyzer was installed.

- Test 5. A checkout burn to test system modifications after Test 4 and verify satisfactory flow of preheated (90 - 100°F) "Orange" Herbicide. Satisfactory results.

- Test 6 (Record Burn I). A satisfactory low temperature ($TC_{AVG}$ = 2273°F) record burn at a fuel/air ratio of 0.086, and applied caustic of 3.05 times theoretical. Gas and liquid sampling accomplished satisfactorily. The area was monitored for phosgene and none was detected. Testing terminated at darkness.

  - Disassembly of the burner revealed an accumulation of about 7.9 pounds of carbon residue around the combustion chamber, about 15 inches from the step, in an annular pattern. The residue

was brittle and easily removed from the wall. A residue specimen was sent to West Coast Technical Service for analyses. Patterns of these residue deposits were repeated during Burns II, III, and IV and are discussed in paragraph 10.1. A permanent heat exchanger system was added to preheat the "Orange" Herbicide to at least 90°F as shown in Figure 1. Modifications were made to the combustion chamber to ensure better air cooling. It was also noted that corrections were required to fuel flowmeter readings for viscosity effects. The fuel flowmeter was recalibrated and numerical corrections applied to all prior fuel mass flow data. The TMC Beckman HC analyzer was reinstalled.

- Test 7 (Record Burn II). A satisfactory duplicate low temperature ($TC_{AVG}$ = 2286°F) record run at fuel/air ratio of 0.086 and applied caustic at 3.18 times theoretical. Scrubber exit gas and liquid sampling accomplished. The combustion gas sampling probe plugged part way into the test but an adequate sample was obtained. The new "Orange" preheating system performed well and fuel temperature was maintained at about 98°F.

  - The burner was again disassembled. A carbon deposit similar to that from Burn I was again present and weighed about 9 pounds. The deposit was removed and a specimen sent to West Coast Technical Service for analyses. To lengthen the test time available with the caustic supply tank, it was loaded with a higher concentration of NaOH. Caustic solution mass flow rates could then be reduced and total scrubber water flow maintained by an increased flow of tap water.

- Test 8 (Record Burn III). A satisfactory medium temperature ($TC_{AVG}$ = 2567°F) record burn at a fuel/air ratio of 0.106 and applied caustic at 2.06 times theoretical. Sampling accomplished satisfactorily.

  - Burner disassembly revealed another carbon deposit of 12.9 pounds which was removed and analyzed by WCTS. It was decided to preheat the fuel much higher to see if increased fuel temperature affected the quantity, size or shape of the deposit.

- Test 9 (Record Burn IV). A satisfactory replicate medium temperature ($TC_{AVE}$ = 2508°F) record burn at a fuel/air ratio of 0.105 and and applied caustic at 2.16 times theoretical. Herbicide fuel temperature was preheated to about 177°F for this burn. This test condition appeared to move the flame closer to the inlet (step) of the combustion chamber as evidenced by the increased temperature at the inlet to the reaction tailpipe. Sampling was accomplished satisfactorily and noise measurements were taken around the test pad and in the control room.

- Burner assembly again revealed a sizeable annular carbon deposit of 2.8 pounds which was removed and sent to WCTS for analyses. The poppet nozzle was removed and the slot nozzle manifold installed for subsequent testing. It was felt that the slot nozzles would provide improved high flow combustion, and that the slot nozzle fuel pattern in the incinerator would alleviate the carbon residue problem.

- Test 10 (Record Burn V). A very satisfactory high temperature ($TC_{AVE}$ = 2734°F) record burn at a fuel/air ratio of 0.120 and applied caustic at 2.23 times theoretical. Combustion with the slot nozzles was very smooth and the temperature profile down the system indicated faster burning in the incinerator. Higher $TC_{AVE}$ was limited by the requirement of 30 percent minimum excess air. Scrubbed effluent gas and water sampling was completed satisfactorily. The combustion gas sampling probe plugged part way into the run and only a partial sample was obtained.

  - Examination of the burner revealed only four small carbon deposits, these deposits being of finer grain, more flaky, and much less brittle than earlier ones. It was decided to add another medium temperature burn with the slot nozzles for comparison to Tests 8 and 9 (Record Burns III and IV).

- Test 11 (Record Burn VI). A satisfactory, but shortened, medium temperature ($TC_{AVE}$ = 2454°F) record burn at a fuel/air ratio of 0.106. Caustic solution flow was reduced to provide only 1.73 times theoretical. However, an acid smell was noticed by stack gas monitoring personnel and caustic solution flow was increased to 2.23 times theoretical about one-half hour into the burn. This return to prior applied caustic conditions corrected the acid odor problem. After about one and one-half hours of operation a buildup of chamber pressure, with corresponding decrease of burner $\Delta P$, was noted which indicated a restriction in the venturi scrubber. Testing was terminated to investigate the problem. Gas and liquid sampling had been completed.

  - Examination of the system revealed no significant restriction or other problem. It was theorized that a restriction had built up in the venturi from condensed caustic (a condition present some what during all tests) which had broken loose during shutdown, or that a piece of carbon residue from the combustion chamber had likewise caused a temporary restriction. About 1.95 pounds of carbon residue was removed from the combustion chamber, which was not as much as deposited during similar burn conditions while using the poppet nozzle.

- Test 12 (Record Burn VII). A satisfactory replicate high temperature ($TC_{AVE}$ = 2772°F) record burn at a fuel/air ratio of 0.120 and applied caustic at 2.26 times theoretical. This was the last of the required burns, although additional supplies of "Orange" Herbicide remained. Sampling was completed satisfactorily and noise measurements taken.

- Test 13 (Record Burn VIII). This burn was completed satisfactorily at replicate high temperatures ($TC_{AVE}$ = 2759°F) and at a fuel/air ratio of 0.118. The applied caustic was 1.29 times theoretical and the $HCl/Cl_2$ odor was again noticed from the stack gas monitoring personnel. The air mass flow was decreased to 1.0 pps to provide data comparisons with other high temperature runs which had higher combustion chamber velocities and lower stay time. Sampling was completed satisfactorily.

- Test 14. A satisfactory burn at an estimated $TC_{AVG}$ of 2700°F as required to destroy the first batch of JP-4/"Orange" Herbicide rinse solution, which was calculated by specific gravity of the solution to contain approximately 11% "Orange" Herbicide by weight. Testing was conducted at a fuel/air ratio of 0.060 and applied caustic of approximately 3.4 times theoretical. On-line gas sampling only was utilized which indicated very satisfactory scrubbed effluent gas properties (hydrocarbon at 10 ppm).

- Test 15. A satisfactory burn at an estimated $TC_{AVG}$ of 2700°F to complete the destruction of JP-4/"Orange" rinse solutions (less than 8% "Orange" by weight). Testing was conducted at a fuel/air ratio of 0.050. Satisfactory on-line sampling data were collected for both combustion chamber and scrubbed effluent gases.

  - The fuel tank was loaded with approximately 80 gallons of clean JP-4 and circulated through the system.

- Test 16. A final satisfactory burn at an estimated $TC_{AVG}$ of 2700°F to complete the cleaning of the fuel system using undiluted JP-4. Testing was conducted at a fuel/air ratio of 0.050. This completed all contractual testing requirements.

## 8.0 GAS SAMPLING RESULTS AND COMMENTS

### 8.1 Combustion and Scrubbed Effluent Gas Sampling Results (Prepared by USAF EHL/M)

Gas sampling equipment and field sampling personnel were furnished by the USAF EHL/M. The combustion and scrubbed effluent gas monitoring program is presented in detail in Appendix D. Organic analyses of gas and particulate samples were performed by WCTS. (See Appendix G and results discussed in detail in Appendix I). The results below were summarized from the discussions in Appendices D and I. The gas sampling train used for "Orange" Herbicide and related herbicidal compounds was laboratory tested with nb esters of 2,4-D and 2,4,5-T, and the acids of 2,4-D and 2,4,5-T (Appendix D).

#### 8.1.1 Gas Sampling Results:

Combustion and scrubbed effluent gas sampling was conducted satisfactorily except during Burn V. During Burn V the

air cooled sampling probe (combustion gas) clogged during sampling and a small (6 liters) sample was obtained. Otherwise, all sample volumes provided a detection level $\leq 0.65 \times 10^{-9}$ grams per liter of sample gas (STP) for each of five "Orange" Herbicide compounds: TCDD, nb-2,4-D and nb-2,4,5-T esters, and nb 2,4-D and 2,4,5-T acids. The detection level for related herbicidal compounds was $\leq 1.3 \times 10^{-9}$ grams per liter (STP) (Appendix G and I).

No "Orange" Herbicide compound was detected in any combustion or scrubbed effluent gas sample. Monochlorophenol (1.06 µg/l) was detected in the combustion gas of Burn I but not in the combustion gas of Burns II through VIII.

8.1.2 Herbicidal Compounds in Related Sampling Equipment:

Microgram quantities (0.7 and 6.5 µg) of the nb-2,4-D and nb-2,4,5-T esters were found in the rinse from a cold trap used during Burn I. The cold trap was used to condition sample gas for the Beckman 109A hydrocarbon analyzer. The cold trap was used during two "Orange" Herbicide checkout burns. It was not rinsed before use in the successful record Burn I. The nb-esters were not considered to have been deposited during record Burn I (see discussion, Appendix I).

Microgram quantities (1.38 and 0.7 µg) of dichlorophenol were detected in the rinse of the combustion gas air cooled sampling probes from Burns II and III. This compound was concluded to have been formed in the probes by reaction of $Cl_2$ and (Cl) on the nonchlorinated aromatic hydrocarbons condensed by the probe (see discussion, Appendix I).

Microgram quantities (1.2, 0.1 and 0.1 µg) of dichlorophenol were also detected in the rinses of the cold traps (Beckman 109A) from Burns I, II and III. This compound was concluded to have been formed as discussed in the preceding paragraph (see Appendix I).

Microgram quantities (1.3 and 0.1 µg) of dichlorophenol were detected in the water from the scrubbed effluent gas particulate source sampling train impingers from Burns IV and VI. An evaluation of all available data indicated that this compound was not associated with "Orange" Herbicide incineration (Appendix I).

8.1.3 Nonchlorinated Aliphatic and Aromatic Hydrocarbons and Biphenyl in Gas Samples:

Biphenyl was detected in all scrubbed effluent gas samples at an average mass concentration of $46 \times 10^{-9}$ grams per liter (STP).

Aliphatic hydrocarbons in the combustion and scrubbed effluent gases centered around $C_{10}$, ranging from $C_7$ through $C_{15}$ (Appendix G).

Aromatic hydrocarbons in the combustion and scrubbed effluent gases centered around a $C_4$ benzene substituted sidechain ($C_6H_5$ ($C_4H_9$)). The sidechain appeared saturated (Appendix G).

8.1.4 Relative "Orange" Herbicide Pyrolysis Efficiencies and General Comments:

Relative "Orange" Herbicide pyrolysis efficiencies (RPE) were calculated (based on carbon mass collected in the TCDD sampling train and carbon mass feed into the incinerator) for each burn. These relative efficiencies ranged from 99.98% in Burn II to 99.999% in Burns VI, VII and VIII (Appendix I). The RPE was considered relative since the TCDD sampling train did not efficiently collect light, volatile pyrolyzates. See Appendix I for a thorough discussion of RPE.

Additional preheat of "Orange" Herbicide fuel from ~90°F to 175°F significantly improved the RPE.

Hydrocarbon penetration through the caustic scrubber (relative to penetration through the TCDD sampling trains) increased significantly as the RPE improved (Appendix I).

Beckman 109A hydrocarbon data were not relatable to RPE's (Appendix I).

8.1.5 Particulate, $NO_x$ and $CO_2$ Emissions:

Particulate emissions from the eight burns averaged 0.076 grains per standard cubic foot of scrubbed effluent gas and had a standard deviation of 0.035. The particulate matter, by visual observation, appeared to be mostly sodium salts. No aromatic hydrocarbons were detected in the particulate mass. An average 6 µg of unchlorinated aliphatic hydrocarbons was detected in an average particulate mass of 105 mg (filter maintained at 320°F).

Nitrogen oxide ($NO_x$) emissions from all eight burns averaged 53.4 ppm with a standard deviation of 18.9 ppm. The emissions increased to about 100 ppm in Burns VII and VIII when the theoretical combustion temperature ($TC_{THEO}$) increased from ≈3000°F to above 3200°F.

The $CO_2$ concentration (% by volume) averaged 12.1% in Burns IV, V, VI and VII. An average 9.9% of the $CO_2$ was absorbed in the caustic scrubber (see Appendices D and E).

8.2 On-Line Gas Sampling (Prepared by TMC)

The Beckman analyzer data for CO, $NO_x$, and HC for the record burns are presented in Table 2. These were readings from the scrubbed effluent gas only. Both the high and low values observed

during the burn are presented. During temperature stabilization using natural gas at the beginning of each burn, hydrocarbon readings were high due to inefficient, low temperature combustion. Once combustion on "Orange" Herbicide was established, the hydrocarbon data took some time to stabilize at lower values due to the time required to sweep the analyzer input lines and traps. The low values presented were representative of the stabilized incineration process.

Considerable difficulty was experienced in trying to analyze combustion chamber gases. The system was initially set to maintain the sample gas temperature at 300°F into the analyzer, but condensation of acid and $H_2O$ within the analyzer was experienced. Consequently, a cold trap was installed in the sample line and the heating tape removed from the sample line between the cold trap and analyzer. Sample line heating was maintained from the sample probe to the cold trap. Heavy hydrocarbons were condensed and collected in the cold trap. Therefore, the cold trap was rinsed after each run and the rinse was analyzed for hydrocarbons.

Beckman sampling analyses were used throughout the program to sample scrubbed effluent gas since this was the final system effluent. This type of analyses was intended only to provide an operational indicator of system combustion stability. Scrubbed effluent gas hydrocarbon data were generally higher than noted during combustion of JP-4 which could be expected considering the potential products of "Orange" Herbicide combustion. In the Beckman 109A analyzer, the magnitude of instrument response caused by a given carbon atom depends on the chemical environment of the atom in the molecule. The data presented from the Beckman indicated the hydrocarbon content of the sample in ppm of carbon, and must be divided by an "effective carbon number" (proportional to carbon count) of the sample compounds to obtain the true ppm. Therefore true data values would be proportionally reduced for compounds of high carbon count. Also, in some compounds certain other atoms will change the analyzer's sensivity to carbon. As noted in paragraph 8.1, these data could not be used to provide comparisons of relative pyrolysis efficiencies for the system.

The $NO_x$ readings generally followed the expected tendency to increase at higher combustion temperatures, remaining below 62 ppm for $TC_{AVG}$ up to 2500°F and rising to 168 ppm at a $TC_{AVG}$ of 2759°F.

## 9.0 SCRUBBER WATER SAMPLING RESULTS (Prepared by USAF EHL/K)

All water sampling and inorganic analyses were conducted by USAF EHL/K using their own equipment and specially prepared sample containers. The water monitoring program and discussion of inorganic analyses are presented in Appendix E. Organic analyses of scrubber water samples were performed by WCTS, see Appendix G, and the results are discussed in detail in Appendix I. Results below were summarized from the discussions in Appendices E and I.

## 9.1 Inorganic Quality of Spent Scrubber Water (SSW)

The consistency of SSW inorganic parameters throughout a given burn agreed with the smoothness with which burn operation parameters were maintained. The only exceptions occurred when the applied caustic was increased during Burn VI. Of all measured SSW physical and inorganic parameters, only temperature, specific gravity, and chlorides remained relatively constant between burns. All other measured parameters were acceptably correlated by least squares regression analyses to only one incinerator operating parameter; the ratio of applied NaOH to that required to neutralize the theoretically expected HCl ($N_U/N_T$). Table 3 summarizes the range of measured parameters in SSW for all burns.

All loadings in Table 3 except chlorides, suspended solids, total iron, and hydroxyl alkalinity increased or decreased linearly about 30% as $N_U/N_T$ increased to three or decreased to two, respectively. The exceptions varied non-linearly with $N_U/N_T$ and were dependent upon complete neutralization of HCl and the adsorption of $CO_2$ into the scrubber water. Approximately 10% (s = 4) of the combustion gas $CO_2$ was absorbed by the scrubber water.

Evaluations of scrubber water flow rates showed that, dependent on fuel to air mass ratios, about 1350 gallons (s = 175) of scrubber water were needed for each drum of herbicide burned. About 1000 gallons (s = 200) or 75% of this water was not volatilized and was therefore recovered as spent scrubber water.

Suspended solids were present in moderate concentrations (56-97 mg/l). However, there were finely sized black carbon particles which imparted a distinct grey color to the SSW. Elevated iron concentrations (160-400 mg/l) in Burns VI and VIII attributed intense rust colors to the water. These solids concentrations were reduced by 77% with primary settling.

Inorganically measured mass balances of sodium, hydroxide, and chlorine throughout the incinerator system were all accounted for within five percent of their theoretical or measured input values. These balances validated the overall accuracy of scrubber water collection and analyses.

After five drums of herbicide had been burned, about 5000 gallons of SSW were discharged into 1.4 million gallons of relatively excellent quality facility waste water. The waste water's quality changed significantly in pH, total and carbonate alkalinity, sodium, chlorides, specific conductance, and total dissolved solids but its specific gravity, total solids, chlorine residual (0.0 mg/l), hydroxyl alkalinity (0.0 mg/l), and bicarbonate alkalinity were unchanged. These chemical quality changes were, however, not detrimental to the waste water's intended industrial uses. The water's quality met industrial sewer ordinance codes after receiving nearly 25,000 gallons of SSW. Chemical quality changes of the final sample collected indicated that the waste water's quality had already begun to adjust back toward the carbonate equilibrium system. Such adjustment would naturally lower all measured parameters except conservative sodium and chlorides to near original conditions.

TABLE 3: INORGANIC LOADING AND RANGE OF QUALITY IN SPENT SCRUBBER WATER

| Parameter (mg/l unless noted) | Range of Quality | Loading - Pounds Per Drum of Herbicide Burned @ $N_U/N_T = 2.0$ |
|---|---|---|
| Temperature ($^oF$) when collected | 164 | N/A |
| pH | 10.5-11.8 | N/A |
| Specific Gravity | 1.057 | N/A |
| Specific Conductances (μmho/cm) | 11.3-15.8 | N/A |
| Total Solids or Total Dissolved Solids (x $10^3$) | 61-87 | ≈590 |
| Suspended Solids | 56-97* | 0.66 |
| Chlorides (x $10^3$) | 16.5-28.0 | 166 |
| Free and Total Chlorine Residuals | 250-500 | 1.9 |
| Sodium (x $10^3$) | 32-38** | 254 |
| Iron, Total | 3.0- 5.0*** | 0.03 |
| Total Alkalinity (x $10^3$ as $CaCO_3$) | 32.0-52.5+ | 278 |
| Carbonate Alkalinity (x $10^3$ as $CaCO_3$) | 22.4-36.4++ | 232 |
| Hydroxyl Alkalinity (x $10^3$ as $CaCO_3$) | 9.6-16.1+++ | 47 |
| Bicarbonate Alkalinity (x $10^3$ as $CaCO_3$) | 0*+ | 0.00 |

* Increased to 500-800 when $N_U/N_T$ <2.0.

** Decreased to 25.0 when $N_U/N_T$ decreased to 1.29.

*** Increased to 400 when $N_U/N_T$ decreased to 1.29.

\+ Decreased to 12.0 when $N_U/N_T$ decreased to 1.29.

++ Averaged 70 (± 8) % of Total Alkalinity but increased to 90 (s = 10)% of Total Alkalinity when $N_U/N_T$ <2.0.

+++ Averaged 30 (± 8)% of Total Alkalinity but decreased toward zero when $N_U/N_T$ <2.0.

*+ Was zero but increased to 8% of Total Alkalinity as $N_U/N_T$ decreased to 1.29.

9.2 Organic Quality of SSW

Combustion gas hydrocarbons apparently condensed through the venturi, were impacted into the scrubber water, and were slightly dissolved into the warm (165°F) caustic. As discussed in Section 11 some pyrolyzates (unchlorinated aromatics) in the combustion gases reacted with the oxidants in the combustion gas (HCl, $Cl_2$, and monatomic chlorine) and the caustic to produce hydrolyzates: monochlorophenol and dichlorobenzene. A detailed summary of these organic masses is presented in Table I-8. The average concentration of these pyrolyzates and hydrolyzates expressed as carbon in the spent scrubber water averaged 0.60 mg/l for Burns I, II, and III and decreased to an average of 0.02 mg/l for Burns IV through VIII. None of these hydrocarbon compounds were detected in suspended solids in the scrubber water. Comparison of both water and gas hydrocarbon analyses showed that improved combustion efficiency in the last five burns significantly reduced the hydrocarbons delivered into, and collected by, the scrubber.

No TCDD and none of the esters or acids of 2,4-D or 2,4,5-T were detected in any of the spent scrubber water samples or suspended solids except the total burn composite of Burn III. The detection limit of each compound averaged 0.045 µg/l for an overall average detection limit of 0.23 µg/l for the five compounds. A thorough discussion of this sample and the most probable source of its positive TCDD (0.25 µg/l) are presented in Appendix I. The source of the TCDD was concluded to have been combustor coke deposit which broke away from the combustion chamber, settled in the scrubber, and provided the TCDD to the scrubber water. This heavily contaminated combustor coke, found only in Burn III, was attributed to fuel flow conditions and the incinerator poppet nozzle which in this instance produced poorer combustion and mixing within the combustion chamber than was observed in any of the other burns. This situation is discussed in Section 10.

10.0 COMBUSTION CHAMBER COKE DEPOSIT RESULTS AND DISCUSSION

10.1 Quantity and Quality (Prepared by EHL/K)

The relationships regarding quantity and quality of the coke deposits removed from the combustion chamber are discussed in detail in Appendix I. A summary of results regarding coke deposits is presented below.

The central poppet nozzle was utilized for Burns I through IV. The deposits removed from the combustion chamber averaged 3.03 pounds of coke per drum of "Orange" Herbicide incinerated. These quantities of coke were twenty times the average produced in Burns V through VIII while utilizing the radial slot fuel nozzles. None of the coke samples lost weight until heated to 525°C and all left an ash content of <0.06% when heated to 725°C. The coke deposits

from Burns I, II, and IV had a steel gray color and were grainy, hard, and brittle. The deposits from Burns V - VIII were darker (like carbon black), of finer particle size, and much more easily crushed. Except for Burn III deposits, none of the coke had a herbicidal odor. Burn III coke also had "soft spots" which were not observed in coke from other poppet nozzle burns (I, II, and IV).

Except for Burn III, the total hydrocarbon contaminants in the coke deposits were small amounts of pyrolyzates per 100 gm of deposit: unchlorinated aromatics, <512 µg; unchlorinated aliphatics, <87 µg; and biphenyl, <17 µg. See Table G-9, Appendix G. Burn III coke deposit, however, contained these pyrolyzates in lesser amounts but also contained 1100.2 µg of herbicide esters and acids of 2,4-D and 2,4,5-T per 100 gm of deposit. Of these original herbicide compounds 551 µg was normal butyl 2,4-D ester and 542 µg was normal butyl 2,4,5-T ester. Although TCDD was not detected, the existence of these esters indicated TCDD presence--probably below the detection limit of 23 µg/100 gram of sample analyzed. Burn III's coke quantity, 3.28 pounds per drum of herbicide incinerated, was 10% greater than the other deposits encountered while using the central poppet nozzle. The coke's appearance, odor, and chemical quality indicated that lower than usual temperatures had existed around the coke. For these reasons, the coke was implicated as the source of TCDD found in the Burn III spent scrubber water samples. (See paragraph 12, Appendix I.)

The cause for coke deposits and their characteristics was attributed primarily to physical characteristics of the fuel injected and the injection nozzles. These relationships are discussed in the following paragraph.

10.2 Fuel Injection Characteristics Relative to Coke Depositing (Prepared by TMC)

Since the quantity and quality of the coke deposited in the combustion chamber was dependent primarily on the type of fuel injection nozzles utilized, the characteristics attributable to each nozzle type relative to observed data is discussed below.

10.2.1 Poppet Nozzle Injection:

Air entered the combustion chamber through the smaller diameter inlet and expanded into the larger diameter combustion chamber, hence the sudden expansion mechanism. See Figure B-3, Appendix B. Fuel and air mixing was obtained by mounting the poppet nozzle on the centerline of the inlet with the exit of the nozzle near the point of expansion. Mixing occurred somewhat as a result of the momentum of the fuel toward the walls of the chamber and primarily as a result of air recirculation into the region immediately downstream of the sudden expansion. The central poppet nozzle injects fuel into the air stream in a conical pattern and

should produce a finely atomized fuel spray immediately upon leaving the nozzle. It was apparent from the deposits in the combustion chamber from Burns I through IV that some portion of the unreacted "Orange" Herbicide spray was penetrating the air recirculation stream and was pyrolyzing on the chamber walls, thus developing deposits and generating a partial obstruction at about 1½ to 2 diameters from the inlet step. This situation was attributed to the extreme viscosity of the "Orange" Herbicide fuel (see Figure B-7) which required high fuel nozzle driving pressures, and likewise the lack of quick fuel spray atomization necessary for proper burning. This situation generally does not occur with conventional fuels of low viscosity (<1.0 centistoke). The deposition of coke deposits is quite common in conventional commercial incinerator/boilers using high viscosity fuel oils.

The partial obstruction deposited in the combustion chamber tended to limit recirculation of the air and also affected the fuel and air mixing mechanism of the poppet nozzle. The entering air anticipated the restriction thereby reducing the recirculation and changing the mixing characteristics of the zone around the nozzle. Burner performance was thus degraded. Also, as this restriction increased during the burn, it is certain that some of the deposits broke loose due to the increasing gas velocity and turbulence through the "orifice" and were propelled into the scrubber tank.

The poppet nozzle was selected for Burns I - IV on the basis of prior experience indicating satisfactory results at fuel/air mass ratios up to about two thirds of stoichiometric; approximately the ratio required for the middle temperature burns (2500°F). For Burns I and II, a fuel/air mass ratio (0.086) of approximately one half stoichiometic was utilized which, although causing coking of the combustion chamber, did not allow raw herbicide or TCDD to exit the reaction tailpipe. During Burn III, the fuel flow was increased to provide a fuel/air mass ratio (0.106) of approximately two thirds stoichiometric. Deposits increased some 10% over Burns I and II which was attributable to the increased momentum (penetration) of the fuel stream. The increased coking would have caused lower combustion efficiencies and more tendency to break deposits loose. It is apparent that the increased severity of the depositing situation occurring in Burn III resulted in the presence of herbicide in the Burn III deposit and the TCDD in the spent scrubber water which was composited during the later portion of the burn when combustion efficiency had decayed. It is probable that TCDD was present in the deposit but at an undetectable concentration. Likewise it is probable that herbicide broke loose from the deposits, or remained after initial combustion, but was thermally degraded before reaching the scrubber or reacted with the scrubbing solution, whereas TCDD passed unreacted into the scrubber. The fact that TCDD was not found in the combustion gas sample or the first hourly spent scrubber water composite sample indicated that it was produced during the last two hours of operation after these samples were collected.

Burn IV was a duplicate of Burn III except that the "Orange" Herbicide was preheated to approximately 175°F as compared to about 90°F for Burn III. No herbicide or TCDD was found in any effluent sample and the combustion chamber coking was reduced some 10% from Burn III. This increased temperature reduced the viscosity by a factor of 16, thus providing much faster atomization and combustion of the herbicide and a decrease in solid liquid penetration. Burn VI was a duplicate of Burn III also except that the poppet nozzle had been replaced by slot nozzles as discussed below.

10.2.2 Slot Nozzle Injection:

The slot nozzle configuration is described in Appendix B. These nozzles, utilized in Burns V through VIII, injected the fuel radially toward the combustion chamber centerline at the sudden expansion step thereby mixing the fuel and air primarily by injection rather than by recirculation. This method of injection resulted in more efficient mixing near the burner inlet and more efficient combustion within the first diameters length of the combustion chamber. The deposits from Burns V through VIII were much smaller, sparsely distributed, of finer softer grain, and did not contain herbicide. This data indicated that carbon formation occurred in a well mixed combustion gas stream that did not permit significant penetration of liquid fuel to the chamber walls. Likewise, restrictions in the chamber which altered the air flow path did not affect the mixing and burning to the extent noted for poppet nozzle operation. The fuel temperature (viscosity) and fuel/air mass ratio were not as critical regarding combustion destruction efficiency as when using the poppet nozzle. None of the compounds identified in the herbicide feed were found in any of the effluent samples for Burns V through VIII.

11.0 PYROLYZATE AND HYDROLYZATE RESULTS AND DISCUSSION (Prepared by USAF EHL/M and K)

Table 4 presents those detected organic compounds considered to have been pyrolyzates and hydrolyzates in the combustion gas, scrubbed effluent gas, spent scrubber water, spent scrubber water sediment and combustor coke deposit samples taken during "Orange" Herbicide incineration. Two values are given: the average values from Burns I, II and III; and the average values from Burns IV, V, VI, VII and VIII. These burns were so grouped to demonstrate the more efficient pyrolysis of "Orange" Herbicide in the last five burns (see discussion in Appendix I).

The nonchlorinated aliphatics, aromatics, and biphenyls were all considered pyrolyzates since they were undetected in the herbicide fuel and their formation was not dependent on hydrolysis. These aliphatics and aromatics were partially collected in the

TABLE 4: AVERAGE RANGE OF DETECTED HYDROCARBON MASSES CONSIDERED TO BE PYROLYZATES AND HYDROLYZATES OF "ORANGE" HERBICIDE INCINERATION

| Organic Pyrolyzates/Hydrolyzates | Combustion Gas [1] | | Spent Scrubber Water [2] | | Scrubbed Effluent Gas [1] | | Spent Scrubber Water Sediment [3] | | Combustor Coke Deposit [3] | | Average Weight Percent Present in Herbicide Feed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | P | H | P | H | P | H | P | H | P | H | |
| Nonchlorinated Aliphatics ($C_{10}H_{22}$) | 0.96-0.15 | ND | 105.8-7.9 | ND | 0.07-0.09 | ND | ND | ND | 51.0-22.0 | ND | ND |
| Nonchlorinated Aromatics ($C_6H_5(C_4H_9)$) | 4.81-0.25 | ND | 123.8-4.6 | ND | 0.08-0.08 | ND | ND | ND | 105.0-126.0 | ND | ND |
| Biphenyl (unchlorinated) | ND | ND | ND | ND | 0.01-0.06 | ND | ND | ND | 8.75-4.86 | ND | ND |
| Dichlorobenzene | ND | ND | ND | 300.5-2.8 | ND | ND | ND | ND | ND | ND | ND |
| Monochlorophenol | ND | 1.0** | ND | 22.2-0.1 | ND | ND | ND | ND | ND | ND | ND |
| Dichlorophenol*** | ND | ND | ND | ND | ND | ND | ND | ND | 2.3-1.5 | ND | 1.46 |
| 2,4-D Dichlorophenoxy Acetic Acid*** | ND | ND | ND | ND | ND | ND | ND | ND | 2.5* | ND | 0.73 |
| 2,4,5-T Trichlorophenoxy Acetic Acid*** | ND | ND | ND | ND | ND | ND | ND | ND | 2.4* | ND | 0.52 |
| Phenoxy Acetic Acid (unchlorinated) | ND | ND | ND | ND | ND | ND | ND | ND | 0.5* | ND | ND |

ND - Not detected. For detectable limits see Tables G-2 through G-9.

* In Combustor Coke Deposit, Burn III only.

** Burn I only.

*** These compounds were in "Orange" Herbicide - may not have been pyrolyzates.

Note: The first value in each column was an average of Burns I, II and III. Second value in each column was an average of Burns IV, V, VI, VII and VIII.

Reported as mass of compound

1. µg per liter of gas (STP)
2. µg per liter of spent scrubber water
3. µg per 100 grams

STP - 70°F, 29.92" Hg, and Dry

scrubber while the biphenyls completely penetrated through the scrubber. The respective penetration of these pyrolyzates through the scrubber was probably due to their relative solubilities and vapor pressures in hot NaOH solution. (See Appendix I.) The biphenyl pyrolyzate undoubtedly existed in the combustion gases but its detection was considered to have been masked via gas chromatograph peak interference (see Comments section of Appendix G).

Monochlorophenol and dichlorobenzene were consistently detected in the spent scrubber water but never in the herbicide feed or in any of the combustion or scrubbed effluent gas samples except for the monochlorophenol in Burn I combustion gas. Since the precursor(s) (unchlorinated aromatics) of these compounds were present in the combustion gas along with HCl, $Cl_2$, and monatomic chlorine, it was reasoned that condensation and hydrolyses of these combustion gas products occurred in the venturi scrubber to produce monochlorophenol and dichlorobenzene as hydrolyzates.

Since the 2,4-D and 2,4,5-T chlorophenoxy acetic acids and dichlorophenol averaged 2.71% by weight of the blended "Orange" Herbicide feed, these compounds may or may not have been pyrolyzates. These compounds were found only in the combustor coke deposit. The phenoxy acetic acid was however not detected in the blended herbicide feed samples. Thus this acid was considered a pyrolyzate formed when combustion chamber mixing was its poorest and combustor coke deposit was at its maximum (Burn III).

Ionol and didecylphthlate were detected in all combustion and scrubbed effluent gas samples and all spent scrubber water samples. However, as discussed in Appendices G and I, these compounds were considered environmental contaminants and not pyrolyzates or hydrolyzates.

## 12.0 BIOASSAY, NOISE TESTING, AND DRUM CLEANING/DISPOSAL RESULTS AND DISCUSSION (Prepared by USAF EHL/K)

### 12.1 Bioassays

Dynamic bioassays of up to 96 hours were conducted with three-spined stickleback fish (Gasterosteus aculeatus) in the spent scrubber water. Static bioassays were also conducted with brine shrimp (Artemia salina) in spent scrubber water for periods up to 24 hours. Plant biomonitoring was initiated several days prior to Burn I, during all burns, and five days after Burn VIII. Monitored flora consisted of the indigenous plants around TMC's perimeter and ten young tomato plants at each of sixteen locations evenly distributed around the incinerator facility. Results and discussion of these bioassays and plant biomonitoring will be published by EHL/K under separate cover.

[The EHL/K report on biological monitoring has been included as Appendix M to the Final Environmental Statement]

## 12.2 Noise Testing

Incinerator noises were predominately in the 2000-8000 Hertz bands and had an overall noise level of 91 (± 2) dbA at a distance of twelve feet. A fifty-foot radius around the incinerator was a hazardous noise area to unprotected personnel occupationally exposed to the noise. The control room effectively attenuated incinerator noises so that no speech interference levels were observed in the control room. Calculations were made to determine the noise levels at various distances from one or more incinerators. See Appendix J.

## 12.3 Drum Cleaning Analyses and Comments

Appendix F presents and discusses the drum cleaning procedures, drum disposal, and analyses of rinse samples in detail. An abbreviated summary of these results is presented here.

During initial transfer of "Orange" Herbicide to the fuel feed tank, a drum pumping device was used which left usually less than two quarts of herbicide in each drum. Before the cleaning phase each drum was upended and allowed to free drain until steady dripping stopped. Each drum was then rinsed three times with various amounts of JP-4 for five minutes each on a barrel rolling device. Rinse quantities of clean JP-4 in each drum rinse set were 5/5/5, 3/3/3, 2/2/2, and 5/3/2 gallons. Each rinse was drained into a holding tank for subsequent incineration. Samples were taken of each rinse solution midway during the draining.

The cleaned drums were safely disposed of in an environmentally approved manner in the Los Angeles County "Class 1" Landfill Number 5 at Calabasas, CA.

Evaluation of drum rinse sample analyses provided an estimate of total herbicide mass left in a freshly drained drum: 450 (± 25) grams. On a proportional basis, slightly more of the herbicide's 2,4,5-T nb ester was removed during rinsing than the 2,4-D nb ester. Smaller rinse volumes produced significantly more variable results. Nonetheless, a given total volume of rinse removed about the same amount of herbicide whether it was used in subdivided volumes or in a single volume with the restriction that a total volume was ≤5 gallons, from 6 to 10 gallons, or from 9 to 15 gallons. The percent efficiency of herbicide removed increased with total rinse volume applied: range 45% for 2/2 gallons to 79% for 5/5 gallons. A third drum rinse of ≤5 gallons did not improve the herbicide removal efficiency any more than 3%.

Analyses of TCDD in the rinse solutions was beyond the scope of this study. With TCDD solubilities similar to that of the herbicide esters, it was indicated that as much as 1.25 mg of TCDD may have been left in the best rinsed drums. This amount of TCDD in these drums represented the worst case, however, since these drums contained herbicide with the highest TCDD contamination known to exist in Air Force stocks.

All rinse samples have been stored at EHL/K should any further analyses of them be needed to select a drum disposal method.

## 13.0 OTHER TEST PROGRAM COMMENTS (Prepared by TMC)

### 13.1 "Orange" Herbicide Properties

Problems were caused by the high viscosity of "Orange" Herbicide with the unexpectedly low ambient temperatures at the start of testing. Figure B-6 shows viscosity vs. temperature and indicates that even at 100°F the viscosity of "Orange" Herbicide is very high (16 centistokes) compared to other conventional fuels. At 65°F the viscosity rises to 48 centistokes. The temperature/viscosity characteristic was also quite evident during transfer operations. The flow problems in the incinerator system were alleviated by heating the herbicide feed to 90°F or higher. However, the herbicide remained quite difficult to atomize even at these elevated temperatures.

No filtration or plugging problems were noted in the fuel feed system during the program. Although a parallel filter system was available, a 5 micron filter pot selected for initial use was utilized without cleaning throughout the entire program. The maximum pressure loss noted during testing was about 20 psid across the filter. This absence of filtration problem was attributed to the complete flushing of the fuel feed tank during system assembly and the filtering of the "Orange" Herbicide during loading.

No slot nozzle plugging problems were experienced. All testing using slot nozzles was performed with herbicide temperatures about 90 to 110°F. The nozzle slots were 0.009 inch wide. Slot nozzle combustion was very smooth and no indications of plugging were noted. Removal of the manifold after testing revealed the slots had remained clean. The fuel slot nozzles were placed inside the natural gas nozzles as described in Appendix B. This arrangement kept the fuel slot nozzles cooled and precluded the possibility of "Orange" Herbicide being exposed to a hot metal surface during initial injection and thus prevented the formation of any deposits in the nozzle slot. This feature and the 5 micron filtering system was felt to have prevented any slot nozzle plugging problem.

### 13.2 Herbicide Handling

The safety program established for this effort is described in Appendix H. There were no problems experienced in handling of the "Orange" Herbicide during the program. There was no spillage or other release of the herbicide to the environment, except for minor drips normally occurring during transfer or fuel system modifications. These drips were promptly absorbed with a

rag soaked in JP-4. Contaminated rags and other materials were kept in a sealed container and disposed of by the Air Force at test program completion. All contaminated utensils employed during transfer or systems operations (funnels, hoses, drip pans, etc.) were thoroughly rinsed in JP-4 after each use and the rinse solution incinerated.

### 13.3 Effect on Incinerator Materials

A total of 44 hours of operation, including 30.5 hours on undiluted herbicide, was accumulated during the program with 16 complete start/stop transients. During this period no structural problems were noted in the units themselves or at gasketed mating flanges. There were no emergency shutdowns or shortened runs due to physical incinerator problems. Examination of the incinerator during and after the program indicated no evidence of scaling or other physical deterioration indicating impending failure.

General experience with Type 310 stainless steel, and our specific experience with Marquardt incinerators made of 310 stainless, indicate long term durability at the temperatures experienced, particularly at the low stresses and creep rates created by near ambient pressure operation. Even at a chamber pressure as high as 16 psig, the creep rate is 1% per 100,000 hours at 1500°F. Also, the maximum skin temperature noted on the uncooled reaction tailpipe throughout the program was 1700°F which was below the temperature (2000°) at which oxidation scaling becomes appreciable.

## 14.0 CONCLUSIONS (Prepared by USAF EHL/K, EHL/M and TMC)

### 14.1 Destruction of "Orange" Herbicide by Incineration

"Orange" Herbicide was effectively and safely destroyed by incineration. No "Orange" Herbicide constituent was detected in any system effluent when operating with the slot nozzles or the poppet nozzles except for the combustor coke deposit and spent scrubber water sample of Burn III. Very favorable relative pyrolysis efficiencies were obtained, ranging from 99.98% to 99.999%. Chlorinated phenolic compounds were undetected in all of the scrubbed effluent gas samples and detected only in one combustion gas sample (monochlorophenol at $1.06 \times 10^{-6}$ grams/liter in Burn I). The spent scrubber water from all burns contained monochlorophenol but at a level not exceeding $0.14 \times 10^{-6}$ grams/liter in the last five burns or $53 \times 10^{-6}$ grams/liter in any of the burns.

## 14.2 Engineering Data

Preheat of "Orange" Herbicide fuel prior to injection in the combustion chamber was an important combustion efficiency parameter. The RPE was improved significantly (from 99.99 to 99.999%) when the "Orange Herbicide fuel was preheated to between 90° and 175°F. Preheat of "Orange" Herbicide fuel to at least 90°F was required to accomplish acceptable fuel injection characteristics.

The method of fuel injection was an important combustion efficiency parameter. The radial slot nozzles produced a higher RPE (Appendix I) and only about 1/20 the mass of combustion chamber coke deposits produced when central poppet nozzles were used. The slot nozzles provided satisfactory results at higher fuel/air mass ratios and combustion temperatures and therefore permitted a higher destruction rate of the "Orange" Herbicide.

Basic flow control was quite simple in that only fuel and air mass flow regulation was required once steady state was achieved. Transients were performed without incident due to the ease of ignition of "Orange" Herbicide into an established flame. The manual control systems were quite satisfactory in these regards and the only real flow control monitoring needed was to correct for minor changes in flow caused by changes in facility air storage pressure or changing fuel properties. It was concluded that "Orange" flow regulation is no problem as long as temperature is maintained within a reasonable band as determined by system sizing and is properly filtered to prevent plugging of fuel nozzles. Basic incinerator control therefore consisted of fuel and air flow regulation with monitoring of the combustion gas temperature to verify the presence of combustion and provide a relative indication of combustion and consistency of operating parameters. Air and fuel mass flow depended on delivery system pressure. The burner system pressure provided an indication of combustion gas flow and downstream conditions. These control parameters were conventional and could be readily automated using existing process industry control components. Such systems quite routinely monitor and control flow and combustion processes and take appropriate corrective action in the event of system anomalies. From purely a combustion point of view, this incineration process was not much different than when using conventional fuels. However, the serious differences were in the structural integrity (safety) of the incinerator and the safety aspects of storage and delivery of the "Orange" Herbicide.

Scrubbing of the combustion gases and neutralization of acids was accomplished satisfactorily. Optimization of this system was not within the scope of this effort and it is recognized that other types of scrubbers may be more desireable.

The on-line gas analyses equipment used was adequate for CO and $NO_x$ monitoring of scrubbed effluent gas only. Gas analyses equipment incorporating additional features would be required for sampling of combustion gas and for representative hydrocarbon sampling of the scrubbed and combustion gases. Application of on-line sampling analyses to a production process would require additional study beyond the scope of this effort.

### 14.3 Effects on Incinerator Materials

Considering the absence of structural or sealing problems in the physical combustion chamber enclosures, the lack of evidence indicating physical deterioration in the materials utilized, the qualities of the materials used, and prior experience in similar systems, it was concluded that the basic incinerator design would provide a unit of considerable longevity. There are design considerations that would be required, "external" to the basic combustion process, which could further ensure longevity and provide a reliable unit. Such design factors do not appear to be particularly unusual or exotic in nature. It was also concluded that durability would be enhanced by long term continuous operations where start-stop transients are minimized.

### 14.4 Mass Discharge Rates of "Orange" Herbicide Constituents

TCDD was detected in the spent scrubber water from Burn III at $0.25 \times 10^{-6}$ grams/liter. Otherwise, no "Orange" Herbicide constituent was detected in any scrubbed effluent gas sample or in any spent scrubber water sample. "Orange" Herbicide constituents were detected only in the combustion chamber coke deposit from Burn III but these deposits were contained and the mass of the "Orange" Herbicide constituents in the 12.9 pounds of coke was 64.4 mg.

Table 5 presents the maximum potentially undetected "Orange" Herbicide constituents that could have been discharged without being detected. The TCDD in the spent scrubber water from Burn III was included in the discharge. The average mass that could have been discharged in the scrubbed effluent gas during each burn was 9.3 mg ($\sigma$ = 2.7 mg). The average mass that could have been discharged in the spent scrubber water during each burn was 3.4 mg ($\sigma$ = 1.4 mg).

### 14.5 Spent Scrubber Water Quality

Spent scrubber water inorganic quality was directly related to applied caustic. Mineral content of spent scrubber waters would be minimized and acid gases effectively scrubbed if applied caustic were 2.0 ($\pm$ 0.1) times that required to nuetralize the theoretically expected amount of HCl. Primary settling, dechlorination, and adjustment of pH to about 9 may be required before discharging the spent scrubber water to natural

TABLE 5: MAXIMUM POTENTIALLY UNDETECTED "ORANGE" HERBICIDE MASS DISCHARGE RATES FROM INCINERATION OF "ORANGE" HERBICIDE
(includes TCDD, nb 2,4-D and nb 2,4,5-T esters, and 2,4-D and 2,4,5-T acids).

| Burn Number | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| SCRUBBED EFFLUENT GAS | | | | | | | | |
| Total Volume (STP) Produced During Burn (x $10^6$ liters) | 6.55 | 7.75 | 8.58 | 9.47 | 7.65 | 5.03 | 7.55 | 8.76 |
| Undetectable Mass Concentration (x $10^{-3}$ µg/l)+ | 1.05 | 0.90 | 1.15 | 0.80 | 1.00 | 3.00 | 1.30 | 1.20 |
| Total Burn Undetectable Mass (x $10^{-3}$ grams)+ | 6.88 | 6.98 | 9.87 | 7.58 | 7.65 | 15.09 | 9.82 | 10.51 |
| Burn Time (minutes) | 191 | 218 | 235 | 236 | 213 | 136 | 213 | 356 |
| Undetectable Mass Discharge Rate (µg/min)+ | 40 | 30 | 40 | 30 | 40 | 110 | 50 | 30 |
| SPENT SCRUBBER WATER | | | | | | | | |
| Total Volume Discharged During Burn (x $10^3$ liters) | 15.7 | 15.0 | 15.1 | 15.9 | 13.5 | 7.2 | 14.3 | 12.1 |
| Undetectable Mass Concentration (x $10^{-3}$ µg/l)+ | 225 | 225 | 430* | 225 | 225 | 225 | 225 | 225 |
| Total Burn Undetectable Mass (x $10^{-3}$ grams)+ | 3.54 | 3.39 | 6.46* | 3.57 | 3.05 | 1.62 | 3.22 | 2.74 |
| Burn Time (minutes) | 191 | 218 | 235 | 236 | 213 | 136 | 213 | 356 |
| Undetectable Mass Discharge Rate (µg/min)+ | 20 | 20 | 30* | 20 | 10 | 10 | 20 | 10 |

*Only gas or water sample in which any subject compounds were detected: 0.25 x $10^{-6}$ gm/l

+These values expressed as the total of the five herbicide constituents

USAF EHL/M and K

waterways. For burns using the slot nozzles, the total average hydrocarbons were less than 20 µg/l and no hydrocarbons were detected in the water's suspended carbon particles. Of the 20 µg/l total hydrocarbons, less than 1.5 percent of them could have been undetectable compounds of the original herbicide feed.

### 14.6 Pyrolyzates and Hydrolyzates

All of the detected unchlorinated aliphatics, aromatics, and biphenyls were considered pyrolyzates. The total mass of these pyrolyzates in the scrubber water, combustor coke deposit, and scrubbed effluent gas averaged 1.32 gms as carbon per drum of herbicide incinerated in the less efficient burns (I, II, III) and was an order of magnitude less (0.42 gms as carbon per drum) in the more efficient burns (IV through VIII).

All of the detected monochlorophenol and dichlorobenzene were considered hydrolyzates. These compounds were detected in only one effluent from the incinerator (spent scrubber water). Their total effluent mass averaged 0.86 grams as carbon per drum of herbicide incinerated in the less efficient burns (I, II, and III) but decreased three orders of magnitude to an average of 0.006 grams as carbon per drum of herbicide incinerated during the more efficient burns (IV through VIII).

### 14.7 Air Sampling

Data from the Beckman 109A hydrocarbon analyzer was not an indicator of RPE or combustion efficiency (Appendix I).

The formation of dichlorobenzene, dichlorophenol, and monochlorophenol by the reaction of nonchlorinated aromatic hydrocarbons with HCl, $Cl_2$ and (Cl) was indicated in locations of rapid combustion gas cooling. The quantity of these compounds that might be formed in other systems would not be expected to exceed the mass of aromatic hydrocarbons existing in the combustion gas.

### 14.8 Bioassays

Conclusions about bioassay and plant biomonitoring data will be published under separate cover by USAF EHL/K.

### 14.9 Noise Hazards

Unprotected personnel occupationally working within fifty feet of the incinerator(s) should be provided ear protection and be monitored via a hearing conservation program. The conventional masonry control room walls effectively protected the operators from the incinerator's hazardous noise levels (91 ± 2 dbA) and provided them an area quiet enough for reliable communication. Masonry walls around the incinerator pad would preclude ambient incinerator noises from interfering with any adjacent operations.

14.10 Drum Cleaning

Data of this study can be used to determine the volumetric rinses of used or contaminated JP-4 needed to meet any prescribed drum cleaning requirements. Under the following constraints, separate rinse procedures should be used to obtain maximal removal of the 450 (± 25) grams of herbicide remaining in the drums after drainage:

a. Some cleaning required but ≤5 gallons of clean or contaminated JP-4 available per drum. Use the five gallons in a single rinse to obtain 70 percent herbicide removal.

b. Maximal cleaning required but ≤10 gallons of clean or contaminated JP-4 available per drum. Use two rinses of five gallons each to remove 79.1 percent of the herbicide.

c. Third rinses of less than five gallons of JP-4 did not improve overall herbicide removal by more than three percent.

Removing drum ends and spraying the rinse downward through the open drum would provide better rinse drainage. Depending on rinse volumes used, such a rinse application technique might improve herbicide removal efficiencies by 10 to 25 percent over the results of this study.

APPENDIX A
(TO APPENDIX E)

# THEORETICAL COMBUSTION TEMPERATURES AND PRODUCTS FOR "ORANGE" HERBICIDE AND AIR COMBUSTION

A computer program for the calculation of complex chemical equilibrium compositions was used to obtain theoretical combustion temperatures and products for "Orange" Herbicide/air mass ratios. This program is "NASA Report SP-273, Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations by Sanford Gordon and Bonnie J. McBride. 1971."

The chemical composition of the "Orange" Herbicide was assumed to consist of:

50% by volume of N-Butyl 2,4,5-T $C_{12}H_{13}O_3Cl_3$

and

50% by volume of N-Butyl 2,4-D $C_{12}H_{14}O_3Cl_2$

The heats of formation used for each fuel were as follows:

| Fuel | Heat of Formation Cal/Mole |
|---|---|
| N-Butyl 2,4,5-T | -159,000 |
| N-Butyl 2,4-D | -152,000 |

The heats of formation of these compounds were estimated by taking the heats of formation of similar compounds and adding/subtracting the heats of formation of similar/dissimilar groups.

The results of computer analysis are summarized in Figures A-1 through A-4. Figure A-1 presents the theoretical temperature of "Orange" Herbicide and air combustion plotted against "Orange" Herbicide/air mass ratios for ambient air temperatures of 537 and 1000°R. The mass ratios were those of interest in the understoichiometric range which would provide combustion temperatures spanning the 2100° to 2900°F range to meet program requirements. Figure A-2 presents equilibrium products of "Orange" Herbicide/air combustion plotted against theoretical combustion temperature for an ambient air temperature of 537°R. This data was used as a basis for prediction of incinerator combustion gas product composition.

Figures A-3 and A-4 present similar data for the over-stoichiometric combustion of 2,4,5-T herbicide in 537°R ambient air. This data was computed to predict the effects of incomplete combustion or pyrolysis at very fuel rich conditions which could be created by incinerator failure, particularly regarding the formation of phosgene. Mass ratios were analyzed to approximately 1.5 times stoichiometric. Figure A-3 presents theoretical combustion temperatures versus 2,4,5-T herbicide/air mass ratios. Figure A-4 presents equilibrium products of combustion. No phosgene or any other potential gaseous products of incomplete pyrolysis were indicated within the limits of the computer program (less than $5 \times 10^{-6}$ mole fraction).

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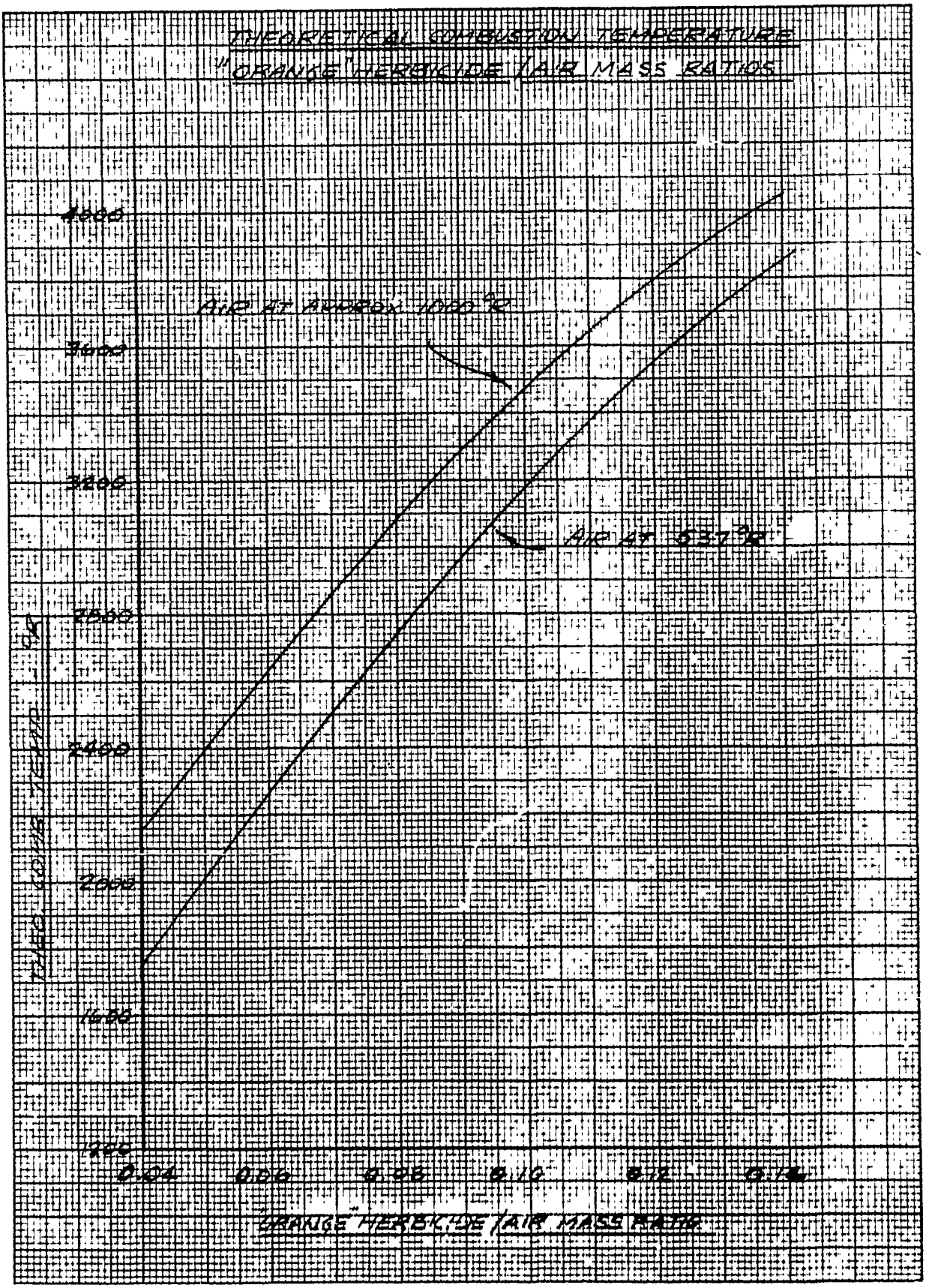
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THE Marquardt CORPORATION

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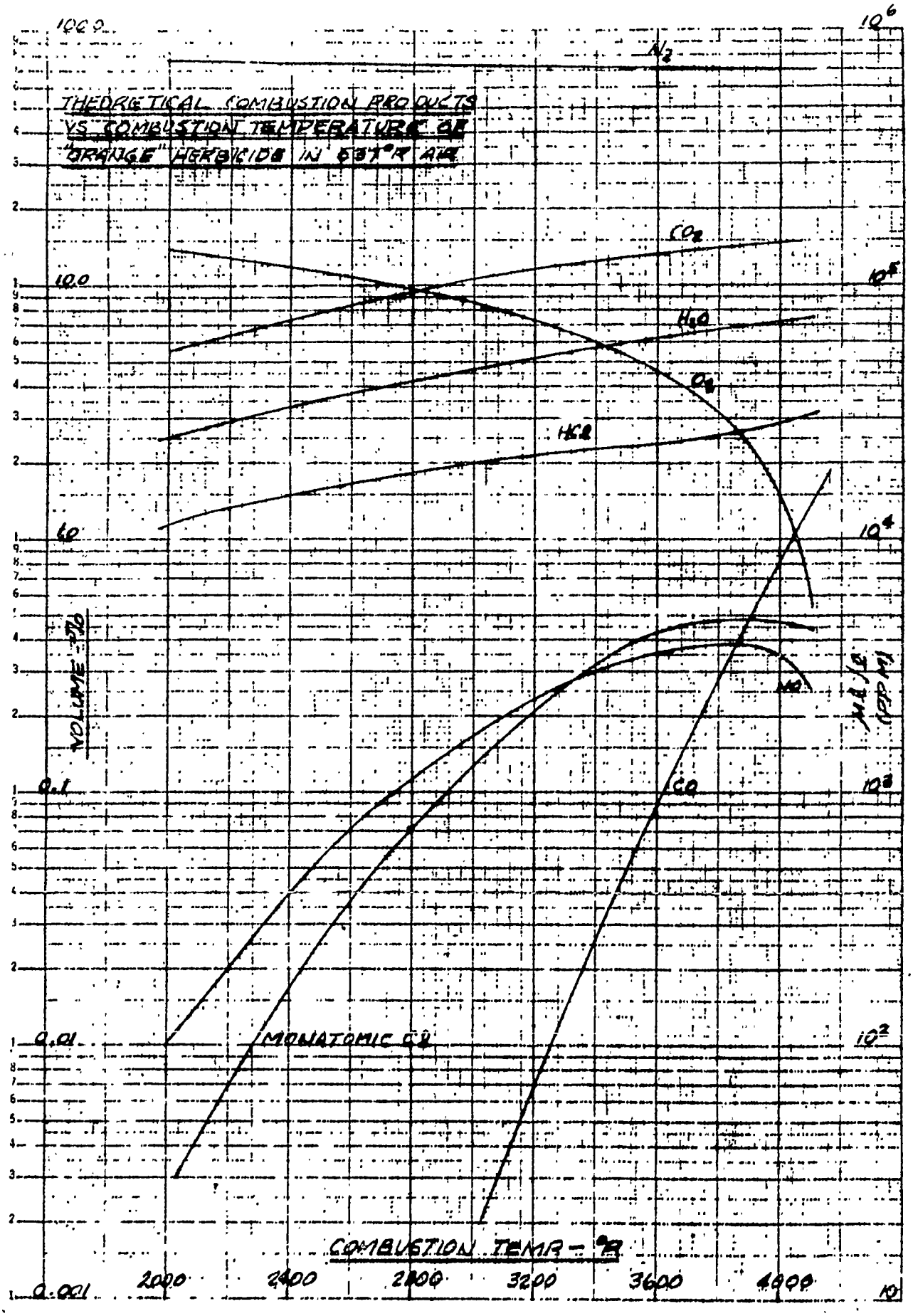
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FIGURE A-1




E(A-4)

FIGURE A-2

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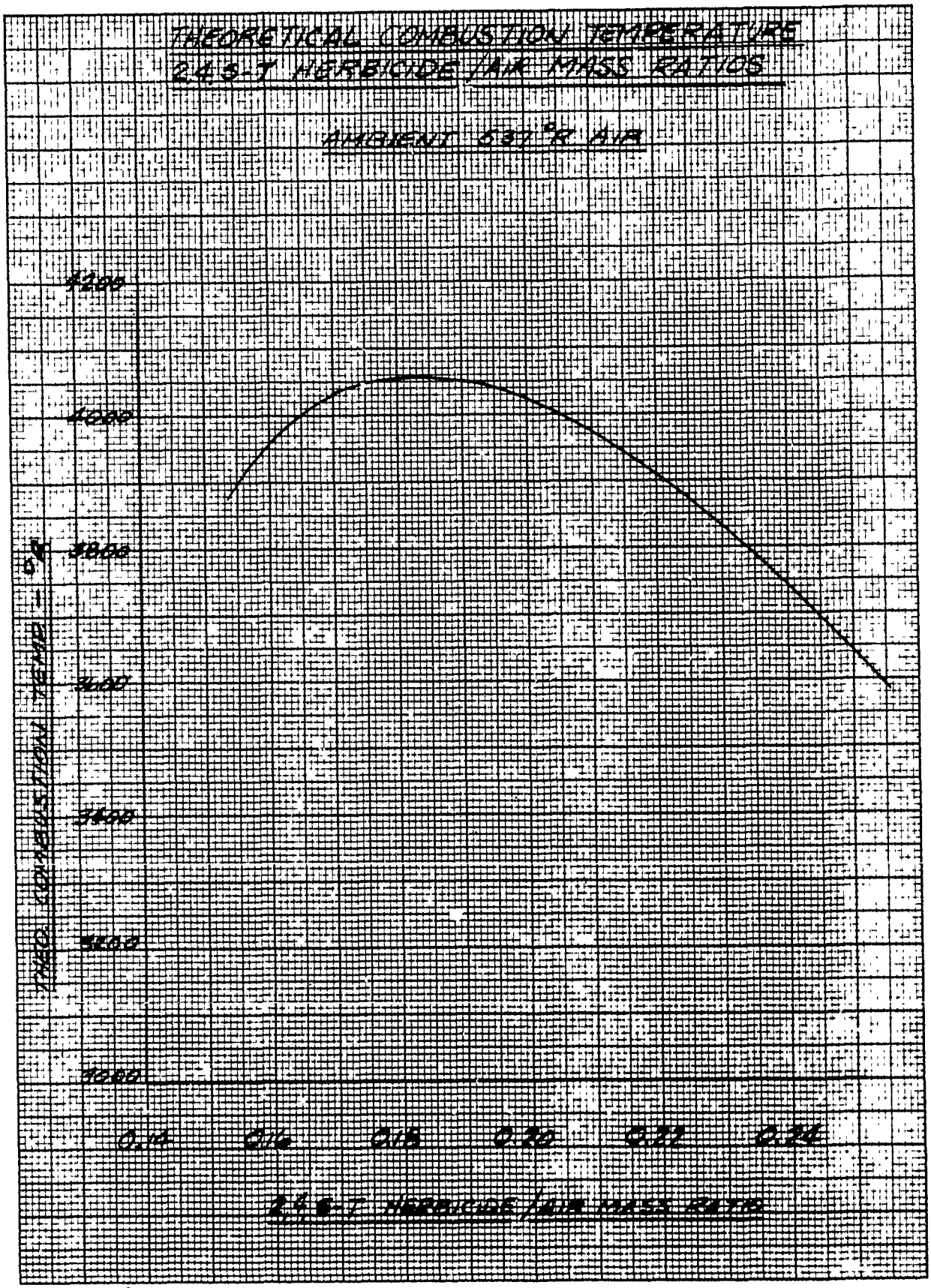
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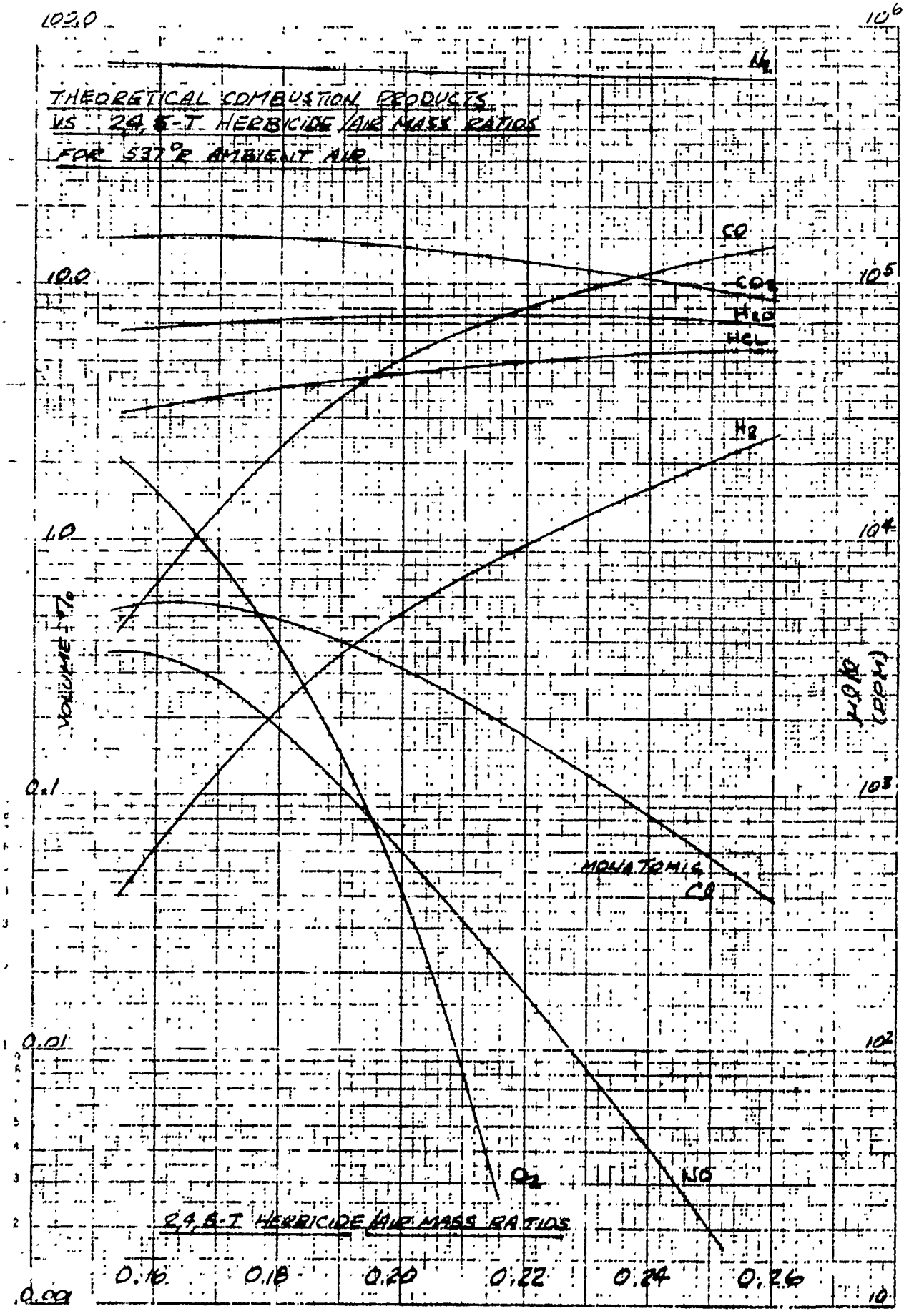
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FIGURE A-3




E(A-6)

FIGURE A-4

APPENDIX B.

(TO APPENDIX E)

## DETAILED DESCRIPTION OF TEST FACILITY FOR "ORANGE" HERBICIDE INCINERATION

A schematic of the complete test facility is shown in Figure B-1. The following discussion will describe the components and systems used during this program.

### SUE® Burner Incinerator and Reaction Tailpipe

The incinerator consisted of a 12-inch diameter SUE® Burner with a 48-inch long air cooled combustion chamber and 180-inch long uncooled reaction tailpipe. The SUE® Burner insert and cooling jacket shown in Figure B-2 was identical to other standard commercial SUE® Burner units used except that the test unit had not been acoustically treated and longitudinal air vanes had been added to aid combustion chamber cooling.

The SUE® consisted of an inlet pipe joined to a larger combustion chamber by a flat expansion plate (see Figure B-3). Fuel was injected through the plate at the "step." Because of this unique injection method, combustible fuel-air ratios were maintained in the recirculation zone, regardless of the overall fuel-air mass ratio. With this method of flame stabilization the burner was capable of operating at average combustion temperatures from 1800°F to the maximum allowable of 2800°F by varying the "Orange" Herbicide/air mass ratio. The maximum allowable temperature was determined by this program's restraint of providing a 30% minimum of excess air.

This SUE® incinerator was equipped with three separate fuel injection arrangements. One set of fuel injectors or nozzles, located in the burner expansion plate, was used to inject the pilot fuel (natural gas). The burner was started with the pilot fuel and a spark type igniter. Two different injection nozzle systems were employed for injecting "Orange" Herbicide. For tests up through Number 9 (Record Burn IV) a central poppet type nozzle was used to inject the herbicide in a finely atomized spray. This nozzle was attached to the inlet plate as shown in Figure B-4 and extended into the burner inlet pipe. Water flowing through the poppet nozzle (Figure B-4) shows its atomization characteristics. For subsequent testing (Test Numbers 10 through 13, Record Burns V through VIII) herbicide was injected with slot type nozzles located inside the natural gas nozzles in the step plate. The slot nozzle manifold and nozzles were located entirely within the natural gas manifold and sprayed into the combustion chamber through the much larger slots in the natural gas nozzles. Refer to Figure B-3. This arrangement kept the fuel nozzles cool at all times due to a small flow of air (0.04 pps) in the outer manifold.

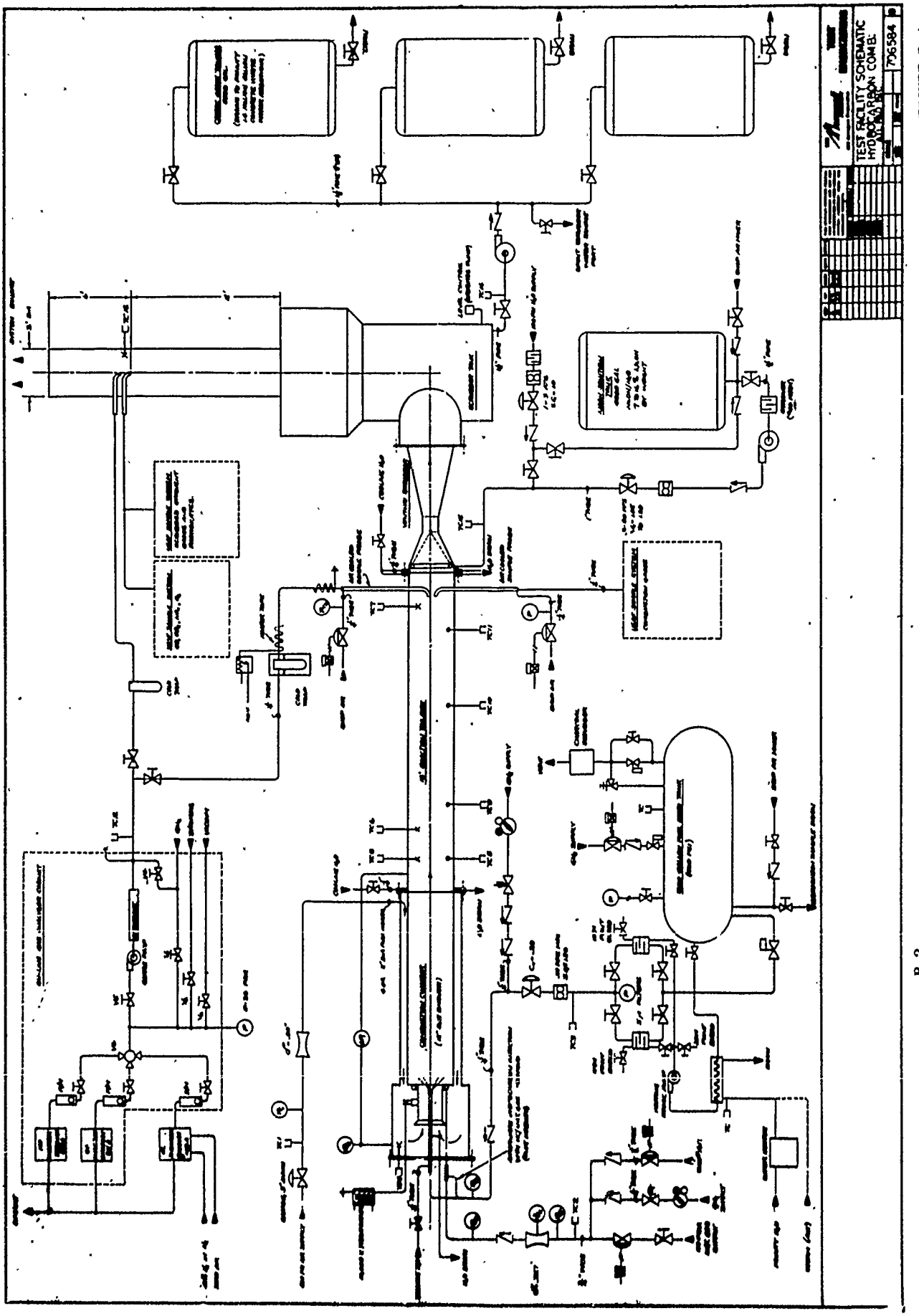



FIGURE B-1

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# COOLING JACKET AND SUE BURNER INSERT

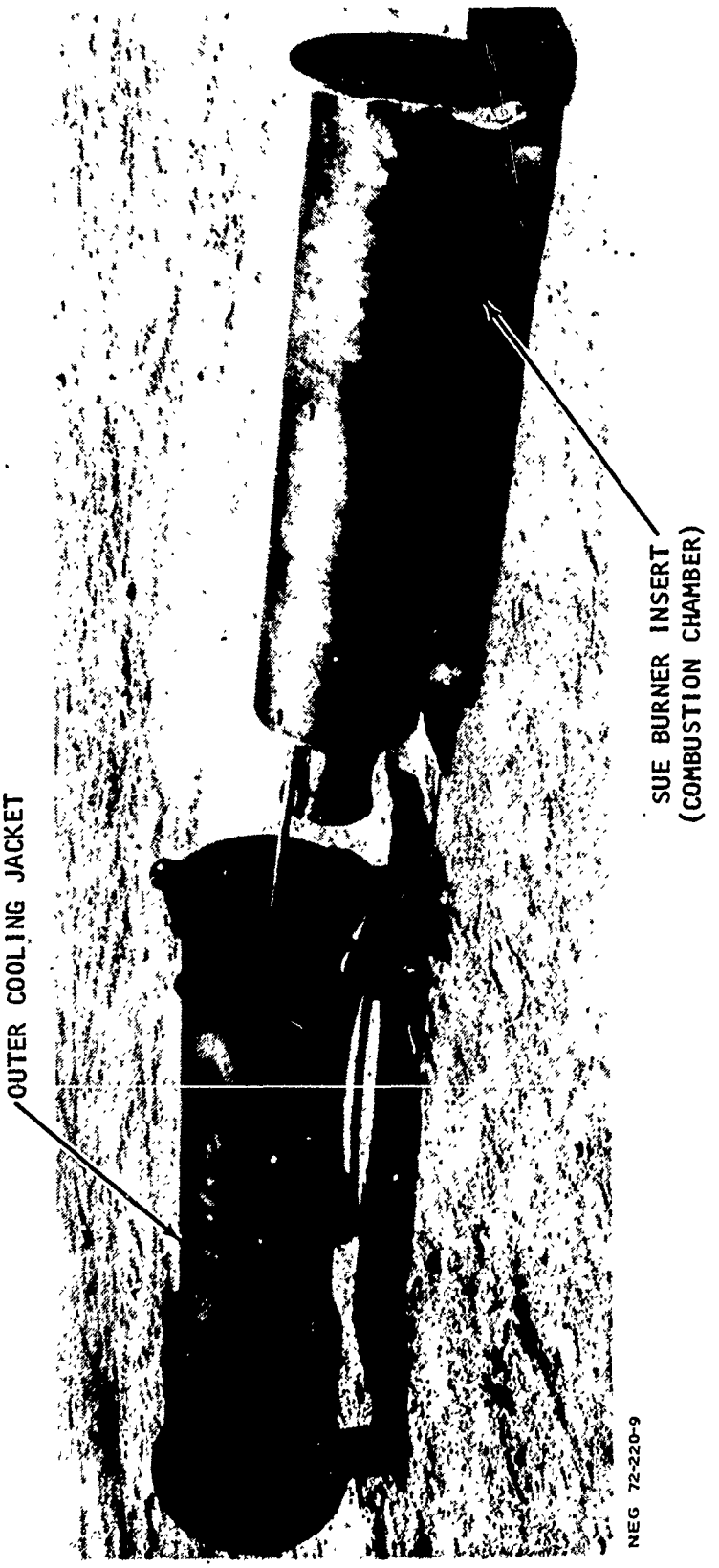
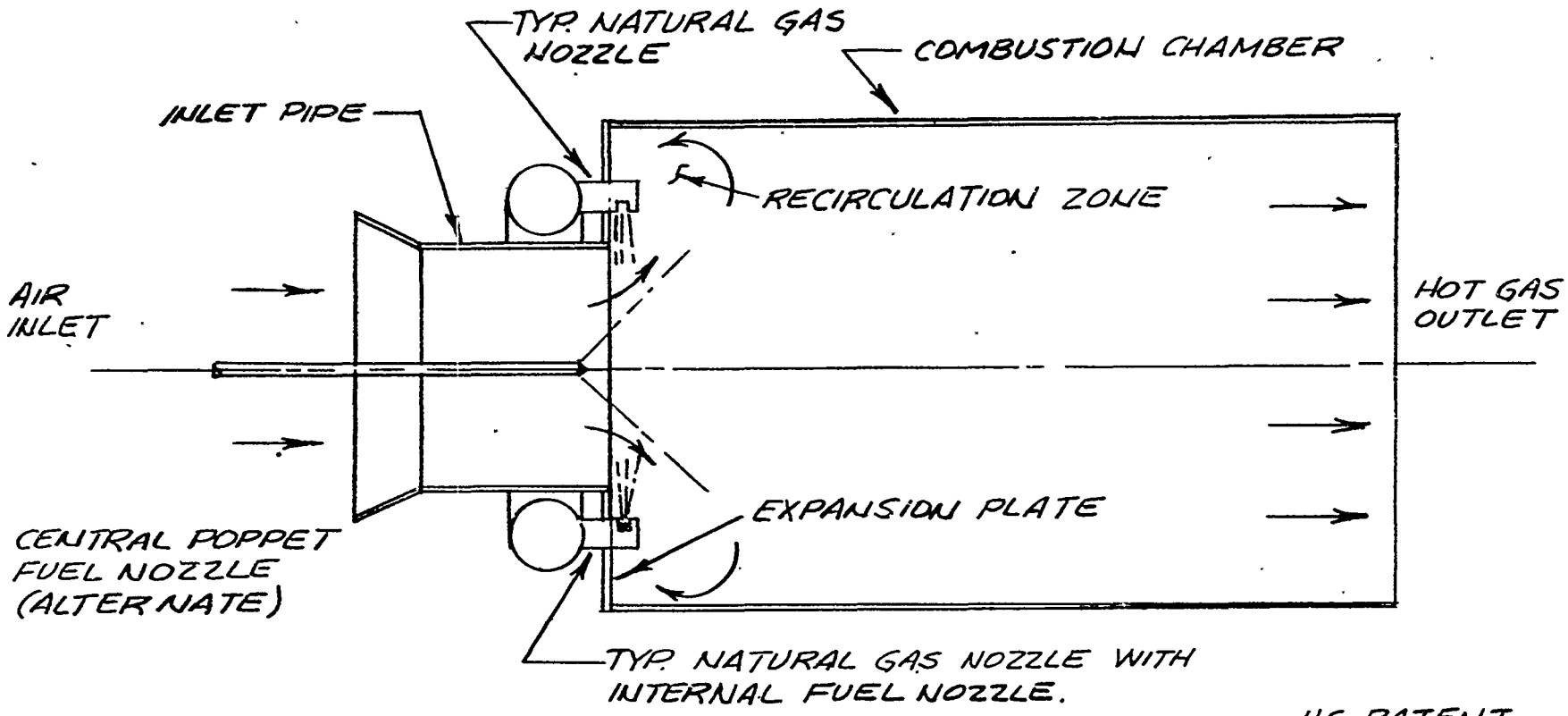





FIGURE B-2




TYPICAL SUE® BURNER CROSS-SECTION

FIGURE B-3

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# CENTRAL POPPET TYPE FUEL INJECTION NOZZLE

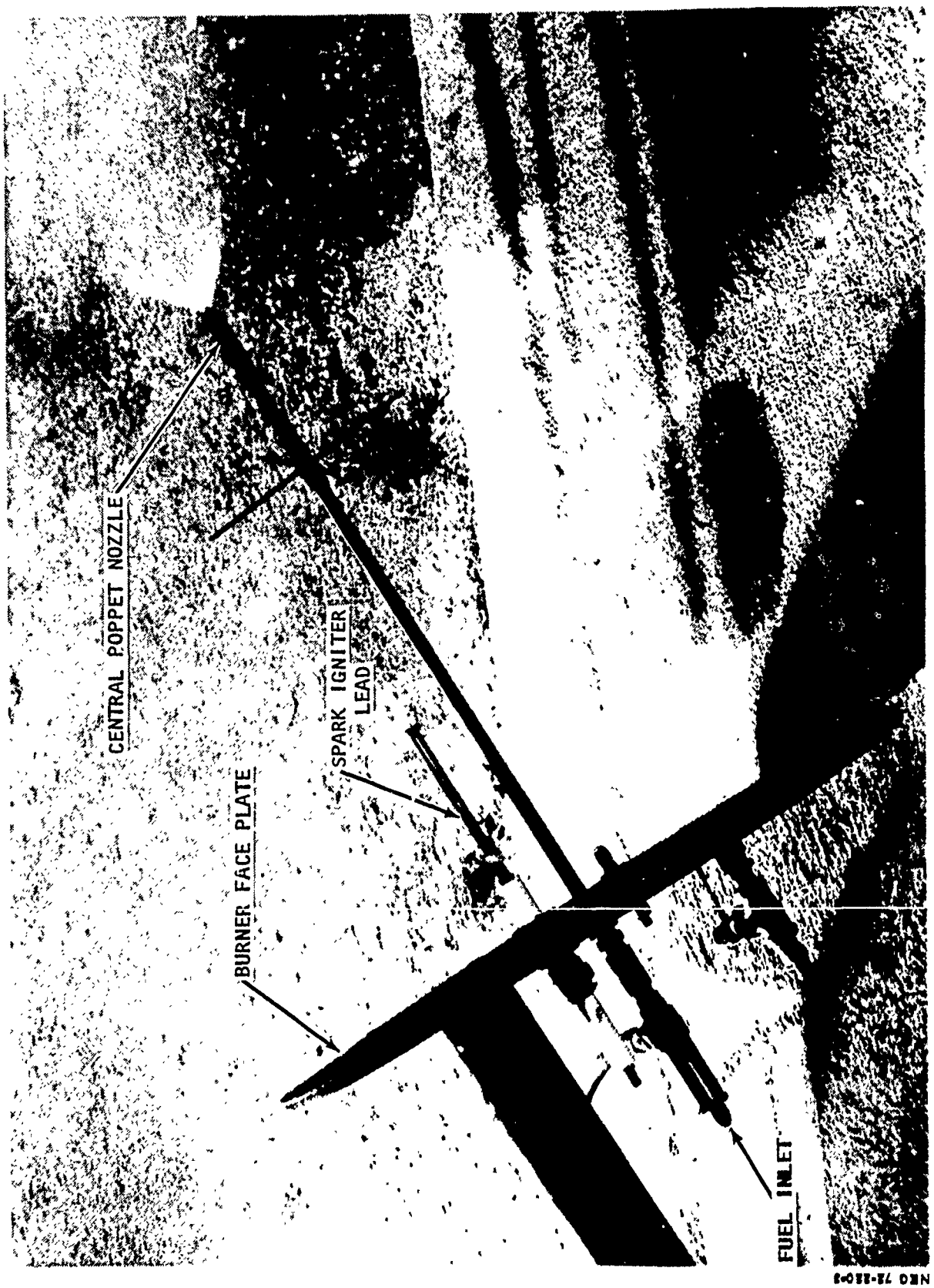





FIGURE B-4

The combustion chamber and reaction tailpipe were fabricated from 310 stainless steel. The combustion chamber was actively cooled by passing the process air over the outside of the chamber prior to its entry into the combustion zone. Thus, the incoming air was preheated 400 to 800°F before entering the combustion zone. The 180-inch long reaction tailpipe was uncooled except by radiation to the surrounding environment. This arrangement simplified construction of the test unit and provided a hot wall for completion of the incineration process in the event combustion was not complete within the 48-inch long combustion chamber. The mating flanges of the reaction tailpipe incorporate internal water cooling which prevented warping and leakage. Flange sealing was accomplished with high temperature asbestos fiber material. Ports were provided in the reaction tailpipe for combustion gas sampling probes and instrumentation.

Venturi Scrubber System

A venturi scrubber was located at the end of the reaction tailpipe, connecting the tailpipe to a scrubber tank. The scrubber tank was approximately eight feet in diameter, 15 feet high and was equipped with an internal water deluge system and a metex screen demistor. The spent scrubber water collected in the tank during a burn was transferred by a cyclic pumping system to holding tanks.

The venturi scrubber shown in Figure B-5 was made according to conventional design from 1/8-inch thick 310 stainless steel. The inside diameter of the inlet and exit sections were 12 inches and the convergent and divergent angles were 40° and 20°, respectively. The throat was 4.4 inches in diameter and 5 inches long. Fresh caustic scrubbing solution mixed with tap water was introduced through a manifold located at the inlet section of the venturi. The mixture was injected through twenty-four 0.094-inch diameter jets directed toward the venturi throat. See Figure B-5. The pressure in the manifold was maintained at approximately 40 psig.

The caustic scrubbing solution cooled and scrubbed the combustion gases as well as neutralized any HCl and $Cl_2$ that may have been present. Varying amounts of cooling tap water and caustic solution could be applied to the scrubber depending on the requirements for a given burn condition.

Caustic Solution Supply System

Caustic solution was supplied to the venturi scrubber from a 4500 gallon tank with a 2 HP pump. The flow was regulated by a remotely controlled valve and metered by a turbine flowmeter. Sodium hydroxide was loaded into the tank and diluted to a solution of desired strength. The tanks contents were mixed by shop air bubbling and the concentration of NaOH determined from the specific gravity of the mixed solution.

VENTURI SCRUBBER

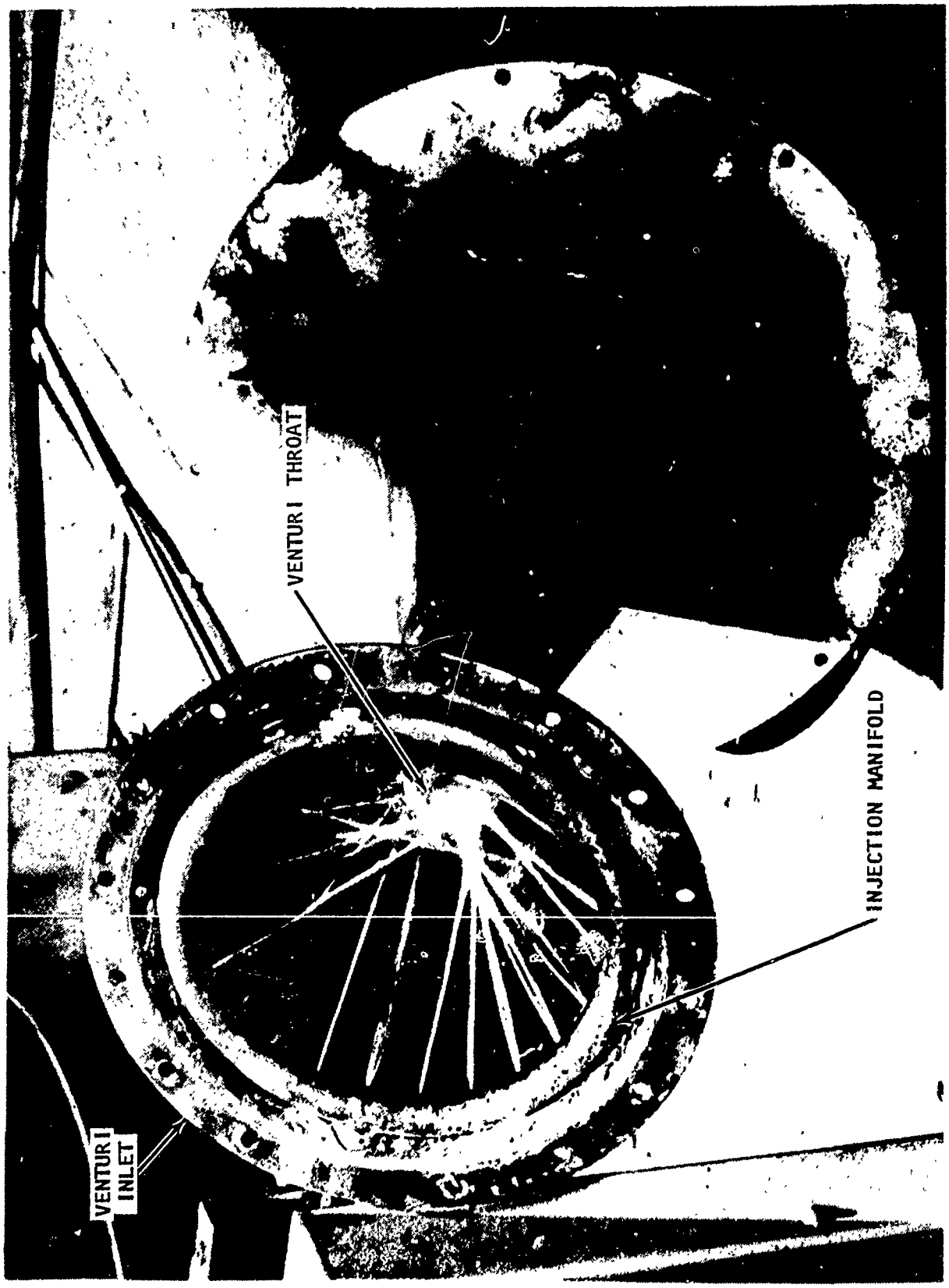





FIGURE B-5

## Scrubber Water Collection System

The spent scrubber water collected in the bottom of the scrubber tank was transferred by a 2 HP pump to one of three holding tanks. The pump was actuated by a float switch in the scrubber tank when the liquid level had reached about eight inches. Lights in the control room indicated when the pump was on so that the pumping cycle could be monitored and scrubber water samples collected. All the scrubber solution from a burn was pumped into a holding tank and held until released by the Air Force, at which time it was drained to the main facility 1.4 million gallon concrete waste water reservoir.

## Air Supply System

For flexibility in varying and measuring the air flow rate, the 600 psig facility air supply system was used. The incinerator could also be operated with a blower if required. As shown on the schematic in Figure B-1, the air mass flow was regulated remotely with a 3-inch Annin valve and was metered by a 0.80-inch throat diameter sonic venturi. Air mass flow could thus be calculated by knowing only air pressure and temperature upstream of the venturi. The air was introduced at the downstream end of the cooling jacket at four locations through 2-inch diameter hoses (see Figure 3). The air cooled the combustion chamber and was thus preheated to 400 - 800°F before entering the combustion zone.

## Herbicide Fuel Supply System

"Orange" Herbicide or JP-4 was stored and supplied from a 500 psig, 300 gallon fuel feed tank. The tank was pressurized with nitrogen at a pressure required to force the fuel through the supply system and fuel injection nozzles. Fuel was delivered through either of two parallel 5-micron filters and controlled by a ½" Annin valve. Fuel mass flow was measured by a turbine flowmeter. A recirculating heater system was used to preheat the "Orange" Herbicide to 90° - 180°F prior to injection into the combustion chamber. A $GN_2$ purge system was incorporated to allow purging of the fuel supply line downstream of the controls during shutdowns.

## Natural Gas Supply Syste.

Natural gas was supplied from the 30 psig facility system as a pilot fuel to establish temperature equilibrium in the incinerator (800°F) prior to injection and ignition of the herbicide. Natural gas flow was terminated after ignition of the herbicide and an air flow established through this system to cool the natural gas nozzles. Remotely controlled Grove regulators were used to control the natural gas or cooling air flows and metering was provided by the same 0.27-inch diameter sonic venturi.

## Instrumentation and Controls

All the parameters required for determining process mass flow rates, pressures, and temperatures were measured and recorded during each run. The parameters measured and the location of each is shown in Figure B-1 and listed in Table B-1.

Heise gauges were used to indicate total and static pressures. Barton gauges were used to measure pressure differentials. Model CF501R Anadex counters were used to indicate herbicide fuel and scrubber waters mass flow rates in pounds per second. Fluid and gas temperatures were recorded on both an 8 point 0 to 600°F and a 16 point 0 to 2400°F Honeywell Brown recorder. Iron constantan thermocouples were used to measure process temperatures below 500°F and chromel-alumel thermocouples were used to measure temperatures between 500 and 2400°F. All gauges, counters and recorders were certified by the Marquardt Instrumentation Laboratory prior to use for this program.

In measuring actual "Orange" Herbicide mass flow rates during a burn, estimated specific gravity and viscosity corrections were applied to the Anadex counters. After the burn, the herbicide mass flow rate was corrected to reflect actual herbicide specific gravity and viscosity as determined by measured herbicide temperature at the flowmeter. Figure B-6 presents "Orange" Herbicide specific gravity as a function of temperature as plotted from measurements taken during the program. Figure B-7 presents "Orange" Herbicide viscosity as a function of temperature.(4)

TABLE B-1

INSTRUMENTATION FOR "ORANGE" HERBICIDE TESTING

| SYSTEM | SYMBOL | FUNCTION | NOTE | SIZE OR RANGE |
|---|---|---|---|---|
| Air | d* | Air Flow Venturi | N/A | 0.80" |
| | $P_{T_1}$ | Upstream Total Pressure | 2 | 0 - 200 psig |
| | TC-1 | Inlet Total Temperature | 1 | 0 - 100°F |
| Natural Gas or Nozzle | d* | Gas Flow Venturi | N/A | 0.27" |
| | $P_{T_2}$ | Upstream Total Pressure | 2 | 0 - 50 psig |
| | $P_{S_2}$ | Throat Static Pressure | 2 | 0 - 50 psig |
| | TC-2 | Inlet Total Temperature | 1 | 0 - 100°F |
| | $P_{T_5}$ | Manifold Pressure | 2 | 0 - 10 psig |
| Orange Herbicide or JP-4 | $w_f$ | Turbine Flowmeter | 2 | .05 - .20 pps |
| | TC-3 | Inlet Fuel Temperature | 1 | 0 - 200°F |
| | $P_{T_4}$ | Manifold Pressure | 2 | 0 - 500 psig |
| | $P_1$ | Supply Tank Pressuree | 2 | 0 - 500 psig |
| | $P_2$ | Supply Pressure D/S Filters | 2 | 0 - 500 psig |
| | $L_1$ | Fuel Tank Liquid Level | 3 | Sight Gauge |
| SUE® Burner | $P_{T_3}$ | Burner Inlet Pressure | 2 | 0 - 10 psig |
| | $\Delta P_1$ | Burner Pressure Drop | 2 | 0 - 25" $H_2O$ |
| | TC-4 | Burner Air Inlet Temperature | 1 | 0 - 1000°F |
| | TC-5,6,7 | Exhaust Gas Temperature | 1, 2 | 0 - 2400°F |
| | TC-8,9 10,11 | Exhaust Duct Skin Temperature | 1, 2 | 0 - 2000°F |

TABLE B-1 (Continued)

INSTRUMENTATION FOR "ORANGE" HERBICIDE TESTING

| SYSTEM | SYMBOL | FUNCTION | NOTE | SIZE OR RANGE |
|---|---|---|---|---|
| Scrubber Systems | $W_C$ | Caustic Solution | 2 | 0.5 - 2 pps |
| | $W_W$ | Water Flowmeter | 2 | 0.5 - 3 pps |
| | TC-13 | Scrubbed Effluent Gas Temperature | 2 | 0 - 200°F |
| | TC-14 | Scrubber Water Exit Temperature | 1 | 0 - 200°F |
| | TC-15 | Caustic Solution Inlet Temperature | 1 | 0 - 100°F |
| Sampling Systems | $P_{T_6}$ | Beckman Probe Cooling Air | 2 | 0 - 100 psig |
| | $P_{T_7}$ | AF Prope Purge Air | 2 | 0 - 100 psig |
| | TC-12 | Beckman Sample Gas Temperature | 2 | 0 - 300°F |

NOTES:
1. Continuously measured and recorded parameter.
2. Continuously measured but manually read/recorded every 30 minutes or whenever deemed necessary by operational changes.
3. Manually measured/checked and recorded whenever deemed necessary.

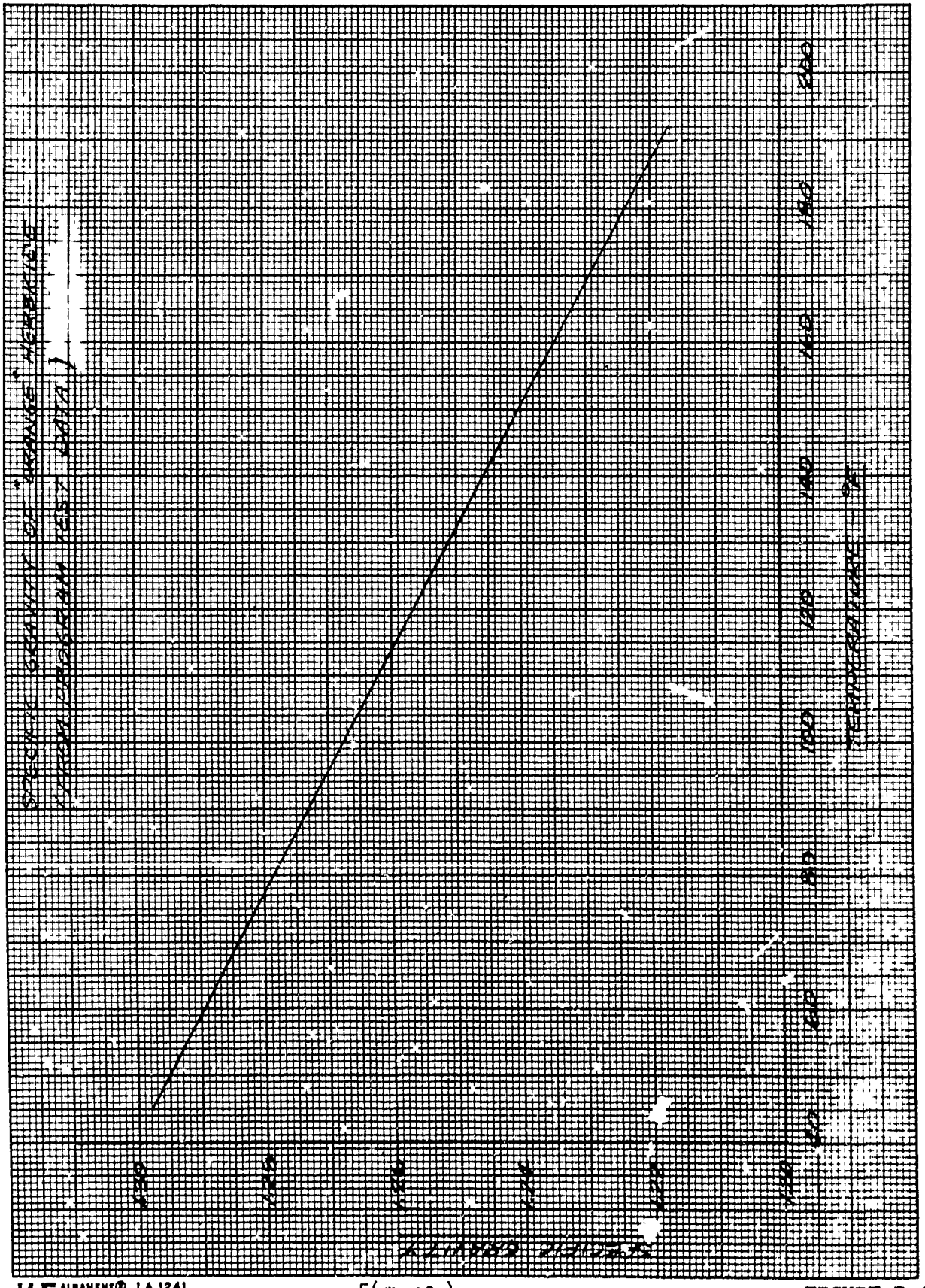
PREPARED BY J.H

CHECKED BY

THE Marquardt CORPORATION

PAGE

DATE 12-14-73




K+E ALBANENE® LA 1241 TRACING PAPER



FIGURE B-6

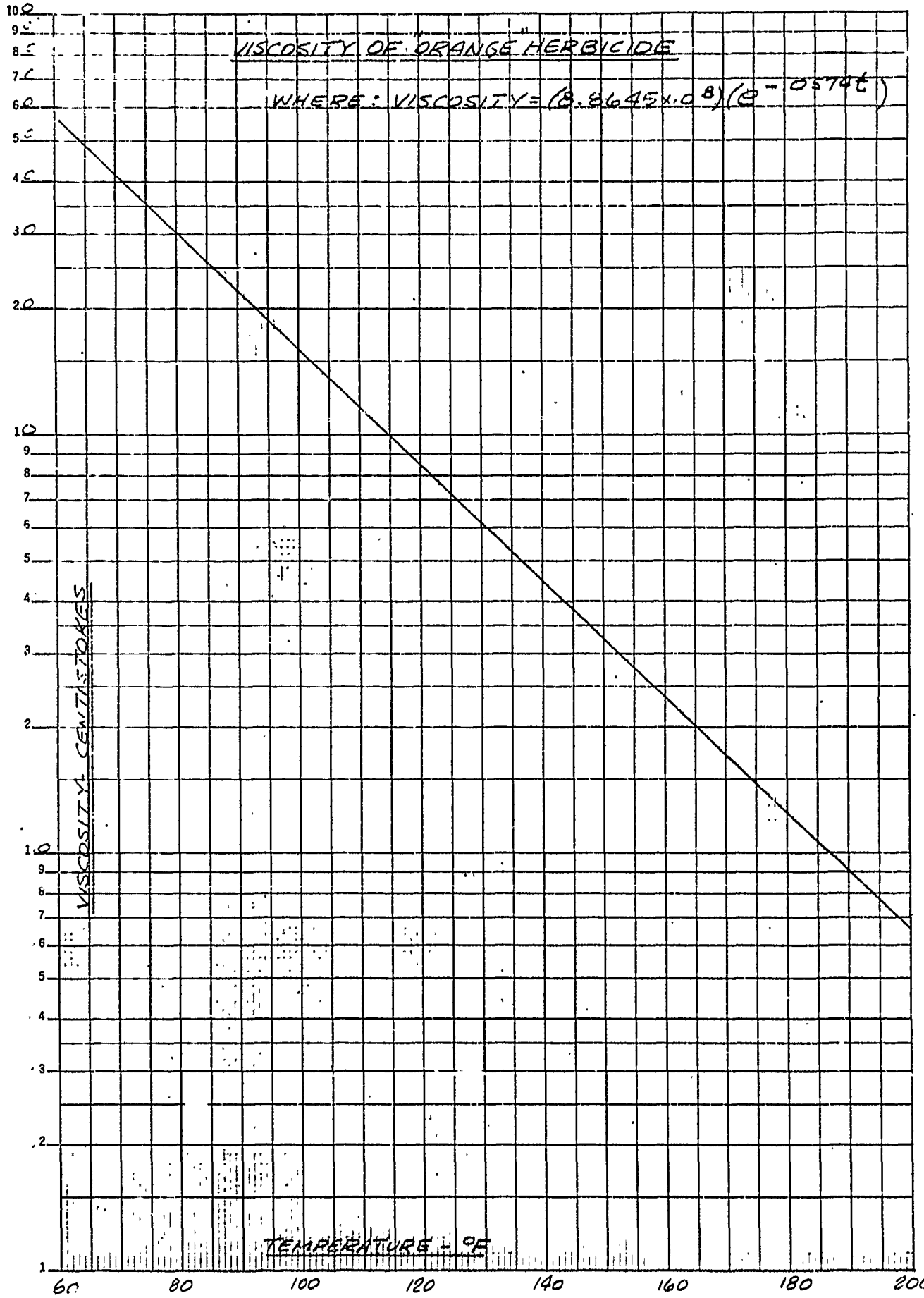

VISCOSITY OF "ORANGE" HERBICIDE
WHERE: VISCOSITY = (8.8645x10^8)(e^-0.074t)
VISCOSITY - CENTISTOKES
TEMPERATURE - °F
10
9
8
7
6
5
4
3
2
1
60
80
100
120
140
160
180
200
K&E SEMI-LOGARITHMIC 359-73
KEUFFEL & ESSER CO. MADE IN U.S.A.
3 CYCLES X 140 DIVISIONS



FIGURE B-7

USAF ENVIRONMENTAL HEALTH LABORATORY

Kelly AFB, TX 78241

# APPENDIX C

(TO APPENDIX E)

## SAMPLE CODE DESIGNATIONS

A set of sampling codes was developed and is presented in Table C-1. Each sample collected by either EHL was assigned a code for laboratory control and reporting analytical results. Samples are referenced to these codes throughout this report.

TABLE C-1: SAMPLING CODES FOR SAMPLES COLLECTED BY EHL'S

| Type/Source of Sample | Code Letters | Interpretation |
|---|---|---|
| | I - (Roman numeral) | Test Burn numbers, I through VIII |
| Blended Herbicide Feed | -BH- | Blended herbicide feed sample. |
| | -number/number/etc. | EHL(K) red drum-head-number for drums placed into feed tank for the test burn. |
| | (Date of Collection) | |
| Scrubber Water | -FSW- | Fresh scrubber water feed sample. |
| | -A. | FSW sample sent to WCTS for analyses. |
| | -B. | FSW sample for EHL(K) analyses. |
| | -SSW- | Spent scrubber water into holding tank(s). |
| | -A- | 20-minute grabs for compositing (1500 ml). |
| | -B- | 20-minute grabs for reserve samples (1500 ml). |
| | -C- | Composite hourly sample (~4500 ml). |
| | -D- | Hourly grabs for EHL(K) analyses (1500 ml). |
| | -TBC- | Total burn period composite (4500 to 6000 ml for WCTS and EHL(K) analyses). |
| | -ARL. | Total burn period composite, ~1200 ml, for ARL analyses. |
| | (Table C-1 cont'd next 2 pages) | |

TABLE C-1: (cont'd)

| Type/Source of Sample | Code Letters | Interpretation |
|---|---|---|
| Scrubber water (cont'd) | -number. | Sequential number from 1 to 3 for each type of grab or hourly composite sample. |
| | -HT- | SSW collected from holding tank. |
| | -1. | HT sample collected from port on side of HT after tank contents had settled for >24 hours. |
| | -2. | HT sample of settled solids collected from bottom of HT after tank contents had settled for >24 hours. |
| | (Time and Date of Collection) | |
| Gases | -CG- | Combustion gases collected via sampling train at end of reaction tailpipe. |
| | -SG- | Scrubbed effluent gases collected via grabs or sampling train in discharge stack. |
| | -number. | Impinger number (1 through 4) in sampling train from which sample was taken. |
| | -ACP. | Sample rinsing of air cooled probe. |
| | -WCP. | Sample rinsing of water cooled probe. |
| | -P- | Particulate sample collected isokinetically from SG. |
| | -CT. | Cold trap sample. |
| | -number(s). | Impinger number (1, 2 and/or 3) in particulate sampling train from which impinger contents were mixed for sample. |
| | -ARL. | Samples collected for ARL analyses. |
| | (Time Period and Date of Collection) | |

TABLE C-1: (cont'd)

| Type/Source of Sample | Code Letters | Interpretation |
|---|---|---|
| Residue from within incinerator | -R- | Chucks/particles of residue collected from within the incinerator. |
| | -A- | Residue sample sent to WCTS for analyses. |
| | -B- | Residue samples kept by EHL(K) for any future analyses. |
| | -CC- | Location of sample from within the incinerator-combustion chamber. |
| | -1. | Orange flakes of residue. |
| | -2. | Carbon/black flakes of residue. |
| | (Date of Collection) | |
| Holding Pond | HP- | Holding Pond |
| | -number. | Sequential number from 1 to 4 for each composited sample collected from holding pond. |
| | (Time and Date of Collection) | |
| Drum Rinsing Samples | Letter- | Alphabetical letter (A,B,C or D) to indicate the set of drums receiving a particular rinse procedure. |
| | -number- | (EHL(K)'s red number on head of drum. |
| | -number- | Sequential number from 1 to 3 to indicate the rinse number for that drum. |
| | -number. | Rinse volume in gallons. |

USAF ENVIRONMENTAL HEALTH LABORATORY

McClellan AFB, CA 95652

# APPENDIX D

(TO APPENDIX E)

## COMBUSTION AND SCRUBBED EFFLUENT GAS MONITORING

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# APPENDIX D

## COMBUSTION AND SCRUBBED EFFLUENT GAS MONITORING

### 1. Introduction

Monitoring the combustion and scrubbed effluent gases from the incineration of "Orange" Herbicide presented several unusual sampling situations. The combined sampling and analytical techniques had to be sensitive at the parts per billion level for several compounds. The sampling environment was hostile regarding temperature, moisture and potential interfering compounds. Finally the contaminants to be monitored in the scrubbed effluent gas could exist as a vapor, an aerosol or both.

A literature review did not reveal a proven source sampling technique for this work. Consequently, it was necessary to develop one. A technique used in "Orange" Herbicide pyrolysis studies at the Environmental Health Laboratory, Kelly AFB, provided a basis for this development.(D-1)

Several sampling techniques were tested. The one finally chosen was absorption in benzene using a modified EPA source sampling train. The following sections describe the sampling requirements, the sampling technique and methodology, the laboratory validation of the sampling technique, and the results of field sampling and inorganic analysis of gases. (See Appendix I for hydrocarbon results.)

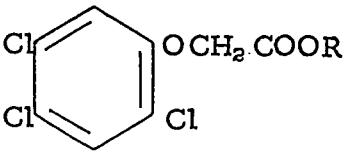
### 2. Sampling Requirements

#### a. Potential Contaminants.

TCDD was considered the potential contaminant of primary importance. It is a trace contaminant in many lots of "Orange" Herbicide, requires greater heat energy for pyrolysis than the basic compounds of "Orange" Herbicide, and is a hypothetical partial degradation product from the incomplete pyrolysis of nb 2,4,5-T and 2,4-D ester. (See Figure D-1.)

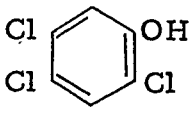
The nb esters of 2,4-D and 2,4,5-T, the principal compound in "Orange" Herbicide, were potential contaminants and had to be monitored.

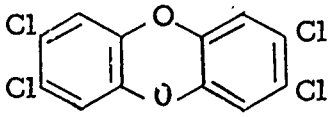
The acids of 2,4-D and 2,4,5-T could be formed from the butyl esters through two mechanisms: cleavage of the ester to the acid and butanol in the presence of heat and moisture; and hydrolysis of the ester in the caustic scrubber. Due to the possible formation of these acids they had to be monitored.

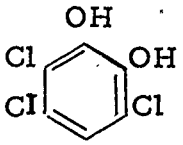


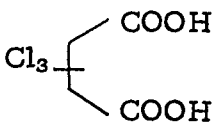
2, 4, 5-T

Oxygen Sufficient









$HOCH_2COOH$

$HOOCCOOH$

HCl

$CO_2$

$H_2O$

$Cl_2$

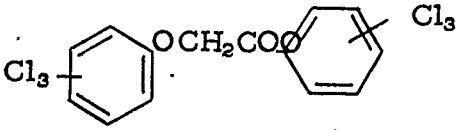
$O_2$

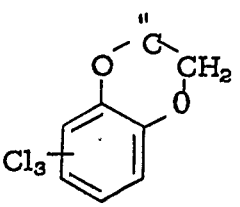
Oxygen Deficient

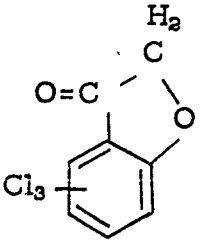
$CH_3COOH$

$Cl_2CH_2COOH$

$CH_2=CH-R$







HCl

CO

FIGURE D-1: HYPOTHETICAL PARTIAL DEGRADATION PRODUCTS OF 2,4,5-T N-BUTYL ESTER(D-2)

Consideration was given to hypothetical partial pyrolysis products. Figure D-1 is a list of hypothetical products from the incomplete pyrolysis of 2,4,5-T ester.(D-2) It would be impossible to design a practical system for each specific hypothetical pyrolysis product. As the final sampling system was developed, it was found that a majority of the hypothetical products would be trapped in the system by condensation or by absorption in the solvent. While the products might not be collected at a 100% efficiency level, they would be detected. If the products were considered significant, later laboratory studies could simulate the field conditions that existed during sampling and the efficiency of collection could be estimated.

Total particulate loading was considered important for two reasons. An environmental statement would require this information and the particulate matter could be qualitatively and quantitively analyzed for additional information.

Finally, to evaluate the overall performance of the incinerator, it was necessary to measure the emissions of the common combustion products, CO, $CO_2$, $NO_x$, $O_2$, $H_2O$ and total hydrocarbons.

b. Sampling Locations.

To evaluate the capability of the incinerator to incinerate "Orange" Herbicide, it was necessary to sample at two locations: in the reaction tailpipe just prior to the caustic scrubber and in the scrubbed effluent gas stack. These locations presented different sampling conditions and necessitated the use of slightly different sampling techniques.

(1) Reaction Tailpipe: In the reaction tailpipe, combustion gas temperatures averaged 1900°F. TCDD and the butyl esters and acids of 2,4-D and 2,4,5-T existed only in the vapor phase. Isokinetic sampling was not necessary to obtain a representative sample.

Samples of combustion gases had to be cooled quickly to depress chemical reactions as the gas traversed the sampling probe to the absorbent. However, the gas sample temperature had to be maintained slightly above the boiling point of TCDD and the butyl esters and acids (>350°F) to prevent condensation of these compounds in the sampling train upstream of the impingers.

Finally, measurements of combustion gas velocity were not attempted in this area because of the high temperature and unavailability of specialized equipment. The gas velocity was obtained from Marquardt theoretical data and the temperature was measured by a thermocouple installed by Marquardt. The sampling train did not need a temperature sensor or a pitot tube.

(2) Scrubbed Effluent Gas: The scrubbed effluent gas temperatures were expected to average 170°F. Any TCDD or butyl esters and acids would tnerefore have existed in the vapor and aerosol phases simultaneously. Isokinetic sampling was required to obtain a representative sample.

The scrubbed effluent gas, after passing the caustic scrubber, would be saturated with water vapor and contain water droplets. To prevent moisture saturation of the particulate filter it was necessary to heat the sample gas above 212°F in the probe to vaporize the water droplets.

3. Sampling Techniques.

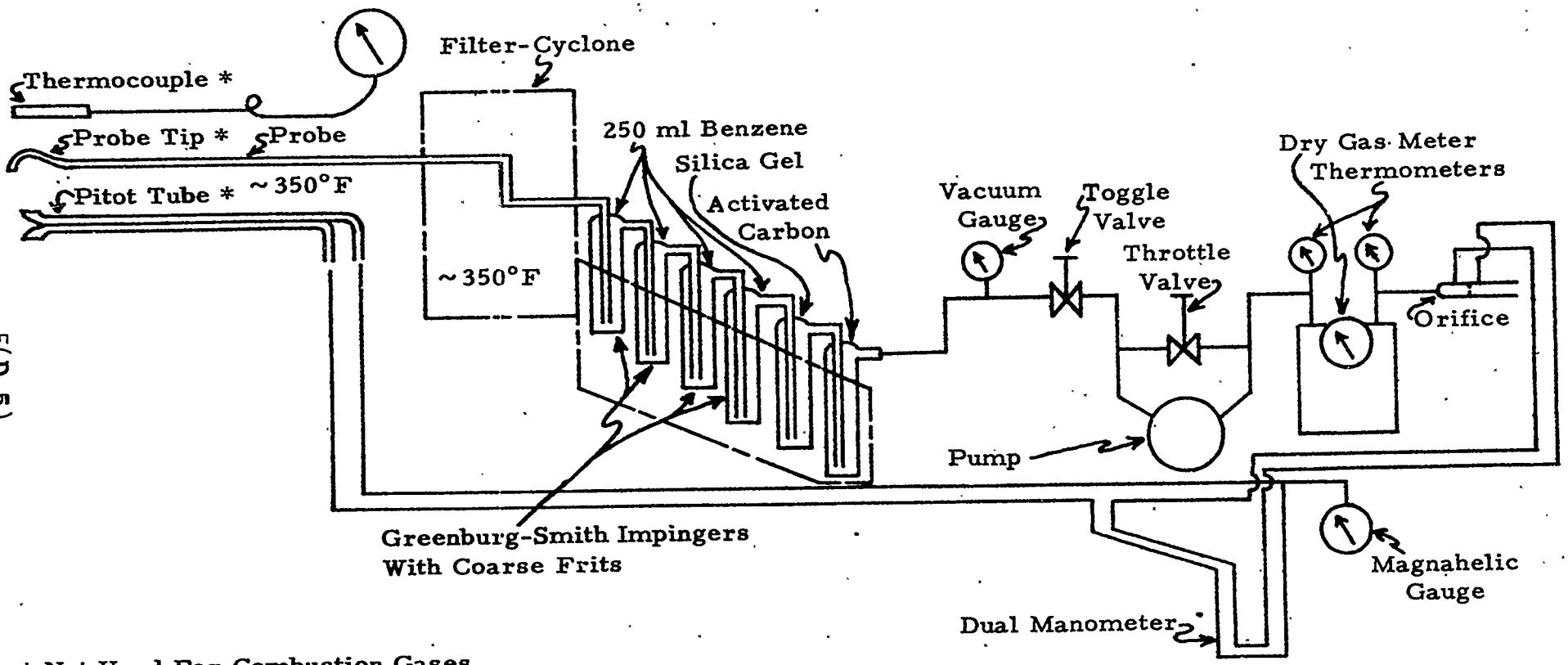
To accomplish the sampling requirements of Section 2, it was necessary to operate three sampling systems simultaneously. One system was used at the reaction tailpipe section to monitor the potential vapors of TCDD and butyl esters and acids of 2,4-D and 2,4,5-T. The other two systems were used on the scrubbed effluent gas stack, one to monitor the potential vapors and aerosols of TCDD and the butyl esters and acids and the other to monitor particulate matter, hydrochloric acid, free chlorine, and total moisture in the stack.

a. TCDD, Ester and Acid Sampling Trains.

The trains used to sample for TCDD and the butyl esters and acids are shown in Figure D-2. The first four Greenburg-Smith impingers were modified with coarse frits and each contained 250ml pesticide quality benzene. Two modified Greenburg-Smith impingers, one containing silica gel and one containing activated carbon, were placed downstream of the four benzene impingers. The main difference between the two sampling trains was the type of probe used. At the reaction tailpipe section, the train box was connected to a stainless steel sampling probe (air cooled in burns I-V and water cooled in burns VI-VIII) via a ground glass joint. The sampling probe was cooled to prevent damage to it in the high temperature of the reaction tailpipe (1900°F). This cooling of the probe also provided the required cooling of the combustion gases (to 300-400°F) in order to suppress any continued combustion reaction within the sampling probe. The sampling train on the scrubbed effluent gas stack was attached to a heated 3-foot glass probe wrapped in asbestos and foil. Since it was necessary to sample isokinetically in the event of aerosol formation, the glass probe had a glass sampling tip of 0.25 inch inside diameter.

b. Particulate Sampling.

The train used for particulate matter, hydrochloric acid, free chlorine, and moisture is shown in Figure D-3. The water



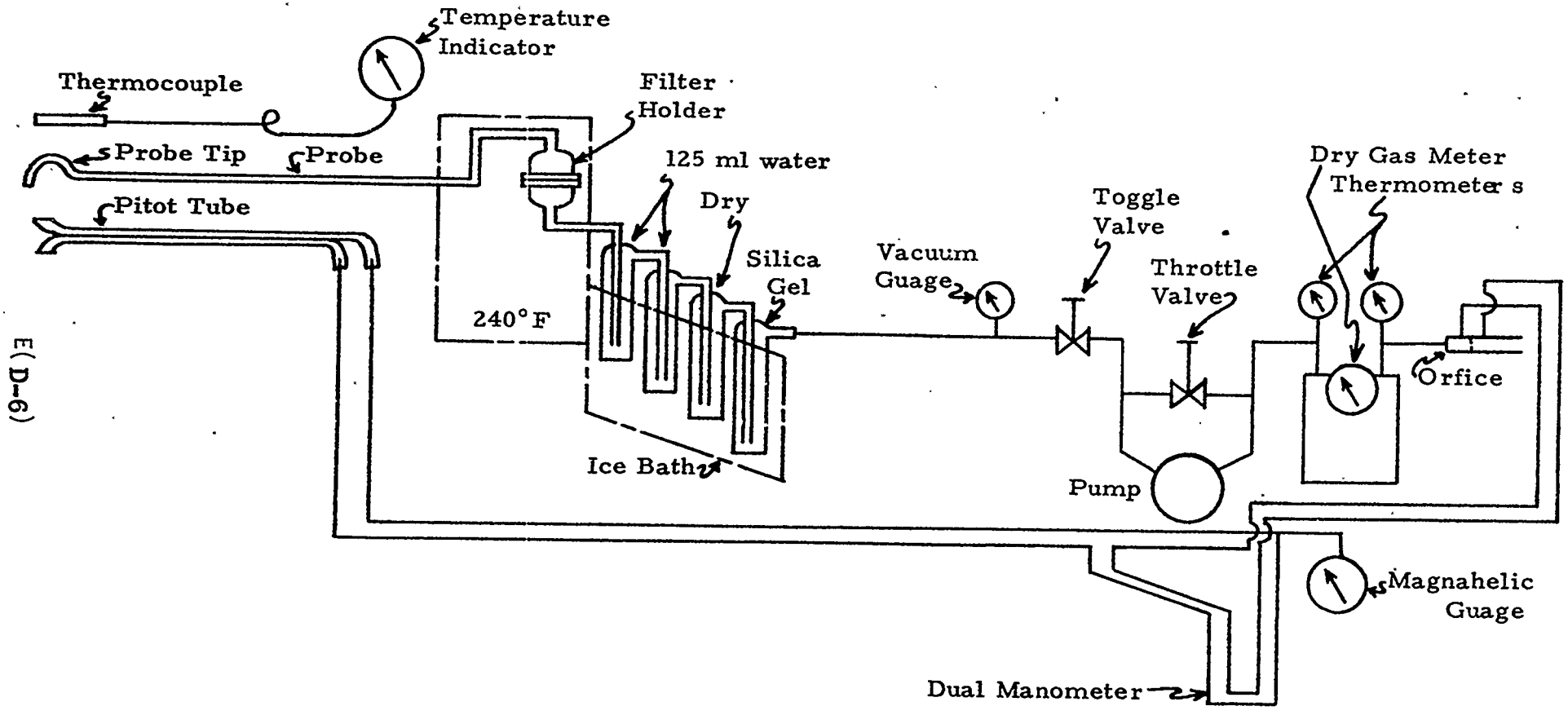

* Not Used For Combustion Gases in Reaction Tailpipe

E(D-5)

**FIGURE D-2: SCHEMATIC OF SAMPLING EQUIPMENT FOR TCDD, BUTYL ESTERS AND ACIDS OF 2,4-D AND 2,4,5-T**

"ORANGE" HERBICIDE PROGRAM
NOV 73

Drawn By:
Sgt. Frank Lessing
USAF EHL(M)




E(D-6)

**FIGURE D-3: SCHEMATIC OF EQUIPMENT FOR PARTICULATE SOURCE SAMPLING "ORANGE" HERBICIDE PROGRAM NOV 73**

Drawn By:
Sgt. Frank Lessing
USAF EHL(M)

collected in the first two impingers was used to determine hydrochloric acid and free chlorine concentrations in the stack gas.

c. Other Contaminants.

EPA procedures given in 40 CFR 60 were used to sample and analyze the stack gas for CO, $CO_2$, $O_2$, and $NO_x$. Hydrocarbons were continuously monitored by The Marquardt Company using a Beckman 109 Hydrocarbon Analyzer. (See paragraph 4.1.)

4. Validation of Sampling Technique.

Prior to use in the field, the technique of absorption of the butyl esters and acids (of 2,4-D and 2,4,5-T) in benzene was tested in the laboratory. Other sorbents were also evaluated in an effort to avoid using the very toxic and flammable benzene. See Table D-1. These included adsorption on Chromosorb 102, absorption in acetone, and collection in a cold trap.

A brief explanation of events is given below to explain the order of testing and validating the candidate sampling techniques. The original scope of the combustion gas monitoring project was the detection and quantitization of TCDD and the butyl esters (2,4-D and 2,4,5-T) that might escape pyrolysis in the incineration process. The first nine experiments concentrated on the butyl esters and three candidate techniques were evaluated for collecting these esters. Then, it was speculated that acids might be formed by either hydrolysis of the butyl esters in the caustic scrubber or by cleavage of the butyl esters in the presence of heat and moisture in the combustion chamber and reaction tailpipe. The scope was expanded to include the detection and quantitization of the acids (2,4-D and 2,4,5-T). Since absorption in benzene and adsorption on Chromosorb appeared equally effective for the butyl esters, both sorbents were tested for collection of the acids.

a. Testing Procedure.

The validation procedure was based upon mass balance. A known mass of the butyl esters and/or acids was vaporized and drawn through the sampling system. The collection efficiency was determined by comparing the total mass collected in the collection media with the mass vaporized.

The sampling train was operated in the laboratory exactly as it was planned to be used in the field. This procedure insured that the collection efficiency in the field would not be changed due to different operating conditions.

b. Sample Gas Generation.

Two small glass containers were used to hold incividual samples of the butyl esters and acids. The containers were

TABLE D-1

DESCRIPTION OF SAMPLING TECHNIQUES TESTED IN THE LABORATORY

| Experiment # | Description |
|---|---|
| 1. | Series of 4 fritted Greenburg-Smith impingers, each charged with 250ml pesticide quality benzene. Butyl esters collected. |
| 2. | Repeat of Experiment 1. |
| 3. | Series of 4 Greenburg-Smith impingers, 1 and 2 were standard, 3 and 4 were modified,* each charged with 250ml benzene. Butyl esters collected. |
| 4. | Series of 4 Greenburg-Smith impingers, 1 was standard,** 2, 3 and 4 were fritted. 1 was charged with 250ml of 10% NaOH solution, 2, 3 and 4 with 250ml benzene. Butyl esters collected. |
| 5. | Same as 4 except all impingers were fritted and 1 was charged with 250ml of a 2.5% CaOH solution. Butyl esters collected. |
| 6. | Repeat of Experiment 1. |
| 7. | A fiberglass filter, 6" in diameter, followed by the series of impingers described in 1. The filter had 31 gms of 40/80 mesh activated carbon spread evenly on it. Butyl esters collected. |
| 8. | Repeat of Experiment 1. |
| 9. | Chromosorb 102, 12 gms packed in the filter section glassware, followed by the impinger series described in 1. Butyl esters collected. |
| 10. | Same as 1. Acids of 2,4-D and 2,4,5-T collected. |
| 11. | Same as 1. Butyl esters and acids collected. |
| 12-16. | Same as 9 except butyl esters and acids collected. |
| 17. | Cold trap, acetone in an alcohol-dry ice bath followed by the series of impingers described in 1. |
| 18. | Same as 9 except only 2,4-D acid collected. |

TABLE D-1 (Continued)

| Experiment # | Description |
|---|---|
| 19. | Series of 4 impingers, 1 was standard charged with 250ml acetone, 2, 3 and 4 were fritted and charged with 250ml benzene. Acids and esters collected. |
| 20. | Same as 19 except impinger 1 was charged with benzene. |
| 21. | Repeat of Experiment 18. |
| 22. | Same as 1 except frits on the impingers were changed from fine to coarse frits. Butyl esters and acids collected. |
| 23. | Repeat of Experiment 22. |

*The modified impingers had a glass insert that was not tapered at the end.

**The standard impinger had a glass insert that was tapered at the end and had an impaction plate attached.

attached to the end of the sampling probe by means of a glass tee and ground glass joints. The containers were designed to have identical flow resistance and to require a small vacuum to obtain a flow rate of 1 liter per minute through each. The vacuum prevented the loss of sample vapor through the container air inlet. The rate of sample vaporization was controlled by placing the containers in a portable gas chromatograph oven. The probe from the sampling train was inserted through an asbestos grommet into the oven and the sample containers were connected to it. The butyl esters were vaporized between 80 and 100°C and the acids at 160 to 180°C.

In initial experiments, excess ester was placed in the glass container. The time required to vaporize a given mass was determined and a contaminant concentration calculated from the mass and air flow rates. The results indicated that collection efficiency was independent of contaminant concentration.

c. Sampling System Operation.

Prior to each test, the sample was placed in the glass container and the entire unit was dessicated for two hours. The entire unit was then weighed to the nearest tenth of a milligram.

The probe on the sampling train was maintained at approximately 180 to 190°C. This temperature prevented condensation of the butyl esters or acids on the glassware. When the oven and sampling train components were at the correct temperature, the sampling train was turned on. The sample flow rate was maintained at 2 to 6 liters/minute (STP), and the samples were vaporized to provide contaminant concentrations of 0.1 to 50 ppm in the air being drawn into the sampling probe. At the end of the sampling period, the remaining fraction of the sample was weighed to the nearest tenth of a milligram after dessication for two hours. The net difference in sample weight was used to determine the mass of sample vaporized.

d. Analytical Procedures.

Electron capture gas chromatography was used for quantitative analysis. Two different units were used at different times. One was equipped with a $Ni^{63}$ detector and an 8-foot column packed with 3% OV17. The other unit was equipped with a $T^3$ detector and a 6-foot column packed with 3% SE 30. Both columns were 1/4 inch outside diameter. The column and detector temperatures of the units were maintained isothermally at about 165° and 195°C, respectively.

Peak height comparison was used for quantitative analysis. Area measurement is usually preferred; however, peak height

comparison can be more accurate when the peaks are sharp and narrow.(D-3) The samples in this work were essentially as pure as standards and the resulting peaks were sharp and narrow and not degraded by interfering peaks (see Figure D-5). To obtain maximum accuracy each sample peak height was compared with a standard peak that was within 90 to 110% of the sample peak height. Each sample and standard was injected twice and if the injections differed by greater than 5% of their average, new injections were made until each peak height in a series of three was within 5% of the average. Linearity in the working range was verified before and after each series of samples was analyzed.

e. Analytical Accuracy.

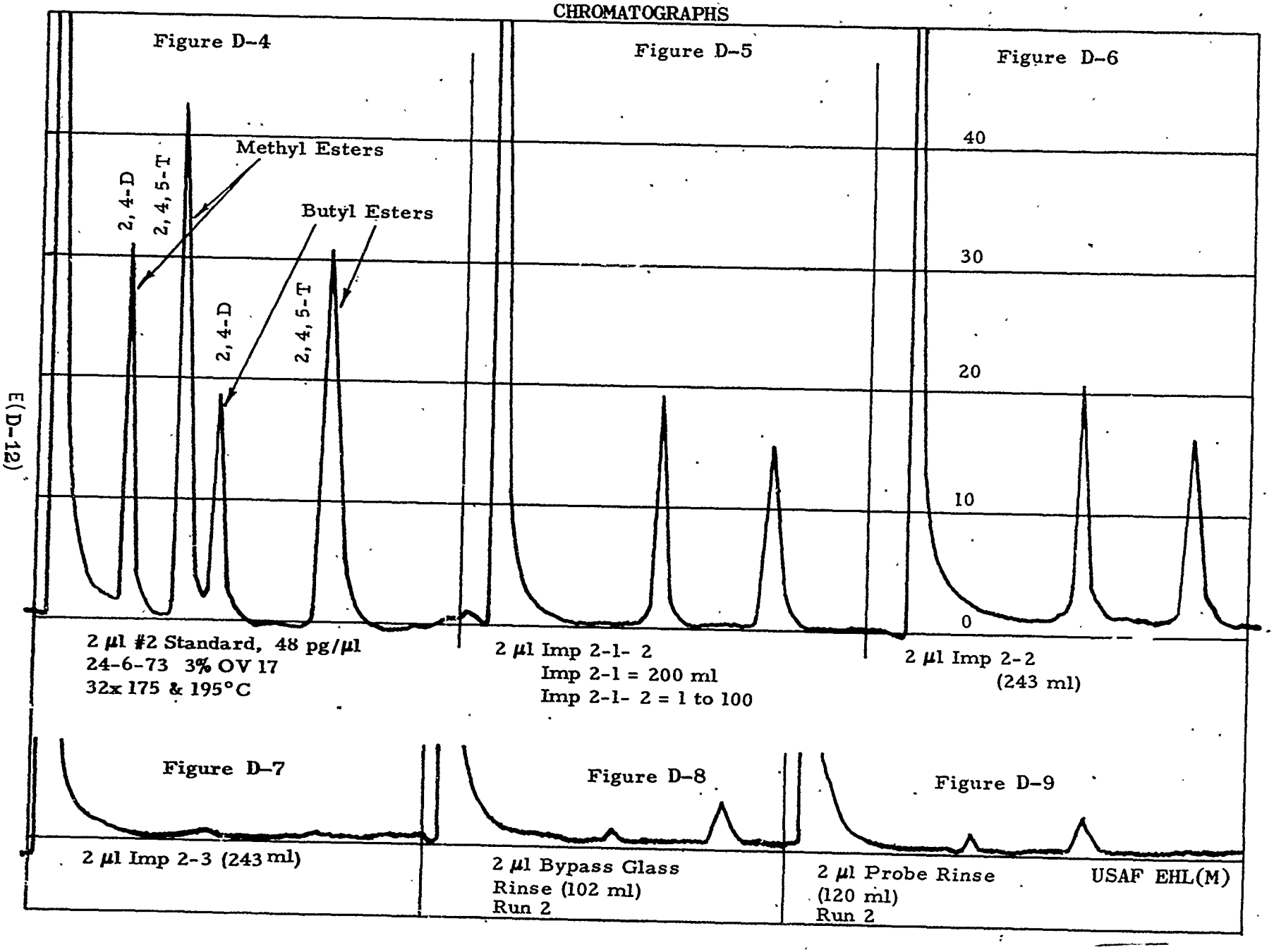
Weighing of samples before and after vaporization, weighing and dilution of standards, dilution of samples for analysis, and peak height variation were all sources of analytical error. However, peak height variation was considered the major source of error.

Figures D-4 through D-6 were used to illustrate this potential error. These figures depict the chromatographs of impingers 1, 2 and 3 from experiment 2. Assume the standard 2,4-D N-butyl ester peak height of 18 divisions in Figure D-4 represented 96 picograms/2 µl, i.e., the true value. The impinger 2-1-2 sample peak height of 19 divisions in Figure D-5 represented (19/18) times 96/2 or 51 picograms/µl. Let the standard peak height be 5% greater than true and the sample peak height be 5% less than before. Then the impinger 2-1-2 sample peak height of 18 divisions represented (18/19) times 96/2 or 45 picograms/µl. The 45 picograms was 11% less than the true value. This potential error applied to the total mass in the sample. The total mass in impinger 2-1-2 was in the milligram range while the mass in impinger 2-2 was in the microgram range. Since the overall efficiency was calculated from milligrams to the nearest tenth, the error in impinger 2-1-2 was significant while the error in impinger 2-2 did not affect the calculation of overall efficiency.

The total mass vaporized during a given test was measured to the nearest tenth of a milligram. This mass always exceeded 4 milligrams; therefore, the maximum error in determining the total mass evaporated was 2.5%.

The mass used in standards was weighed to the nearest microgram on a Cahn balance. Class A volumetrics were used for dilution and dilutions were conducted with hexane and volumetrics at $20^{o} \pm 1$. The error in this procedure was considered less than 1%. Samples were diluted in Class A volumetrics at $21^{o}C \pm 1$. After dilution the samples were placed next to the standards and given time to equalize in temperature with the standards.

# CHROMATOGRAPHS



In view of this brief error analysis, the mass determinations were not considered more accurate than ± 15%. Mass recovery was considered complete if it fell between 85 and 115% of the mass vaporized, and the unconcentrated absorbent volume in the last impinger in the series showed no more than a trace amount of contaminant.

f. Sample Analysis.

A series of four impingers charged with benzene was used in all experiments either as the primary absorption system or as a backup system when Chromosorb 102 or activated carbon was used as the primary collection medium. To determine the quantity of esters collected in each individual impinger, the benzene volume was carefully measured and each impinger rinsed a minimum of 5 times with pesticide grade acetone. For most experiments the rinsings were added to the benzene remaining in the impinger. This sample was diluted, if necessary, and a two microliter portion injected into the chromatograph and analyzed.

For several runs, the acetone rinse was analyzed separately from the benzene in the impinger. This was done to obtain some insight into the collection mechanism. It was believed that the compounds principally absorbed in the benzene, but condensation on the frit was also an important mechanism.

The benzene and acetone rinse from the third and fourth impingers often contained masses of each ester below the detection limit of the chromatograph. These solutions were never concentrated. The volume of benzene and acetone rinse from these impingers averaged 300 milliliters. Based on the detection limit of the gas chromatograph (~5 picograms/µl), the mass contained in these impingers could not have exceeded microgram quantity unless dilution was required. Since dilution was never required, the mass contained in these impingers never exceeded 0.1% of the total vaporized.

The standard $BF_3$ methylation procedure was used to determine concentrations of the acids in the benzene. The benzene and acetone rinses from each impinger were concentrated by rotary vaporization and transferred to a 15 milliliter conical centrifuge tube. The evaporation flask was rinsed with acetone and the rinse added to the tube. The tube content was dried with anhydrous $Na_2SO_4$, and then concentrated to 0.5 milliliters in a hot water bath. After the concentrate cooled, 0.5 milliliters of 14% $BF_3$ in methanol was added and the mixture heated at 50°C for 30 minutes in a water or sand bath. After the mixture cooled, 0.5 milliliter benzene and 4.5 milliliter of 5% aqueous $Na_2SO_4$ solution was added. After phase separation, the organic layer

was removed and the surface washed with 1 milliliter benzene. The organic layers were passed through a micro cleanup column of florisil. Benzene was added to the column effluent to bring the processed sample volume to 5 milliliters. This prepared sample volume was then analyzed with an electron capture gas chromatograph.

When Chromosorb 102 or activated carbon was used as the primary collection medium, the contaminants were extracted from the medium with acetone in a Soxhlet extractor at 30 cycles per hour. Again, samples were taken directly from the volume of acetone in the extractor, usually 200 milliliters, and analyzed for butyl esters. The solution was then concentrated, and, if acids had been collected, put through the methylation procedure. In two experiments where esters and acids were collected simultaneously, the samples were evaluated for butyl esters before and after the methylation procedure. This was done to determine the possibility of transesterification of the butyl esters to methyl esters in the methylation procedure. Significant (<3%) transesterification was not detected in this work or in similar studies at the Air Force Academy.(D-4)

g. Findings and Discussion.

Absorption of the butyl esters (2,4-D and 2,4,5-T) in benzene was evaluated in experiments 1, 2, 6, 8, 20, 22 and 23 (see Table D-2). The collection of the esters was complete in all experiments except 20 where the first impinger in the fritted series had been replaced with a standard impinger. The collection efficiency in this first impinger dropped from an average 93% with the fritted inpinger to 14% with the standard impinger. Also, the last impinger in experiment 20 had a 10% recovery while the last impinger in the other experiments never had more than a trace. Coarse frits were used in experiments 22 and 23 while fine frits were used in experiments 1, 2, 6 and 8. No trace of esters was found in the last impinger of experiments 1, 2, 6 and 8 while a trace was found in the last impinger of experiments 22 and 23. These results indicated a slight but insignificant loss of recovery efficiency with the coarse frits. Consequently, the field sampling unit was designed to use coarse frits because they operated under much less vacuum requirements than the fine frits (3"Hg vs 9"Hg) and significantly decreased the possibility of leaks in the system.

Absorption of the acids in benzene was evaluated in experiments 10, 11, 20, 22 and 23. Results of 10 and 11 were discarded due to errors in analytical procedures. The less than complete recovery in 20 was due to the replacement of the #1 fritted impinger with a standard impinger. In 22 and 23 all impingers were fritted and recovery was complete.

TABLE D-2

LABORATORY TESTING RESULTS

"ORANGE" HERBICIDE PROGRAM

NOV 1973

| Exp # | Overall Efficiency % | | Efficiency, Specific Components, % | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Impinger # | | | | | | | | Other * | | Glassware Washings | | | |
| | | | 1 | | 2 | | 3 | | 4 | | | | Probe | | Bypass | |
| | Esters | Acids | Esters | Acids | Esters | Acids | Esters | Acids | Esters | Acids | Esters | Acids | Esters | Acids | Esters | Acids |
| 1 | 96 | | 76 | | T | | ND | | ND | | | | ND | | 20 | |
| 2 | 105 | | 104 | | <1 | | ND | | ND | | | | T | | T | |
| 3 | 89 | | 48 | | 36 | | 5 | | T | | | | T | | ND | |
| 4 | 99 | | 46 | <1 | 52 | ND | T | ND | ND | ND | | | <2 | | | |
| 5 | 98 | | 97 | <1 | T | ND | ND | | ND | | | | | | | |
| 6 | 106 | | 90 | | 3 | | <1 | | ND | | | | | | 12 | |
| 7 | 103 | | 1 | | 1 | | T | ND | | | 99 | | <2 | | <1 | |
| 8 | 115 | | 113 | | 2 | | T | | ND | | | | ND | | <1 | |
| 9 | 98 | | ND | | ND | | NE | | NE | | 98 | | ND | | ND | |
| 10+ | | 5 | | 4 | | >1 | | ND | | ND | | | | ND | | ND |
| 11+ | | ND | | ND | | ND | | ND | | ND | | | | ND | | ND |
| 12 | | ~1 | | ND | | ND | | ND | | ND | NE | ~1 | | ND | | ND |
| 13 | | ~1 | ND | ND | ND | ND | ND | ND | ND | ND | NE | ~1 | | | | |
| 14 | | ~1 | ND | ND | | | | | ND | ND | NE | ~1 | | | | |
| 15 | SAMPLE LOST DUE TO CONTAMINATION | | | | | | | | | | | | | | | |
| 16 | 87 | | ND | | ND | | ND | | ND | | 87 | | ND | | ND | |
| 17 | NE | NE | 12 | 12 | NE | NE | NE | NE | 6 | 4 | | | ND | ND | ND | ND |
| 18 | NE | 22 | NE | ND | NE | ND | NE | ND | NE | ND | NE | 22 | | ND | | ND |
| 19 | 62 | 97 | 13 | 39 | 21 | 37 | 13 | 13 | 15 | 8 | | | ND | ND | ND | ND |
| 20 | 80 | 89 | 14 | 32 | 38 | 32 | 18 | 15 | 10 | 10 | | | | | | |
| 21 | | 35 | | ND | | ND | | | | | | 35 | | <1 | | <1 |
| 22 | 90 | 90 | 86 | 83 | 4 | 7 | <1 | <1 | T | T | | | ND | ND | ND | ND |
| 23 | 89 | 91 | 87 | 75 | 2 | 13 | <1 | 3 | T | T | | | | | | |

T - Trace, None Quantitable Mass

ND - None Detected

NE - Not Evaluated

Efficiency = $\frac{\text{Mass Recovered}}{\text{Mass Vaporized}}$ X 100

Mass Measured to 0.1 Milligram

* Other Collection Medium

\+ Experiment results were discarded due to errors in analytical procedures.

USAF EHL(M)

In experiment 19, the first impinger was a modified one charged with acetone. Recovery of acids was 95% while ester recovery was only 62%. Experiment 20 was a duplicate of 19 except the first impinger was charged with benzene. Recovery of esters improved while recovery of acids appeared to decline with the change to benzene. In both experiments, less than 85% of the esters and acids was recovered in the last impinger and recovery was therefore not considered complete.

Adsorption of the butyl esters on 40/60 mesh activated carbon was evaluated in experiment 7. Carbon was spread evenly on a fiberglass filter and the assembly was maintained at 350°F in the filter section. The carbon effectively adsorbed the esters with less than 3% of the esters breaking through to the benzene impingers. The esters were not easily extracted from the carbon and twenty-four hours of Soxhlet extraction was necessary to achieve total ester recovery. This medium was not further evaluated for acid adsorption because of the later experience with adsorption on Chromosorb.

A cold trap of acetone in an alcohol-dry ice bath was evaluated in experiment 17. The acetone was contained in a modified impinger. The impinger insert was a ½ inch inside diameter glass tube that extended to within ½ inch of the impinger bottom. After a sample volume of only 85 liters had been collected, the impinger insert became totally blocked with ice. Also, the collection efficiency in the trap was only 12%. This sampling technique was discarded due to the icing problem which would be severe in scrubbed effluent gas sampling and the low collection efficiency in the trap.

Adsorption of butyl esters on Chromosorb 102 was evaluated in experiment 9 and for the esters and/or acids in experiments 12, 13, 14, 15, 16, 18, and 21. The Chromosorb was packed in the bypass glassware in the filter section and maintained at 370°F during sampling. Even at this elevated temperature, the Chromosorb effectively adsorbed the butyl esters in experiments 9 and 16. Due to the negative recovery of the acids in experiments 12, 13 and 14, recovery of the butyl esters was not evaluated. In experiments 9 and 16, problematic extraction of the esters from the Chromosorb required sixteen hours of Soxhlet extraction at 30 cycles per hour to effect >85% recovery.

Experiments 18 and 21 were conducted in an attempt to determine the reason for negative acid recovery in experiments 12, 13 and 14. Apparently chemical alteration of the acids was occurring on the Chromosorb due to the significantly elevated adsorption temperature. As a simple test, the Chromosorb was carefully weighed before and after adsorption of the acids. The weight gain indicated

complete mass recovery and no acids were detected in the backup benzene train; however, the Chromosorb was discolored at the upstream interface and only 22 and 35% of the acids were recovered in experiments 18 and 21, respectively. The temperature in experiment 21 was 320°F compared to 370°F in experiment 18. A relationship between temperature and recovery of the acids was indicated during these Chromosorb experiments.

In experiments 2, 6, 7 and 8 the acetone impinger rinse was evaluated separately from the benzene in the #1 impinger. The percent of esters collected in the acetone rinse relative to the total collected in the impinger benzene was 12, 6, 30 and 44% respectively. In experiments 2 and 6 the impinger insert remained in the benzene for several minutes before the benzene was removed. This allowed the esters condensed on the frit to become dissolved in the benzene. In experiments 7 and 8 the benzene was removed immediately after sampling ceased. These data indicated that condensation on the frit was an important collection mechanism. This procedure was not used in the acid experiments; however, condensation on the frit was indicated. The resistance in the sampling system increased or the sample flow rate decreased as sampling progressed. Also, the first acetone rinse percolated through the frit slowly. By the fifth rinse, the acetone passed through the frit freely. The only obvious cause of these anomalies was condensation of the acids on the frit. Since the acids had a much higher boiling temperature than the butyl esters, the condensation mechanism was important in acid collection and accounted for the excellent collection efficiency of acids in benzene even though the solubility of the acids was less than 1% in benzene.

A caustic scrubber was simulated in experiments 4 and 5 by replacing the benzene in the first impinger with caustic solution. A standard impinger and a 10% NaOH solution was used in experiment 4 and a fritted impinger and a 2.5% $Ca(OH)_2$ solution was used in experiment 5. The purpose of these two experiments was to evaluate the possible hydrolysis of the butyl esters in a caustic scrubber. In both experiments the hydrolysis, if it occurred, was less than 1%. The methyl esters that were detected could have been formed from transesterification of the butyl esters remaining in the solution after extraction. No conclusions could be drawn from these experiments.

Experiments 8 and 22 evaluated the presence of water vapor on sampling efficiency. Fifty milliliters of water were placed in the first impinger. The oven air used to generate samples was also saturated with water vapor by allowing a beaker of water to boil in the oven throughout the sampling period. The sampling efficiency was not degraded by this water.

In the pyrolysis of the butyl esters large amounts of HCl would be produced. To test the effect that HCl might have on the collection efficiency of the butyl esters, five milliliters of concentrated HCl were poured through the first impinger frit just before sampling in experiment 6. As the data indicated, no effect was noticed. There was no reason to suspect that HCl would have any effect upon absorption of the 2,4-D and 2,4,5-T acids.

h. Conclusions.

Complete absorption (>85%) of the butyl esters and acids of 2,4-D and 2,4,5-T in benzene, using a series of four fritted Greenburg-Smith impingers, was documented. Test data were conclusive for contaminant concentrations between 0.1 and 50 ppm (by volume) and flow rates between 2 and 6 liters per minute (STP). Collection efficiency was not a function of contaminate concentration or flow rate.

Substitution of a standard impinger for the first fritted impinger in the impinger series decreased absorption efficiency to <85%. Test data were not sufficient to document the precise decrease in efficiency.

TCDD, in view of its chemical similarities to the butyl esters, should be as effectively absorbed in the benzene-fritted impinger system as were the esters. Due to its extreme toxicity, impinger collection of TCDD was not tested in the laboratory.

Water in the impingers and/or the sample gas did not degrade sampling efficiency. Test data verified this at benzene to water ratios of greater than 5 by volume.

The presence of HCl in the benzene did not affect the absorption of butyl esters and there was no reason to suspect that HCl would affect the absorption of the acids. In a very strong acid solution the esters could be hydrolyzed to their respective acids. If only the acids of 2,4-D and 2,4,5-T are detected in the field sampling impingers where HCl will be high, the sampling condition will be duplicated and further evaluated in the laboratory.

5. Sampling Procedure.

Sampling was designed to monitor TCDD and the butyl esters and acids of 2,4,-D and 2,4,5-T simultaneously in the reaction tailpipe section upstream of the scrubber and in the scrubbed effluent gas stack downstream of the scrubber. This sampling scheme in combination with simultaneous scrubber water sampling provided data required to perform certain material balances of the incineration process.

a. Prior to Run:

Minimizing potential contaminants that would interfere with gas chromatographic analyses was essential. All glassware in the TCDD systems was soaked in hot, soapy water, rinsed 5 times with distilled water, and rinsed 5 times with pesticide quality acetone. The first four impingers were charged with 250ml pesticide quality benzene. The last two impingers were charged respectively with silica gel and activated charcoal and weighed. The entire train was then sealed with aluminum foil until sampling commenced. The particulate sampling train was prepared in accordance with procedures established in 40 CFR 60.

Prior to sampling, all three sampling trains were leak tested in accordance with procedures recommended in 40 CFR 60. To verify that no leak occurred in the TCDD sampling train on the stack, the water collected during sampling was compared with the quantity of water collected in the particulate train during the same burn. The water collected in the reaction tailpipe TCDD sampling train was compared to the theoretical amount predicted by the contractor's calculations.

b. During Run:

Sampling was begun after herbicide combustion parameters in the incinerator had stabilized and remained so for a period of time, usually 45 to 60 minutes into the burn.

All three sampling systems were activated as near the same time as possible. The two TCDD sampling systems were always activated within five minutes of each other to provide simultaneous samples pre- and post scrubber.

The sampling system used at the reaction tailpipe section was operated at a sampling rate of 8 to 20 liters per minute and was constant for each burn. Loss of benzene due to evaporation necessitated the low sampling rate and also controlled the duration of sampling. The total sample volume for each burn usually exceeded 500 liters at conditions in the reaction tailpipe section.

The particulate and TCDD sampling systems used on the scrubbed effluent gas stack were operated isokinetically. The system used to sample for TCDD and the butyl esters and acids (of 2,4-D and 2,4,5-T) was not traversed across the stack. Movement of this system would have broken the unprotected glass probe, so it was necessary to conduct single point sampling. This was acceptable because temperature and velocity traverses across the stack showed uniform velocity and temperature profiles. The glass probe tip was sized to keep the sample flow rate between 4 and 6 liters per minute to prevent benzene loss. Sample volume for each burn was between 200 and 400 liters at stack conditions.

The particulate sampling train was traversed across one diameter of the stack. Eight points were sampled with a sampling time of 10 minutes at each point. Because of the presence of the other sampling train in the stack, it was impossible to sample along the other diameter. The average sample volume was 500 liters at standard temperature and pressure, and dry. This train was operated in accordance with procedures recommended in 40 CFR 60 for isokinetic stack sampling.

c. After Run:

Upon completion of the sampling run, the trains used to sample for TCDD and the butyl esters and acids (of 2,4-D and 2,4,5-T) were cleaned according to the following procedures. The final volume of benzene and water in each impinger was measured. Each impinger was then rinsed five times with pesticide quality acetone followed by a deionized water rinse. The volume of this rinse was recorded and added to the benzene and water for that particular impinger. All glassware from the probe tip to the first impinger was rinsed with about 200ml of acetone and the rinsings added to the liquid from the first impinger. This volume was also recorded. All glass connectors between impingers were rinsed into the preceding impinger. Both impingers containing silica gel and activated carbon were weighed. This weight was used to determine the amount of benzene vapors that were adsorbed on the silica gel and carbon. If more benzene was lost from the impingers than was recovered, a sample volume adjustment was necessary. However, the data indicated that all benzene vapors were recovered in the adsorption media.

The particulate train samples were handled in accordance with recommended EPA procedures. Additionally, a small sample of water from the first two impingers in this train was analyzed for hydrochloric acid and free chlorine by the Environmental Health Laboratory, Kelly AFB, Texas. After the particulate sample filter was dessicated and weighed the particulate matter was qualitatively and quantitatively analyzed by WCTS.

6. Field Sampling Results and Discussion

a. Results.

(1) Particulates. These data are presented in Table D-3. The Federal particulate emission standard for incinerators used in Federal government activities is 0.2 grains per standard cubic foot of dry flue gas corrected to 12% carbon dioxide (40 CFR 76). The particulate emissions in the incinerator's scrubbed effluent gases during these tests averaged 0.076 gr/scf (standard deviation = 0.035), and were thus well below the Federal standard. Also, these particulates, by visual observation, appeared to be mostly sodium salts that had been entrained in the scrubbed effluent gas during the scrubbing process in the caustic scrubber (see second paragraph, page G-7, Appendix G).

TABLE D-3

SCRUBBED EFFLUENT GAS PARTICULATE SAMPLING DATA

"ORANGE" HERBICIDE INCINERATION TESTS

12 - 30 NOV 73

| | STACK | | | | | PARTICULATES | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Gr/SCF | | |
| Burn# | Temp °F | Dry Gas Fraction | Pressure Inches Hq | Flow Dry @ Stp $ft^3$/min | Sample Volume Dry @ Stp $Ft^3$ | lbs/hr | | @12%$CO_2$ | %Isokinetic* |
| I | 161 | 0.66 | 30.07 | 1551.2/1211.8 | 22.58 | 0.72 | 0.054 | + | 72.7/ 93.1 |
| II | 166 | 0.62 | 30.04 | 1465.0/1256.2 | 13.66 | 0.64 | 0.051 | + | 93.1/109.0 |
| III | 163 | 0.65 | 30.09 | 1415.4/1290.1 | 24.49 | 0.39 | 0.032 | + | 86.4/ 95.0 |
| IV | 163 | 0.65 | 29.96 | 1515.9/1417.9 | 26.05 | 0.71 | 0.055 | 0.055 | 85.8/ 91.7 |
| V | 156 | 0.71 | 30.28 | 1719.1/1269.1 | 27.26 | 1.39 | 0.095 | 0.095 | 79.2/107.0 |
| VI | 175 | 0.53 | 30.20 | 1222.5/1306.9 | 15.69 | 0.91 | 0.087 | 0.087 | 85.1/ 79.6 |
| VII | 170 | 0.59 | 30.12 | 1447.0/1252.5 | 20.85 | 1.05 | 0.085 | 0.082 | 71.9/ 83.1 |
| VIII | 151 | 0.74 | 30.09 | 1589.9/ 896.5 | 20.28 | 1.98 | 0.145 | + | 63.7/116.5 |

Stack Area: 1003.8 Square Inches.

Velocity is at stack conditions.

*1st number is based on actual velocity pressure measurements/2nd number is based on velocities calculated from theoretical data (see Appendix I for discussion).

+Not calculated due to erroneous $CO_2$ measurements during Burns I, II, III, and VIII.

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(2) Butyl Esters and Acids (of 2,4-D and 2,4,5-T) and TCDD. Sample volume data are presented in Table D-4. Neither TCDD, the butyl esters nor the acids (of 2,4-D and 2,4,5-T) were detected in any of the combustion or scrubbed effluent gas samples. Detection limits for these compounds during the different burns are presented in Tables G-2 and G-3 in Appendix G. Also see further discussion in Appendix I.

(3) Hydrocarbons. Results and discussion of these data are presented in Appendix I.

(4) CO, $CO_2$ and $O_2$. These data are presented in Tables D-5 and D-6. Concentrations of CO, $CO_2$ and $O_2$ in the scrubbed effluent gas for burns IV, V, VI and VII were indicative of efficient combustion. A sampling probe leak invalidated CO, $CO_2$ and $O_2$ results for burns I, II, III and VIII.

(5) $NO_x$. These data are presented in Table D-5. $NO_x$ emissions from incinerators are normally low due to the low combustion temperature (<2900°F). $NO_x$ emissions from the incinerator during "Orange" Herbicide incineration were low (<100 ppm) and in agreement with combustion temperatures and the excess air.

b. Discussion.

(1) Particulates. Isokinetic sampling was difficult due to the low velocity pressure (0.008 to 0.01 inch of water pressure) which could not be read more accurately than ± 10% in the scrubbed effluent gas stack. A greater than 100% carbon recovery (Table D-6) as calculated from measured gas velocity pressures and mole fractions of $CO_2$ and CO in the scrubbed effluent gas indicated that gas velocity pressures were read consistently high and that the scrubbed effluent gas velocities were greater than the actual velocities. To evaluate this possibility revised, scrubbed effluent gas velocities for each burn (see Table D-3) were calculated based on theoretical combustion data (Marquardt) and a chlorine mass balance. The ratio of measured/calculated scrubbed effluent gas velocities averaged 1.15 with a standard deviation of 0.14. Thus it was concluded that measured velocity pressures were read high. A thorough discussion of the revised, calculated scrubbed effluent gas velocities is given in Appendix I.

The EHL(M) thermocouple used to obtain the scrubbed effluent gas temperature was reading 20°F too high (discovered during recalibration after this program). The dry gas fraction used to establish isokinetic sampling parameters had to be calculated from the water vapor saturation value of the scrubbed effluent gas at the sampling temperature. With the incorrect temperature, the indicated dry gas fraction was smaller than the actual. Calculations based on these data indicated that scrubbed effluent gas sampling had been performed at less than isokinetic flow. Fortunately, with the aforementioned revised scrubbed effluent gas

TABLE D-4

TCDD, BUTYL ESTER & ACID (OF 2,4-D & 2,4,5-T) SAMPLING VOLUMES, RATES, AND TIMES

"ORANGE" HERBICIDE INCINERATION TESTS

12 - 30 NOV 73

| Burn # | Sample | SAMPLE VOLUME, Liters | | | Date Nov | Start Time Duration | RATE, Liters/Min | |
|---|---|---|---|---|---|---|---|---|
| | | Meter Con'd | Stack Con'd | Dry @ STP | | | Dry @ STP | Stack Con'd |
| I | CG | 184.4 | 512.6 | 137.4 | 13 | 1445/61 | 2.25 | 8.40 |
| | SG | 139.3 | 188.3 | 106.6 | | 1455/59 | 1.81 | 3.19 |
| II | CG | 45.0 | 131.1 | 34.0 | 16 | 1550/17 | 2.00 | 7.71 |
| | SG | 158.3 | 228.5 | 120.4 | | 1622/55 | 2.19 | 4.15 |
| III | CG | 294.2 | 790.9 | 223.2 | 19 | 1432/64 | 3.49 | 12.36 |
| | SG | 126.9 | 174.8 | 97.2 | | 1428/57 | 1.70 | 3.07 |
| IV | CG | 334.0 | 956.9 | 250.3 | 20 | 1357/60 | 4.17 | 15.95 |
| | SG | 176.2 | 242.7 | 134.4 | | 1345/60 | 2.24 | 4.05 |
| V | CG | 7.9 | 24.6 | 6.0 | 27 | 1350/10 | 0.60 | 2.41 |
| | SG | 145.3 | 179.7 | 111.1 | | 1356/60 | 1.85 | 3.00 |
| VI | CG | 220.9 | 582.1 | 165.9 | 28 | 1158/31 | 5.35 | 18.77 |
| | SG | 50.7 | 81.3 | 36.3 | | 1207/36 | 1.01 | 2.26 |
| VII | CG | 150.7 | 437.2 | 112.15 | 29 | 1007/23 | 4.89 | 19.00 |
| | SG | 115.5 | 165.3 | 82.6 | | 1030/56 | 1.48 | 2.95 |
| VIII | CG | 169.4 | 615.0 | 128.2 | 30 | 0952/33 | 3.88 | 18.64 |
| | SG | 124.0 | 142.3 | 90.4 | | 0957/58 | 1.56 | 2.45 |

CG: Combustion Gas, Prescrubber (Reaction Tailpipe)
SG: Scrubber Gas, Postscrubber (Scrubbed Effluent)
Duration, in minutes

## TABLE D-5

## CO, $CO_2$, $O_2$, $H_2O$ AND $NO_x$ SAMPLING RESULTS

## "ORANGE" HERBICIDE INCINERATION TESTS

## 12 - 30 NOV 73

| Burn # | Sample | CONCENTRATION % BY VOLUME | | | | $NO_x$ | Temp | Inches Hg |
|---|---|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $O_2$ | $H_2O$ | ppm | °F | Pressure |
| | CG | <0.01 | 9.1 | 9.7 | 4.3 | --- | 1875 | 36.9 |
| I | SG | ----- | --- | --- | 34 | 44.2 | 161 | 30.07 |
| | CG | <0.01 | 9.6 | 9.1 | 4.5 | --- | 1850 | 35.4 |
| II | SG | ----- | --- | --- | 38 | 43.3 | 166 | 30.04 |
| | CG | <0.06 | 11.5 | 6.6 | 5.4 | --- | 1975 | 41.0 |
| III | SG | ----- | --- | --- | 35 | 50.6 | 163 | 30.09 |
| | CG | 0.07 | 11.5 | NA | 5.4 | --- | 1840 | 35.9 |
| IV | SG | 0.90 | 12.0 | 4.8 | 35 | 48.7 | 163 | 29.96 |
| | CG | 0.16 | 12.9 | 4.7 | 6.1 | --- | 2140 | 38.1 |
| V | SG | 0.90 | 12.0 | 4.8 | 29 | 44.8 | 156 | 30.28 |
| | CG | 0.03 | 11.5 | NA | 5.4 | --- | 1780 | 38.1 |
| VI | SG | 0.90 | 12.0 | 4.8 | 47 | 46.3 | 175 | 30.20 |
| | CG | 0.14 | 12.7 | 4.9 | 6.0 | --- | 2200 | 41.0 |
| VII | SG | 0.90 | 12.4 | 4.8 | 41 | 95.9 | 170 | 30.12 |
| | CG | 0.19 | 12.7 | 4.8 | 6.0 | --- | 2160 | 32.8 |
| VIII | SG | ----- | --- | --- | 26 | 100.5 | 151 | 30.09 |

NOTES:
SG - Values are average of 4 measurements
CG - Values are theoretical (see main report paragraph 2.6)
NA - Not available
CG - Combustion gas pre-scrubber
SG - Stack gas post-scrubber

TABLE D-6

CARBON MASS BALANCE ON SCRUBBED EFFLUENT GASES

"ORANGE" HERBICIDE INCINERATION TEST

12 - 30 NOV 73

| Burn # | Flow* Dry @ STP $ft^3$/min | $CO_2$ Volume % | CO Volume % | $CO_2$ Mass as C lbs/min | CO Mass as C lbs/min | Feed Rate Fuel lbs/min | Feed Rate Air lbs/min | Recovery** % |
|---|---|---|---|---|---|---|---|---|
| IV | 1515.9/1417.9 | 12.0 | 0.9 | 5.65/5.28 | 0.42 | 4.80 | 0.01 | 126/119 |
| V | 1719.1/1269.1 | 12.0 | 0.9 | 6.41/4.73 | 0.48 | 5.45 | 0.01 | 126/ 96 |
| VI | 1222.5/1306.9 | 12.0 | 0.9 | 4.56/4.87 | 0.34 | 4.80 | 0.01 | 102/108 |
| VII | 1447.9/1252.5 | 12.4 | 0.8 | 5.57/4.82 | 0.40 | 5.48 | 0.01 | 109/ 95 |

*First number based on measured velocity pressures/second number based on Marquardt theoretical data, see discussion, Appendix I.

**Does not include carbon mass as $CO_2$ removed by the caustic scrubber or the carbon mass as particulate matter and as hydrocarbon gases escaping in the scrubbed effluent gas.

velocities, recalculated isokinetic sampling flows were 96.9% (s= 12.9%) and no adjustments of particulate data were necessary.

(2) Butyl Esters and Acids (of 2,4-D and 2,4,5-T) and TCDD. All sample volumes were sufficient to detect ≤5 ppb of these compounds, except for the six liters of combustion gas sampled from burn V when the air cooled sampling probe clogged part way through the desired sampling period. Although the air cooled sampling probe clogged during burn II, a sufficient sample volume was obtained.

A set of three identical sampling probes was used in burns I through V. The same probe was used in burns II and V. Since the clogging problem was isolated to one probe used in burns II and V, it seemed probable that the sampling conduit was crimped or the 90° bend was too sharp allowing particulate matter to build up. A new water cooled probe was used in burns VI, VII and VIII. This new probe had a 3/16' ID conduit versus the 1/8" ID conduit in the air cooled probe. The larger conduit allowed the high pressure in the reaction tailpipe section to be transmitted to the sampling train. The sample flow rate had to be increased to neutralize the positive pressure in the sampling train.

(3) Hydrocarbons. See Appendix I.

(4) CO, $CO_2$, $O_2$. A sampling probe leak developed in burns I, II, III and VIII. The CO, $CO_2$ and $O_2$ data for these burns were considered invalid.

$CO_2$ and $O_2$ concentrations in the scrubbed effluent gas of burns IV, V, VI and VII were in excellent agreement (even though $CO_2$ was absorbed in the scrubber) with the theoretical values calculated by The Marquardt Company. However, CO values were not in agreement. The measured concentrations of CO were significantly greater than the theoretical values (Marquardt). These data indicated that actual combustion efficiency was slightly less than theoretical efficiency.

(5) $NO_x$. These data were taken in anticipation of higher combustion temperatures than were actually attained. $NO_x$ emissions from the incinerator were low (<100 ppm) and would not be expected to pose any environmental impact.

7. Definitions and Formulas

Butyl Esters: Includes N-Butyl 2,4,5 Trichlorophenoxy-acetate and N-Butyl 2,4 Dichlorophenoxy-acetate.

TCDD: 2,3,7,8 - tetrachlorodibenzo-p-dioxin.

Acids: Free acids of 2,4,5 Trichlorophenoxy-acetate and 2,4 Dichlorophenoxy-acetate.

STP: 70°F and 29.92 inches of Hg.

Isokinetic Sampling: Extracting a gas sample from a flowing gas stream at the same velocity of the gas flow.

Meter Conditions: Temperature and pressure of gas being measured by the dry gas meter.

Stack Conditions: Temperature, pressure, and moisture content of the gas at the sampling point.

DGF: Dry gas fraction, the mole fraction of dry gas in the sample volume.

Gr/scf: Grains per standard cubic feet dry.

40 CFR 60: Code of Federal Regulations, Protection of the Environment, Part 60, Standards of Performance for New Stationary Sources.

Conversion From Volume at Standard Conditions To Volume at Stack Conditions:

$$V_{stk} = V_{stp} \times \frac{T_{stk}{}^{\circ}R}{530} \times \frac{29.92}{P_{stk,\ in\ Hg}} \times \frac{1}{DGF}$$

Conversion From Volume at Meter Conditions To Volume at Standard Conditions:

$$V_{stp} = V_m \times \frac{530^{\circ}R}{T_m} \times \frac{P_m}{29.92}$$

## 8. References

D-1. Incineration of Orange Herbicide, R. A. Callahan, July, 1972, USAF Environmental Health Laboratory, Kelly AFB, Texas

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D-6. Perry's Chemical Engineers Handbook, 4th Edition, McGraw-Hill.

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D-8. Thermal Decomposition of Orange Herbicide, B. J. Stojanovic, M. V. Kennedy, W. C. Shaw, June, 1972, State College, Mississippi.

D-9. Controlled Test Atmospheres, Gary O. Nelson, 1971, Ann Arbor Science Publishers, Inc.

USAF ENVIRONMENTAL HEALTH LABORATORY

Kelly AFB, TX 78241

# APPENDIX E

## (TO APPENDIX E)

## SCRUBBER WATER MONITORING

E(D-29)

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E(D-30)

# APPENDIX E

## SCRUBBER WATER MONITORING

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# APPENDIX E

## SCRUBBER WATER MONITORING

1. INTRODUCTION: This appendix describes the equipment, procedures, and techniques used to collect scrubber water samples for chemical analyses and bioassay studies. Methods and results of chemical analyses performed by EHL(K) are also described, presented, and related to the combustion system operating parameters.

2. CLEANING OF SAMPLE CONTAINERS

a. Containers for Chemical Samples: Upon receipt of the bottles from the manufacturer, EHL(K) washed all bottles and caps once with detergent and rinsed them thoroughly several times with hot tap water. Bottles and caps were then dried for about an hour in a 110°C drying oven. Dried bottles and caps were finally rinsed twice with pesticide grade quality hexane. New aluminum foil was likewise rinsed with pesticide grade hexane and then used to line all bottle caps before the caps were placed on the bottles.

b. Containers for Bioassay Samples: The contractor provided reconditioned 55-gallon drums which had been steamed cleaned. EHL(K) then rinsed these drums with a 25% by weight NaOH solution and then thoroughly flushed them with copious amounts of tap water.

3. DESCRIPTION OF SAMPLE BOTTLES FOR CHEMICAL SAMPLES: All water and residue samples collected for chemical analyses were composited and stored for analyses in new, especially cleaned glass bottles. Dark amber, wide mouth glass bottles of 250, 1250, 1500, and 2000 ml capacity were used with molded black plastic caps lined with plastic ringlite. Clear, wide mouth glass bottles of three gallon capacity were also used and had metal screw caps lined with plastic ringlite. The clear bottles were always stored at room temperature in their cardboard shipping containers to keep light away from the collected samples. Bottle caps lined with new aluminum foil were used if the bottle contents were to be analyzed for herbicide and its associated products. Aluminum foil was discarded and not used on the caps of other sample bottles because the alkaline samples would dissolve the aluminum and thus cause analytical interferences with the inorganic analyses.

4. SAMPLE COLLECTION AND COMPOSITING

a. Fresh Scrubber Water: A 1500 ml sample of fresh scrubber water was collected prior to commencing record burn tests I, II, III and IV. The supply tank had just been well mixed via agitation with shop air and the samples were taken from the tank's side port.

b. Scrubber Water Discharge to Holding Tanks

(1) Spent scrubber water samples were collected from a sample port downstream of the scrubber discharge pump, see paragraph 3.7 and Figure 6 of the report. Sampling was begun after a period in which incinerator operation had stabilized to equilibrium conditions and a cycle of accumulated spent

scrubber water had been pumped from the bottom of the scrubber tank. This period was usually thirty minutes after the caustic scrubber water flow and herbicide ignition had begun. The rate of spent scrubber water accumulation in the bottom of the scrubber tank was such that the float actuated discharge pump cycle was approximately seven minutes in the "ON" mode followed by about thirteen minutes in the "OFF" mode. This twenty minute pumping cycle varied ±2 minutes for all record test burns. The discharge pump was allowed to run about one minute and the sample port line was purged before a "pump cycle grab sample" was collected.

(2) Grab sample volumes collected during each pump cycle were: 1500 ml for compositing into a hourly composite, about 1300 ml for a reserve sample, and three to five gallons for compositing a drum of total burn period sample to be used for bioassay studies. A 1200 ml volume (or a proportional fraction) of each hourly composite was used to prepare a total burn period composite (TBC).

c. Scrubber Water Collected From Holding Tanks: After at least 24 hours of quiescent settling, a 1500 ml sample was collected from the side port on a holding tank. This sample was for EHL(K) chemical analyses. At the same time, the bottom valve on the holding tank was opened slowly and a 1500 ml sample of settled particulates was collected. A fraction of this particulate sample was analyzed by WCTS for hydrocarbons and the remaining fraction of this sample was kept by EHL(K) for any future analyses.

d. Holding Pond Waters: Six two-quart grab samples were collected one foot below the surface and at equal distant points around the holding pond. These six grabs were blended to form a composited holding pond sample. The holding pond was so sampled once before any spent scrubber water had been discharged into it. Spent scrubber water from the following groups of record test burns were then discharged into the holding pond and a holding pond composite sample collected 24 hours after the last record burn's water had been discharged: I and II; III and IV; V, VI and VII.

5. EHL/K METHODS AND EQUIPMENT FOR INORGANIC ANALYSES OF SCRUBBER AND HOLDING POND WATER SAMPLES: Tables E-1 and E-2 list the techniques and equipment used by EHL/K to measure physical and analyze inorganic chemical parameters of collected water samples. Additional comments are:

a. The analyses of diluted samples for specific conductance were multiplied by two different factors to relate the two different dilutions back to the original sample strength. These factors were different because specific conductance readings are nonlinear with dilutions (see Table 154 of reference cited in Table E-1). Analyses of 1/99 dilutions were multiplied by 80.44 while 10/90 dilutions were multiplied by 8.73.

b. Solids analyses that required filtration were filtered through 0.6μ glass fiber filter disks. Since the volatile solids fractions from burns I and II were such an insignificant fraction of their respective total solids, the volatile solids were not analyzed in subsequent samples.

c. Total dissolved solids were measured per Standard Methods (TDS-Ms) and with a meter (TDS-Mt) in order to compare the meter's results to the conven-

TABLE E-1: EHL/K TECHNIQUES OF ANALYSES OF WATER SAMPLES

| Inorganic or Physical Parameter | Volume of Sample Analyzed (ml) /Dilution Volume (ml) | | | | | Reference to Procedures Followed** (pages/method) |
|---|---|---|---|---|---|---|
| | FSW* | SSW* | HT* | HP* | SG-P* 1 & 2 | |
| Temperature | N/A | N/A | N/A | N/A | NT | N/A |
| pH | 100/0 | 100/0 | 100/0 | 100/0 | " | 500 |
| Specific Gravity | 250/00 | 250/0 | 250/0 | 250/0 | " | 550 |
| Specific Conductance | 1/99 | 10/90 | 10/90 | 100/0 | " | 323-327 |
| Total Solids (TS) | 10/0 | 10/0 | 10/0 | 10/0 | " | 535-541 |
| Volatile Total Solids (VTS) | NT | 10/0 | 10/0 | NT | " | " |
| Total Dissolved Solids (TDS) - Meas. | 10/0 | 10/0 | 10/0 | 10/0 | " | " |
| Total Dissolved Solids (TDS) Meter | 1/199 | 1/199 | 1/199 | NT | " | NA |
| Volatile Total Dissolved Solids (VTDS) | NT | 10/0 | 10/0 | NT | " | 535-541 |
| Suspended Solids (SS) | NT | 100/0 | 100/0 | NT | " | " |
| Volatile Suspended Solids (SS) | NT | 100/0 | 100/0 | NT | " | " |
| Chlorides | 1/99 | 1/99 | 1/99 | 100/0 | 100/0 | 377/203B |
| Total Chlorine Residual | 2/0 | 1/249 | 1/249 | 2/0 | 2/0 | 385/204B |
| Free Available Chlorine | 2/0 | 1/249 | 1/249 | 2/0 | 2/0 | " |
| Sodium | 1/2499 | 1/999 | 1/999 | 1/9 | NT | 317/153A |
| Iron, Total | 20/0 | 20/0,1/249 | 20/0 | 20/0 | " | 211/129A |
| Total Alkalinity | 2/98 | 2/98 | 2/98 | 100/0 | " | 370/pH meter |
| Hydroxyl Alkalinity | 2/98 | 2/98 | 2/98 | 100/0 | " | " |
| Bicarbonate Alkalinity | 2/98 | 2/98 | 2/98 | 100/0 | " | " |
| Carbonate Alkalinity | 2/98 | 2/98 | 2/98 | 100/0 | " | " |

*See Appendix C for definition of these sample codes.

NT -- Not Tested

**Standard Methods for the Examination of Water and Wastewater, 13th Ed, American Public Health Association, 1015 18th St NW, Washington DC 20036 (1971).

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TABLE E-2: EQUIPMENT USED BY EHL/K TO ANALYZE WATER SAMPLES

| Measured Parameter | Equipment Description |
|---|---|
| Temperature | Immersion mercury thermometer |
| pH | Beckman Century SS pH Meter with combination 0-14 pH electrode. Meter Model 76. Standardized with pH buffers 4.0, 7.0, 10.0, and 12.45. |
| Sp. Gravity | Hydrometers: For liquids 1.000-1.200, and for liquids 1.200-1.400 |
| Sp. Conductance | Delta Scientific Conductivity Monitor/Recorder, Model 3314-01, Serial No. 2277. |
| TDS-Mt | Total Dissolved Solids Meter, Model 512T5, Serial No. 062137, Myron L. Company. |
| Chlorine Residuals | Hellige Chlorine Comparator |
| Sodium | Atomic Absorption, Perkin Elmer, Model 403. |
| Iron, Total | " " " " " " |
| Weights | Mettler Balance, Model H-10Tw, accurate to 0.1 mg. |

USAF EHL/K

tional standard method. This was done because the standard method was very time consuming and subject to larger errors because of weighing and calculations based on a 10 ml sample. Figure E-1 presents these different TDS values. Although the values differed by an order of magnitude, the meter values were acceptably correlated to the measured values. The error in correlation was acceptable considering the overall error (±15%) in measuring such high concentrations of hygroscopic solids, i.e. sodium hydroxide and sodium salts.

d. EHL/K chlorine residuals of burn I were verified by WCTS analyses using the iodometric method. Since acceptable agreement of these analyses was within ±20 mg/l, subsequent chlorine residual analyses were done using the Hellige chlorine comparator.

e. Alkalinities were analyzed per the potentiometric method using pH titration endpoints of 10.0, 8.3, 4.5, and 4.2. All results were expressed as mg/l as calcium carbonate.

6. ANALYTICAL RESULTS AND DISCUSSION OF SCRUBBER WATERS INORGANIC QUALITY

a. Fresh scrubber water analyses in Table E-3 showed the quality of this highly caustic solution which was prepared to range from 8.7 to 15.5% by weight NaOH. From data in Tables E-4 through E-11, spent scrubber water (SSW) quality was essentially constant between hourly composites, the TBC, and the holding tank sample for a given burn. The only inconsistency was in burn VI when the applied caustic flow rate was increased from 1.73 pps to 2.32 pps. This change in scrubber water quality in burn VI SSW-Cl's indicated the very strong effect that applied caustic had on the SSW quality. Chemical constituents in each burn's SSW holding tank were converted to total mass produced (pounds) and pounds per drum of herbicide burned. This last value was calculated so that the chemical constituents could be compared directly between burns and independent of the volume of scrubber/cooling water produced or the durations of the burns.

b. Although the concentrations of SSW inorganic constituents changed between burns because of different applied caustic and herbicide fuel feed rates, the following concentrations were consistently within the following ranges and worth noting:

(1) pH: 10.5 to 11.8.

(2) Specific Gravity: 1.040 to 1.075

(3) Specific Conductance ($x10^4$ μmho/cm): 11.3 to 15.8

(4) Total Solids or Total Dissolved Solids - both being about equal ($x10^3$ mg/l): 61.0 to 87.0

(5) Suspended Solids (mg/l): 56 to 97. As discussed in Appendix I, these solids contained no hydrocarbons and were essentially carbon containing less than 10% by weight iron. The volatile fraction of the suspended and total solids was considered insignificant. The concentration of suspended solids increased significantly to 500-800 mg/l because of iron content when applied caustic was decreased below two times theoretical requirements.

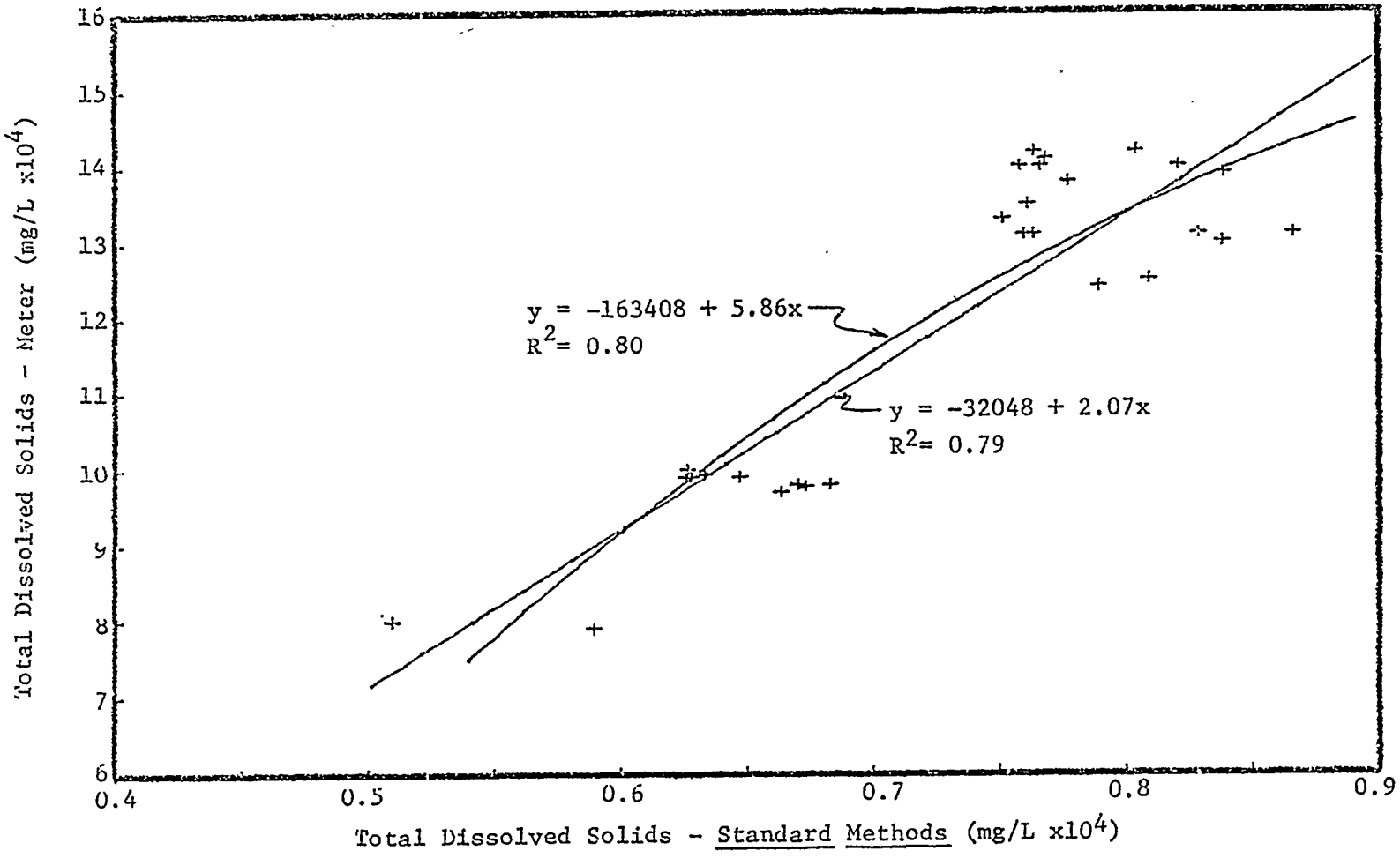



FIGURE E-1: RELATIONSHIP OF TOTAL DISSOLVED SOLIDS MEASUREMENTS ON SPENT SCRUBBER WATER - STANDARD METHODS vs METER

USAF EHL(K)

TABLE E-3: SUMMARY OF EHL/K FRESH SCRUBBER WATER ANALYSES

| | SAMPLE NUMBER | III-FSW B | IV-FSW B | AVERAGE VALUES |
|---|---|---|---|---|
| | Time Collected (hrs) | 1000 | 1450 | |
| | Date Collected (Nov 73) | Mon 19 | Tue 20 | |
| | Date Analyzed (Nov 73) | Sat 24 | Sat 24 | |
| GENERAL | Parameter (mg/l unless noted) | | | |
| GENERAL | Temp ($^0$F) at time: Collected | 66. | 63. | - |
| GENERAL | Analyzed | 72. | 72. | - |
| GENERAL | pH | 13+ | 13+ | 13+ |
| GENERAL | Sp. Gravity | 1.149 | 1.154 | 1.151 |
| GENERAL | Sp. Cond. (x$10^4$. µ mho/cm) | 65.9 | 68.3 | 67.1 |
| SOLIDS | TS (x$10^3$) | 174.77 | 189.37 | 182.07 |
| SOLIDS | VTS (x $10^3$) | - | - | - |
| SOLIDS | TDS, Mt (x$10^4$) | 50.0 | 50.0 | 50.0 |
| SOLIDS | TDS, Ms (x$10^3$) | - | - | - |
| SOLIDS | VTDS (x$10^3$) | - | - | - |
| SOLIDS | SS | - | - | - |
| SOLIDS | VSS | - | - | - |
| IONS/RADICALS | Chlorides (x$10^3$) | 0.014 | 0.014 | 0.014 |
| IONS/RADICALS | Total Chl. Resid. | 0.0 | 0.0 | 0.0 |
| IONS/RADICALS | Free Avail. Chl. | 0.0 | 0.0 | 0.0 |
| IONS/RADICALS | Sodium (x$10^3$) | 97.5 | 97.5 | 97.5 |
| IONS/RADICALS | Iron, Total | 1.45 | 1.61 | 1.53 |
| ALKALINITY | Total Alk ($CaCO_3$) (x$10^3$) | 195.8 | 198.0 | 196.9 |
| ALKALINITY | OH-Alk ($CaCO_3$) (x$10^3$) | 193.3 | 196.3 | 194.8 |
| ALKALINITY | $HCO_3$ -AlK ($CaCO_3$) (x$10^3$) | 0.0 | 0.0 | 0.0 |
| ALKALINITY | $CO_3$ -Alk ($CaCO_3$) (x$10^3$) | 2.5 | 1.7 | 2.1 |

USAF EHL(K)

TABLE E-4: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN I

| | SAMPLE NUMBER | I - SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 1430-1503 | 1520-1555 | 1613-1647 | 1430-1647 | 1430-1706 | 1045 | | |
| | Date Collected (Nov 73) | Tue 13 | Tue 13 | Tue 13 | Tue 13 | Tue 13 | Sat 17 | | |
| | Date Analyzed (Nov 73) | Wed 14 | Wed 14 | Wed 14 | Wed 14 | Wed 14 | Sat 17 | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: Collected | 164. | 164. | 164. | 164. | - | - | - | - |
| GENERAL | Analyzed | 72. | 73. | 73. | 73. | 72. | 75. | - | - |
| GENERAL | pH | 11.65 | 11.75 | 11.60 | 11.70 | 11.85 | 11.50 | - | - |
| GENERAL | Sp. Gravity | 1.060 | 1.060 | 1.060 | 1.060 | 1.060 | 1.055 | - | - |
| GENERAL | Sp. Cond. (x10$^4$ µmho/cm) | 14.9 | 15.1 | 14.8 | 14.9 | 14.8 | 14.0 | - | - |
| SOLIDS | TS (x10$^3$) | 78.77 | 74.28 | 75.77 | 74.94 | 75.61 | 71.23 | 2462.14 | 943.34 |
| SOLIDS | VTS (x 10$^3$) | 4.10 | 4.11 | 6.05 | 4.75 | 5.82 | - | - | - |
| SOLIDS | TDS, Mt (x10$^4$) | 13.1 | 13.3 | 14.1 | 13.5 | 13.1 | 11.8 | 4078.80 | 1562.74 |
| SOLIDS | TDS, Ms (x10$^3$) | 76.35 | 75.13 | 76.82 | 76.10 | 75.97 | - | 2626.02* | 1006.13* |
| SOLIDS | VTDS (x10$^3$) | 6.78 | 5.02 | 7.23 | 6.341 | 5.86 | - | - | - |
| SOLIDS | SS | 74. | 73. | 70. | 72. | - | - | 2.49 | 0.95* |
| SOLIDS | VSS | <10. | <10. | <10. | <10. | <10.0 | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 17.5 | 18.3 | 17.9 | 17.9 | 18.0 | 14.5 | 501.21 | 192.03 |
| IONS/RADICALS | Total Chl. Resid. | 281. | 281. | 281. | 281. | 280. | 225. | 7.78 | 2.98 |
| IONS/RADICALS | Free Avail. Chl. | 281. | 281. | 281. | 281. | 280. | 225. | 7.78 | 2.98 |
| IONS/RADICALS | Sodium (x10$^3$) | 35.0 | 35.0 | 35.0 | 35.0 | 35.0 | 32.0 | 1106.11 | 423.79 |
| IONS/RADICALS | Iron, Total | 5.00 | 4.89 | 4.01 | 4.63 | 4.88 | 0.99 | 0.17* | 0.06* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^3$) | 45.5 | 46.3 | 46.8 | 46.2 | 45.6 | 44.3 | 1531.28 | 586.69 |
| ALKALINITY | OH-Alk ($CaCO_3$) (x10$^3$) | 18.9 | 18.5 | 17.6 | 18.3 | 18.2 | 17.1 | 591.08 | 226.47 |
| ALKALINITY | $HCO_3$ -Alk ($CaCO_3$) (x10$^3$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.00 | 0.00 |
| ALKALINITY | $CO_3$ -Alk ($CaCO_3$) (x10$^3$) | 26.7 | 27.8 | 29.3 | 27.9 | 27.4 | 27.2 | 940.20 | 360.23 |

*Based upon concentration in TBC sample.

TABLE E-5: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN II

| | SAMPLE NUMBER | II -SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 1552-1633 | 1651-1731 | 1751-1831 | 1552-1831 | 1552-1831 | 0900 | | |
| | Date Collected (Nov 73) | Fri 16 | Fri 16 | Fri 16 | Fri 16 | Fri 16 | Tue 20 | | |
| | Date Analyzed (Nov 73) | Sat 17 | Sat 17 | Sat 17 | Sat 17 | Sat 17 | Wed 21 | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: Collected | 164. | 163. | 163. | 163. | - | - | - | - |
| | Analyzed | 72. | 72. | 72. | 72. | 72. | 72. | - | - |
| | pH | 11.40 | 11.45 | 11.55 | 11.50 | 11.50 | 11.50 | - | - |
| | Sp. Gravity | 1.062 | 1.063 | 1.062 | 1.062 | 1.062 | 1.064 | - | - |
| | Sp. Cond. (x10$^4$ µmho/cm) | 15.7 | 15.7 | 15.7 | 15.7 | 15.5 | 15.8 | | |
| SOLIDS | TS (x10$^3$) | 75.97 | 75.62 | 75.10 | 75.56 | 75.74 | 78.32 | 2586.98 | 862.08 |
| | VTS (x 10$^3$) | 1.41 | 1.55 | 2.88 | 1.95 | 0.00 | - | - | - |
| | TDS, Mt (x10$^4$) | 14.0 | 14.2 | 13.8 | 14.0 | 14.2 | 14.3 | 4723.41 | 1574.02 |
| | TDS, Ms (x10$^3$) | 75.82 | 76.36 | 77.72 | 76.63 | 80.40 | - | 2655.68* | 884.98* |
| | VTDS (x10$^3$) | 1.52 | 2.21 | 5.22 | 2.98 | 8.73 | - | - | - |
| | SS | 69.** | 60.** | 58.** | 62. | 65.** | - | 2.15* | 0.72* |
| | VSS | <10. | <10. | <10. | <10. | <10. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 18.5 | 18.1 | 18.4 | 18.3 | 18.3 | 16.0 | 528.49 | 176.11 |
| | Total Chl. Resid. | 250. | 260. | 280. | 263. | 250. | 225. | 7.43 | 2.48 |
| | Free Avail. Chl. | 250. | 260. | 280. | 263. | 250. | 225. | 7.43 | 2.48 |
| | Sodium (x10$^3$) | 37.0 | 36.0 | 37.0 | 36.7 | 37.0 | 36.0 | 1189.11 | 396.26 |
| | Iron, Total | 3.36 | 2.71 | 3.79 | 3.29 | 3.29 | 0.73 | 0.11* | 0.04* |
| ALKALINITY | Total Alk ($CaCO_3$)(x10$^3$) | 52.5 | 52.0 | 52.0 | 52.2 | 52.5 | 51.6 | 1704.39 | 567.97 |
| | OH-Alk ($CaCO_3$) (x10$^3$) | 20.8 | 20.3 | 20.3 | 20.5 | 20.8 | 21.7 | 716.77 | 238.86 |
| | $HCO_3$ -Alk ($CaCO_3$)(x10$^3$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.00 | 0.00 |
| | $CO_3$ -Alk ($CaCO_3$)(x10$^3$) | 31.7 | 31.7 | 31.7 | 31.7 | 31.7 | 29.9 | 987.62 | 329.11 |

* Based upon concentration in TBC sample.
** Average of replicate samples.

USAF EHL(K)

TABLE E-6: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN III

| | SAMPLE NUMBER | III -SSW- | | | | | | HT-1 | |
|---|---|---|---|---|---|---|---|---|---|
| | | C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | lbs | lb/Drum of Herbicide Burned |
| | Time Collected (Hrs) | 1435-1519 | 1535-1616 | 1638-1718 | 1435-1718 | 1435-1/18 | 1000 | | |
| | Date Collected (Nov 73) | Mon 19 | Mon 19 | Mon 19 | Mon 19 | Mon 19 | Tues 20 | | |
| | Date Analyzed (Nov 73) | Wed 21 | Wed 21 | Wed 21 | Wed 21 | Wed 21 | Wed 21 | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: Collected | 164. | 164. | 163. | 164. | - | - | - | - |
| GENERAL | Analyzed | 72. | 72. | 72. | 72. | 72. | 72. | - | - |
| GENERAL | pH | 11.60 | 11.55 | 11.60 | 11.60 | 11.60 | 11.65 | - | - |
| GENERAL | Sp. Gravity | 1.050 | 1.050 | 1.048 | 1.049 | 1.050 | 1.053 | - | - |
| GENERAL | Sp. Cond. (x10$^4$ µmho/cm) | 11.9 | 11.9 | 11.5 | 11.8 | 11.6 | 11.3 | - | - |
| SOLIDS | TS (x10$^3$) | 61.64 | 81.06 | 65.21 | 69.30 | 66.02 | 72.58 | 2414.00 | 614.46 |
| SOLIDS | VTS (x 10$^3$) | - | - | - | - | - | - | - | - |
| SOLIDS | TDS, Mt (x10$^4$) | 9.80 | 9.80 | 9.70 | 9.77 | 9.80 | 9.90 | 3292.73 | 838.14 |
| SOLIDS | TDS, Ms (x10$^3$) | - | 68.29 | 66.36 | 67.32 | 67.01 | - | 2228.75* | 567.31* |
| SOLIDS | VTDS (x10$^3$) | - | - | - | - | - | - | - | - |
| SOLIDS | SS | 76. | 81. | 81. | 79. | 78. | - | 2.59* | 0.66* |
| SOLIDS | VSS | <10. | <10. | <10. | <10. | <10. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 20.1 | 20.1 | 20.0 | 20.1 | 20.1 | 19.6 | 651.89 | 165.93 |
| IONS/RADICALS | Total Chl. Resid. | 280. | 280. | 280. | 280. | 280. | 225. | 7.48 | 1.90 |
| IONS/RADICALS | Free Avail. Chl. | 280. | 280. | 280. | 280. | 280. | 225. | 7.48 | 1.90 |
| IONS/RADICALS | Sodium (x10$^3$) | 28.0 | 27.0 | 28.0 | 27.7 | 24.0 | 30.0 | 997.80 | 253.98 |
| IONS/RADICALS | Iron, Total | 3.49 | 2.86 | 3.21 | 3.19 | 3.37 | 0.85 | 0.11* | 0.03* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^3$) | 33.5 | 32.7 | 32.4 | 32.9 | 32.9 | 32.9 | 1094.25 | 278.53 |
| ALKALINITY | OH-Alk ($CaCO_3$) (x10$^3$) | 6.6 | 5.9 | 6.0 | 6.2 | 6.2 | 5.5 | 182.93 | 46.56 |
| ALKALINITY | $HCO_3$ -Alk ($CaCO_3$) (x10$^3$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.00 | 0.00 |
| ALKALINITY | $CO_3$ -Alk ($CaCO_3$) (x10$^3$) | 26.9 | 26.8 | 26.4 | 26.7 | 26.7 | 27.4 | 911.32 | 231.97 |

*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-7: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN IV

| | SAMPLE NUMBER | IV -SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 1355-1445 | 1505-1553 | 1609 1659 | 1355-1659 | 1355-1659 | 1000 | | |
| | Date Collected (Nov 73) | Tue 20 | Tue 20 | Tue 20 | Tue 20 | Tue 20 | Wed 21 | | |
| | Date Analyzed (Nov 73) | Fri 23 | Fri 23 | Fri 23 | Fri 23 | Fri 23 | Fri 23 | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: Collected | 161. | 160. | 161. | 161. | - | - | - | - |
| | Analyzed | 72. | 72. | 72. | 72. | 72. | 72. | - | - |
| | pH | 11.60 | 11.60 | 11.55 | 11.60 | 11.55 | 11.60 | - | - |
| | Sp. Gravity | 1.052 | 1.052 | 1.052 | 1.052 | 1.052 | 1.051 | - | - |
| | Sp. Cond. (x10$^4$ µmho/cm) | 11.6 | 11.8 | 11.8 | 11.7 | 11.8 | 11.4 | - | - |
| SOLIDS | TS (x10$^3$) | 60.52 | 62.09 | 63.98 | 62.20 | 62.16 | 61.05 | 2140.25 | 545.73 |
| | VTS (x 10$^3$) | - | - | - | - | - | - | - | - |
| | TDS, Mt (x10$^4$) | 10.00 | 9.90 | 9.90 | 9.93 | 9.90 | 10.00 | 3505.72 | 893.90 |
| | TDS, Ms (x10$^3$) | 62.64 | 64.71 | 62.57 | 63.31 | 62.77 | - | 2200.54* | 561.10* |
| | VTDS (x10$^3$) | - | - | - | - | - | - | - | - |
| | SS | 73. | 62. | 56. | 64. | 70. | - | 2.45* | 0.63 |
| | VSS | <10. | <10. | <10. | <10. | <10. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 16.8 | 16.7 | 16.5 | 16.7 | 16.6 | 16.1 | 564.42 | 143.92 |
| | Total Chl. Resid. | 280. | 280. | 280. | 280. | 280. | 225. | 7.89 | 2.01 |
| | Free Avail. Chl. | 280. | 280. | 280. | 280. | 280. | 225. | 7.89 | 2.01 |
| | Sodium | 27.0 | 29.0 | 27.0 | 27.7 | 27.0 | 31.0 | 1086.78 | 277.11 |
| | Iron, Total | 3.07 | 3.07 | 2.57 | 2.90 | 2.86 | 0.74 | 0.10* | 0.03* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^3$) | 34.7 | 35.1 | 34.8 | 34.9 | 34.7 | 33.9 | 1188.44 | 303.03 |
| | OH-Alk ($CaCO_3$) (x10$^3$) | 10.1 | 9.5 | 10.0 | 9.9 | 10.3 | 9.9 | 347.07 | 88.50 |
| | $HCO_3$ -Alk ($CaCO_3$) (x10$^3$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.00 | 0.00 |
| | $CO_3$ -Alk ($CaCO_3$) (x10$^3$) | 24.6 | 25.7 | 24.8 | 25.0 | 24.4 | 24.0 | 841.37 | 214.54 |

*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-8: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN V

| | SAMPLE NUMBER | V -SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 1344-1423 | 1442-1523 | 1542-1614 | 1344 1614 | 1344-1614 | 1310 | | |
| | Date Collected (Nov 73) | Tue 27 | Tue 27 | Tue 27 | Tue 27 | Tue 27 | Wed 28 | | |
| | Date Analyzed (Nov 73) | Wed 28 | Wed 28 | Wed 28 | Wed 28 | Wed 28 | Thur 29 | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: Collected | 164. | 166. | 166. | 165. | - | - | - | - |
| | Analyzed | 72. | 72. | 72. | 72. | 72. | 72. | - | - |
| | pH | 11.50 | 11.55 | 11.45 | 11.50 | 11.40 | 11.45 | - | - |
| | Sp. Gravity | 1.072 | 1.074 | 1.073 | 1.073 | 1.072 | 1.070 | - | - |
| | Sp. Cond. (x10$^4$ µmho/cm) | 13.2 | 13.1 | 13.9 | 13.4 | 13.2 | 13.1 | - | - |
| SOLIDS | TS (x10$^3$) | 91.06 | 86.99 | 87.14 | 88.40 | 86.33 | 86.94 | 2592.50 | 645.38 |
| | VTS (x 10$^3$) | - | - | - | - | - | - | - | - |
| | TDS, Mt (x10$^4$) | 12.5 | 13.0 | 13.9 | 13.1 | 13.1 | 12.7 | 3787.06 | 942.76 |
| | TDS, Ms (x10$^3$) | 80.91 | 83.81 | 83.88 | 82.87 | 86.63 | - | 2583.25* | 643.08* |
| | VTDS (x10$^3$) | - | - | - | - | - | - | - | - |
| | SS | 89. | 97. | 94. | 93. | 87. | - | 2.59* | 0.65* |
| | VSS | <10. | <10. | <10. | <10. | <10. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 23.2 | 23.4 | 23.6 | 23.4 | 23.3 | 22.2 | 661.99 | 164.80 |
| | Total Chl. Resid. | 500. | 500. | 500. | 500. | 500. | 438. | 13.06 | 3.25 |
| | Free Avail. Chl. | 500. | 500. | 500. | 500. | 500. | 438. | 13.06 | 3.25 |
| | Sodium (x10$^3$) | 33.0 | 33.0 | 37.0 | 34.3 | 36.0 | 35.0 | 1043.68 | 259.82 |
| | Iron, Total | 4.36 | 4.30 | 4.59 | 4.42 | 3.78 | 0.93 | 0.11* | 0.03* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^3$) | 44.6 | 46.3 | 46.8 | 45.9 | 45.6 | 44.6 | 1329.94 | 331.08 |
| | OH-Alk ($CaCO_3$) (x10$^3$) | 11.8 | 11.6 | 11.6 | 11.7 | 11.8 | 11.8 | 351.87 | 87.60 |
| | $HCO_3$ -Alk ($CaCO_3$) (x10$^3$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.00 | 0.00 |
| | $CO_3$ -Alk ($CaCO_3$) (x10$^3$) | 32.8 | 34.7 | 35.2 | 34.2 | 33.8 | 32.8 | 978.08 | 243.48 |

*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-9: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VI*

| | SAMPLE NUMBER | VI -SSW- | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | C-1 | C-2 | D-1 | D-2 | D-3 | D-4 | HT-1 |
| | Time Collected (Hrs) | 1108-1156 | 1213-1231 | 1111 | 1133 | 1156 | 1213 | - |
| | Date Collected (Nov 73) | Wed 28 | Wed 28 | Wed 28 | Wed 28 | Wed 28 | Wed 28 | Thur 29 |
| | Date Analyzed (Nov 73) | Thur 29 | Thur 29 | Thur 29 | Thur 29 | Thur 29 | Thur 29 | Thur 29 |
| GENERAL | Parameter (mg/l unless noted) | | | | | | | |
| GENERAL | Temp ($^0$F) at time: Collected | 167. | 165. | - | - | - | - | - |
| GENERAL | Analyzed | 72. | 72. | 72. | 72. | 72. | 72. | 72. |
| GENERAL | pH | 11.40 | 11.40 | 2.0 | 11.3 | 11.3 | 11.3 | - |
| GENERAL | Sp. Gravity | 1.042 | 1.062 | 1.025 | 1.050 | 1.060 | 1.062 | 1.051 |
| GENERAL | Sp. Cond. (x$10^4$ μ mho/cm) | 8.4 | 12.3 | - | - | - | - | - |
| SOLIDS | TS (x$10^3$) | 70.03 | 85.43 | - | - | - | - | - |
| SOLIDS | VTS (x$10^3$) | - | - | - | - | - | - | - |
| SOLIDS | TDS, Mt (x$10^4$) | 8.0 | 12.4 | - | - | - | - | - |
| SOLIDS | TDS, Ms (x$10^3$) | 50.95 | 78.94 | - | - | - | - | - |
| SOLIDS | VTDS (x$10^3$) | - | - | - | - | - | - | - |
| SOLIDS | SS | 799. | 89. | - | - | - | - | - |
| SOLIDS | VSS | <10. | <10. | - | - | - | - | - |
| IONS/RADICALS | Chlorides (x$10^3$) | 21.0 | 23.2 | - | - | - | - | - |
| IONS/RADICALS | Total Chl. Resid. | 38. | 350. | - | - | - | - | - |
| IONS/RADICALS | Free Avail. Chl. | 38. | 350. | - | - | - | - | - |
| IONS/RADICALS | Sodium (x$10^3$) | 22.0 | 35.0 | - | - | - | - | - |
| IONS/RADICALS | Iron, Total | 303.57 | 5.47 | - | - | - | - | - |
| ALKALINITY | Total Alk ($CaCO_3$) (x$10^3$) | 19.5 | 42.8 | - | - | - | - | - |
| ALKALINITY | OH-Alk ($CaCO_3$) (x$10^3$) | 4.3 | 14.6 | - | - | - | - | - |
| ALKALINITY | $HCO_3$-Alk ($CaCO_3$) (x$10^3$) | 0.0 | 0.0 | - | - | - | - | - |
| ALKALINITY | $CO_3$-Alk ($CaCO_3$) (x$10^3$) | 15.2 | 28.2 | - | - | - | - | - |

*A TBC was not prepared for this burn due to the distinct differences in SSW C-1 and C-2. Also, a holding tank liquid sample was not collected because the tank did not fill to the sampling port.

USAF EHL(K)

TABLE E-10: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VII

| | SAMPLE NUMBER | VII -SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | VI/VII -SSW- HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 0947-1027 | 1047-1127 | 1150-1227 | 0947-1227 | 0947-1227 | 1230 | | |
| | Date Collected (Nov 73) | Thur 29 | Thur 29 | Thur 29 | Thur 29 | Thur 29 | Sat 1 DEC | | |
| | Date Analyzed (Nov 73) | Fri 30 | Fri 30 | Fri 30 | Fri 30 | Fri 30 | Sat 1 Dec | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^{0}$F) at time: Collected | 166. | 166. | 172. | 168. | - | - | - | - |
| GENERAL | Analyzed | 72. | 73. | 72. | 72. | 72. | 72. | - | - |
| GENERAL | pH | 11.30 | 11.30 | 11.35 | 11.32 | 11.35 | 11.35 | - | - |
| GENERAL | Sp. Gravity | 1.071 | 1.073 | 1.075 | 1.073 | 1.073 | 1.065 | - | - |
| GENERAL | Sp. Cond. (x10$^{4}$ µmho/cm) | - | - | - | - | 15.1 | 13.7 | - | - |
| SOLIDS | TS (x10$^{3}$) | - | - | - | - | 87.31 | 81.67 | 3859.00 | 612.63 |
| SOLIDS | VTS (x 10$^{3}$) | - | - | - | - | - | - | - | - |
| SOLIDS | TDS, Mt (x10$^{4}$) | 13.9 | 14.0 | 14.0 | 14.0 | 14.0 | 12.0 | 5670.13 | 900.15 |
| SOLIDS | TDS, Ma (x10$^{3}$) | - | - | - | - | 82.08 | - | 3878.37* | 615.71* |
| SOLIDS | VTDS (x10$^{3}$) | - | - | - | - | - | - | - | - |
| SOLIDS | SS | - | - | - | - | 83. | - | 3.92* | 0.62* |
| SOLIDS | VSS | - | - | - | - | 14. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^{3}$) | 23.0 | 24.0 | 23.6 | 23.5 | 23.6 | 22.4 | 1058.42 | 168.03 |
| IONS/RADICALS | Total Chl. Resid. | 438. | 438. | 438. | 438. | 438. | 275. | 12.99 | 2.06 |
| IONS/RADICALS | Free Avail. Chl. | 438. | 438. | 438. | 438. | 438. | 275. | 12.99 | 2.06 |
| IONS/RADICALS | Sodium (x10$^{3}$) | 38.0 | 36.0 | 35.0 | 36.3 | 33.0 | 35.0 | 1653.79 | 262.55 |
| IONS/RADICALS | Iron, Total | 4.48 | 3.43 | 3.84 | 3.92 | 4.53 | 0.77 | 0.21* | 0.03* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^{3}$) | - | - | - | - | 45.8 | 39.8 | 1880.59 | 298.55 |
| ALKALINITY | OH-Alk ($CaCO_3$) (x10$^{3}$) | - | - | - | - | 12.6 | 12.9 | 609.54 | 96.77 |
| ALKALINITY | $HCO_3$ -Alk ($CaCO_3$) (x10$^{3}$) | - | - | - | - | 0.0 | 0.0 | 0.00 | 0.00 |
| ALKALINITY | $CO_3$ -Alk ($CaCO_3$) (x10$^{3}$) | - | - | - | - | 33.2 | 26.9 | 1271.05 | 201.78 |

*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-11: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VIII

| | SAMPLE NUMBER | VIII -SSW- C-1 | C-2 | C-3 | Ave. C-1/C-3 | TBC | HT-1 | HT-1 lbs | HT-1 lb/Drum of Herbicide Burned |
|---|---|---|---|---|---|---|---|---|---|
| | Time Collected (Hrs) | 0946-1041 | 1109-1208 | 1232-1300 | 0946-1300 | 0946-1300 | 1235 | | |
| | Date Collected (Nov 73) | Fri 30 | Fri 30 | Fri 30 | Fri 30 | Fri 30 | Sat 1 Dec | | |
| | Date Analyzed (Nov 73) | Sat 1 Dec | Sat 1 Dec | Sat 1 Dec | Sat 1 Dec | Sat 1 Dec | Sat 1 Dec | | |
| GENERAL | Parameter (mg/l unless noted) Temp ($^0$F) at time: | | | | | | | | |
| GENERAL | Collected | 164. | 164. | 165. | 164. | - | - | - | - |
| GENERAL | Analyzed | 72. | 73. | 72. | 72. | 72. | 73. | - | - |
| GENERAL | pH | 10.95 | 11.05 | 9.05 | 10.35 | 10.80 | 10.80 | - | - |
| GENERAL | Sp. Gravity | 1.044 | 1.046 | 1.041 | 1.044 | 1.044 | 1.041 | - | - |
| GENERAL | Sp. Cond. (x10$^4$ µmho/cm) | - | - | - | - | 8.9 | 8.5 | - | - |
| SOLIDS | TS (x10$^3$) | - | - | - | - | 82.06 | 68.01 | 1816.20 | 406.86 |
| SOLIDS | VTS (x 10$^3$) | - | - | - | - | - | - | - | - |
| SOLIDS | TDS, Mt (x10$^4$) | 7.9 | 8.0 | 7.4 | 7.8 | 7.9 | 7.5 | 2002.86 | 448.68 |
| SOLIDS | TDS, Ms (x10$^3$) | - | - | - | - | 58.92 | - | 1573.45* | 352.48* |
| SOLIDS | VTDS (x10$^3$) | - | - | - | - | - | - | - | - |
| SOLIDS | SS | - | - | - | - | 560. | - | 14.95* | 3.35* |
| SOLIDS | VSS | - | - | - | - | <10. | - | - | - |
| IONS/RADICALS | Chlorides (x10$^3$) | 27.7 | 27.6 | 28.1 | 27.8 | 27.9 | 26.7 | 713.02 | 159.73 |
| IONS/RADICALS | Total Chl. Resid. | 275. | 275. | 275. | 275. | 275. | 138. | 3.69 | 0.83 |
| IONS/RADICALS | Free Avail. Chl. | 275. | 275. | 275. | 275. | 275. | 138. | 3.69 | 0.83 |
| IONS/RADICALS | Sodium (x10$^3$) | 24.0 | 25.0 | 24.0 | 24.3 | 25.0 | 24.0 | 640.92 | 143.58 |
| IONS/RADICALS | Iron, Total | 160.00 | 191.96 | 407.25 | 253.07 | 214.29 | 0.74 | 5.72* | 1.28* |
| ALKALINITY | Total Alk ($CaCO_3$) (x10$^3$) | - | - | - | - | 12.7 | 11.3 | 301.76 | 67.60 |
| ALKALINITY | OH-Alk ($CaCO_3$) (x10$^3$) | - | - | - | - | 0.0 | 0.0 | 0.00 | 0.00 |
| ALKALINITY | $HCO_3$ -Alk ($CaCO_3$) (x10$^3$) | - | - | - | - | 0.1 | 0.9 | 24.03 | 5.38 |
| ALKALINITY | $CO_3$ -Alk ($CaCO_3$) (x10$^3$) | - | - | - | - | 12.6 | 10.4 | 277.73 | 62.22 |

*Based upon concentration in TBC sample.

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(6) Chlorides ($10^3$ x mg/l): 16.5 to 28.0. Chloride concentrations were independent of applied caustic as long as applied caustic was two times theoretical.

(7) Chlorine Residuals (mg/l): 250 to 500. There was no combined available chlorine and thus the free available chlorine residual equalled the total chlorine residual.

(8) Sodium ($10^3$ x mg/l): 32 to 38. Sodium concentrations were directly related to the applied caustic. Burn VIII applied caustic averaged 0.054 pps (less than half the lowest rate of any other burn) to cause the SSW sodium concentration to average only 25.0 x $10^3$ mg/l even though Burn VIII applied water recovery (59.1%) was the lowest of all burns. Sodium masses were considered conservative through the scrubber system except for the minor fractions of sodium salts entrained and exhausted in the scrubbed effluent gases.

(9) Iron, Total (mg/l): 3.0 to 5.0 except up to 400 when applied caustic fell below two times theoretical. Lack of adequate caustic allowed the HCl, $Cl_2$, and any monatomic chlorine of the combustion gas to react with the metal of the scrubber tank walls.

(10) Total alkalinity as $CaCO_3$ ($x10^3$ mg/l): 32.0 to 52.5 except down to 12.0 (±0.7) when applied caustic was less than two times theoretical. As long as applied caustic was twice theoretical, carbonate alkalinity averaged 70(s=8)% of total alkalinity, the remaining alkalinity was hydroxyl, and no bicarbonate alkalinity was detected. At caustic less than twice theoretical, carbonate alkalinity increased to 90(s=10)% of total alkalinity, the remaining alkalinity was bicarbonate, and no hydroxyl alkalinity was detected.

7. EFFECT OF INCINERATOR OPERATING PARAMETERS ON SPENT SCRUBBER WATER INORGANIC QUALITY

a. Table E-12 presents the quality and chemical constituent loading in each burn's total SSW as a function of drums of herbicide incinerated. Values for burns VI and VII were averaged into the VI/VII column. Comparison of data in Table E-12 indicated that all measured parameters except the relatively constant temperatures ($\bar{x}$=164°F), specific gravities ($\bar{x}$=1.057), and chlorides ($\bar{x}$=167 pounds/drum burned) were directly related to applied caustic and independent of F/A or Percent Excess Air. Multiple regression statistics were applied to these data and excellent correlation coefficients were obtained to relate these chemical product loadings to the ratio of applied caustic to that required to neutralize the theoretically expected amounts of HCl($N_U/N_T$) - see Figures E-2 through E-4. Except as discussed in paragraph "e" below, all of these relationships were linear.

b. The following reasoning substantiated why these correlations agreed so well with expectations:

(1) Temperature was a function of combustion gas temperature, combustion gas volume, and total water volumes feed to the scrubber. Since all of these parameters were consistent in relative proportions and gas/water contact time in the scrubber tank was probably consistent, the effluent scrubber water

TABLE E-12: QUALITY AND CHEMICAL LOADINGS IN SPENT SCRUBBER WATER FOR THE TEST BURNS

| BURN NUMBER | I | II | III | IV | V | VI/VII | VIII |
|---|---|---|---|---|---|---|---|
| Unit Operations -Average | | | | | | | |
| $NaOH_{used}/NaOH_{theory}$ | 3.05 | 3.18 | 2.06 | 2.16 | 2.23 | 2.20 | 1.29 |
| Fuel to Air Mass Ratio (F/A) | 0.086 | 0.086 | 0.106 | 0.105 | 0.120 | 0.115 | 0.118 |
| % Excess Air | 89. | 89. | 52. | 53. | 34. | 40. | 37. |
| Spent Scrubber Water - Holding Tank | | | | | | | |
| Physical Parameters | | | | | | | |
| Temp (°F) @ Collection* | 164. | 163. | 164. | 161. | 165. | 166. | 164. |
| pH | 11.50 | 11.50 | 11.65 | 11.60 | 11.45 | 11.35 | 10.80 |
| Sp. Gravity | 1.055 | 1.064 | 1.053 | 1.051 | 1.070 | 1.065 | 1.041 |
| Sp. Conductance ($x10^4$ μ mho/cm) | 14.0 | 15.8 | 11.3 | 11.4 | 13.1 | 13.7 | 8.5 |
| Chemical Mass (lbs) Per Drum of Herbicide Incinerated | | | | | | | |
| Total Solids | 943.34 | 862.08 | 614.46 | 545.73 | 645.38 | 612.63 | 406.86 |
| Total Dissolved Solids-MS* | 1006.13 | 884.98 | 567.31 | 561.10 | 643.08 | 615.71 | 352.48 |
| Suspended Solids* | 0.95 | 0.72 | 0.66 | 0.63 | 0.65 | 0.62 | 3.35 |
| Chlorides | 192.03 | 176.11 | 165.93 | 143.92 | 164.80 | 168.03 | 159.73 |
| Free Available Chlorine | 2.98 | 2.48 | 1.90 | 2.01 | 3.25 | 2.06 | 0.83 |
| Sodium | 423.79 | 396.26 | 253.98 | 277.11 | 259.82 | 262.55 | 143.58 |
| Iron-Total* | 0.06 | 0.04 | 0.03 | 0.03 | 0.03 | 0.03 | 1.28 |
| Total Alkalinity as $CaCO_3$ | 586.69 | 567.97 | 278.53 | 303.03 | 331.08 | 298.05 | 67.60 |
| OH-Alkalinity as $CaCO_3$ | 226.47 | 238.86 | 46.56 | 88.50 | 87.60 | 96.77 | 0.00 |
| $HCO_3$-Alkalinity as $CaCO_3$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 5.38 |
| $CO_3$-Alkalinity as $CaCO_3$ | 360.23 | 329.11 | 231.97 | 214.54 | 243.48 | 201.78 | 62.22 |

*Data/calculation based on analyses of total burn composite (TBC) sample.

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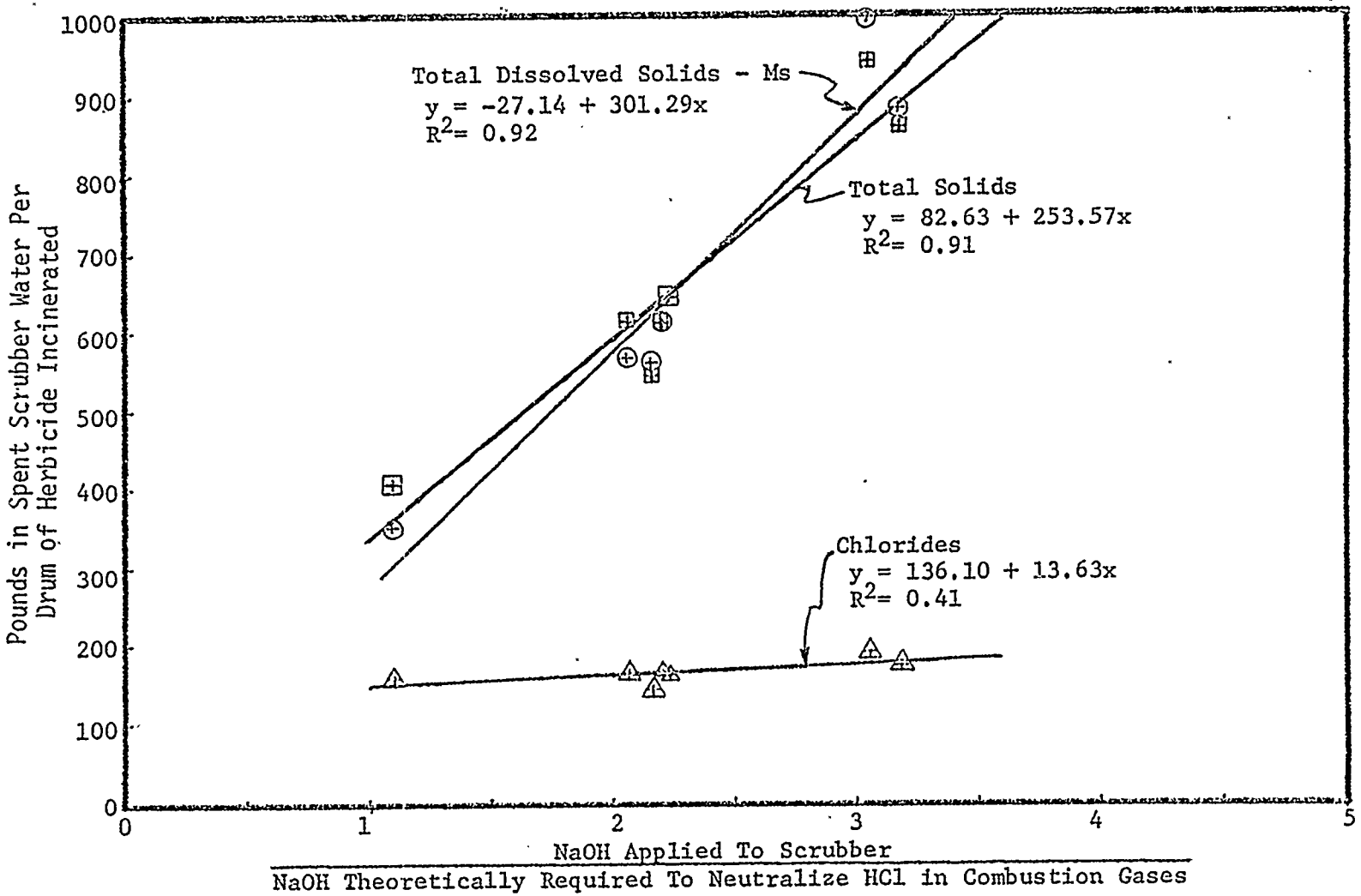



FIGURE E-2 RELATIONSHIP OF CAUSTIC USED TO TOTAL SOLIDS, DISSOLVED SOLIDS, AND CHLORIDES IN SPENT SCRUBBER WATER

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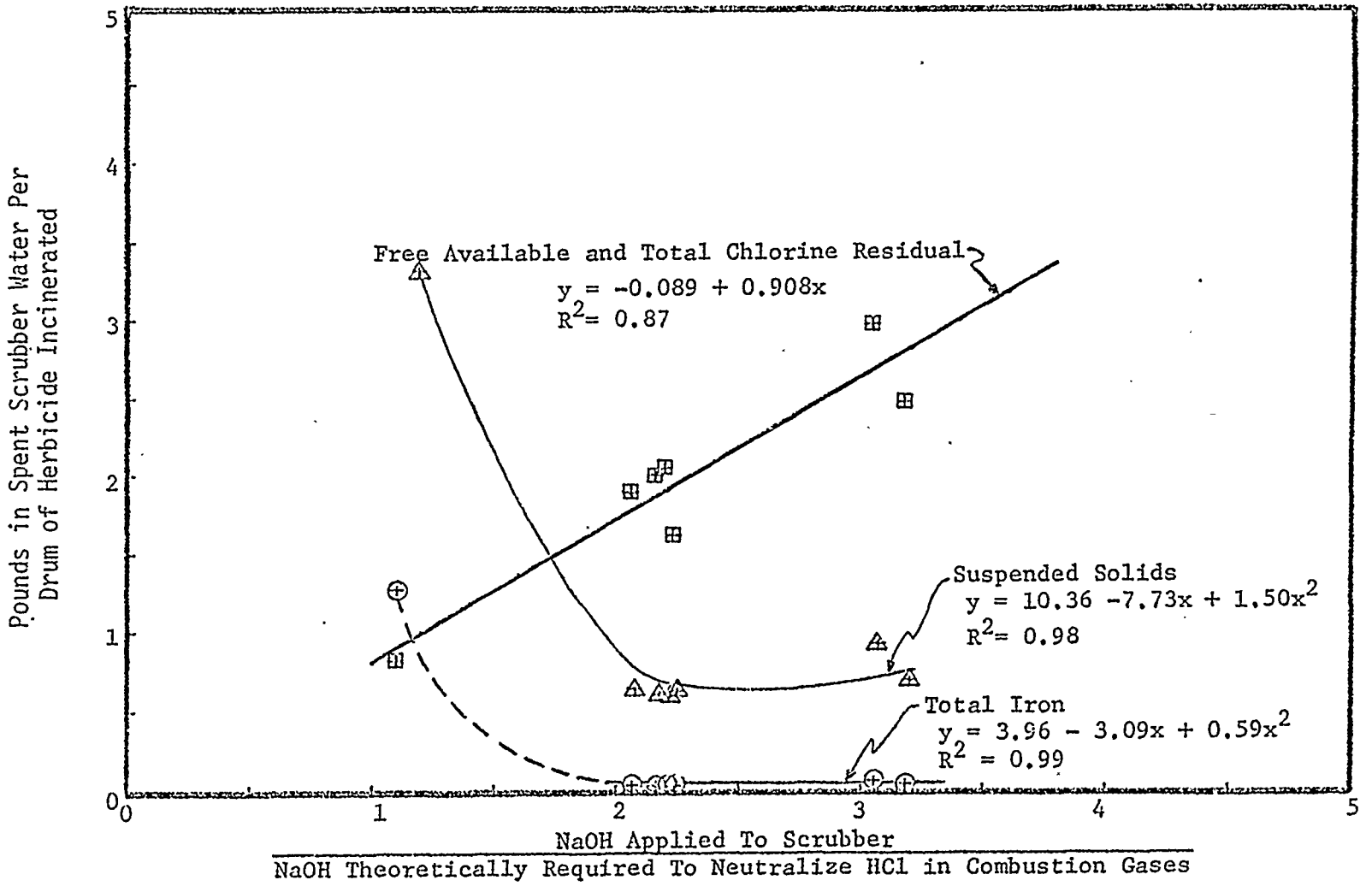



FIGURE E-3 : RELATIONSHIP OF CAUSTIC USED TO CHLORINE RESIDUAL AND TOTAL IRON IN SPENT SCRUBBER WATER

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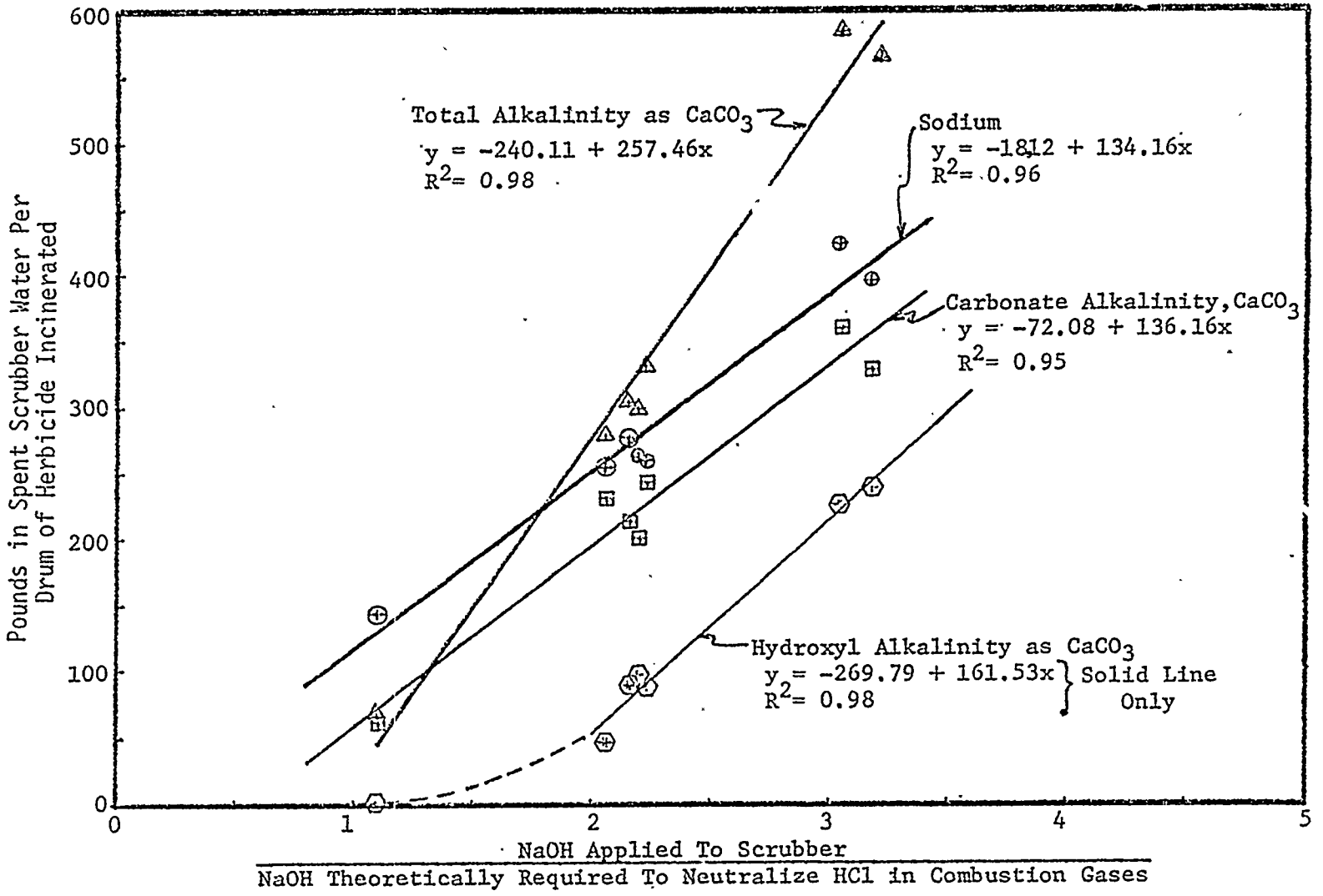



FIGURE E-4 : RELATIONSHIP OF CAUSTIC USED TO ALKALINITIES AND SODIUM IN SPENT SCRUBBER WATER

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temperature was relatively constant.

(2) Specific gravity was dependent on these same parameters plus caustic feed. However, specific gravity is a relatively insensitive measurement and would be expected to change only when the parameters on which it depended had changed more dramatically.

(3) The slightly variable chlorides in pounds per drum of herbicide burned was apparently due to its following consistencies of:

(a) Chlorine weight percent in the herbicide feed,

(b) percent production of HCl, $Cl_2$, and monatomic chlorine from the incinerated chlorinated hydrocarbons, and

(c) efficiency of the caustic scrubber to collect chlorine species as long as the applied caustic was greater than twice theoretical.

Thus, these combined situations allowed collection of chlorides almost independent of any $N_U/N_T$ ratios greater than 1.1.

(4) The inorganic loading of the fresh scrubber water into the spent scrubber water far outweighed any contributions that the herbicide combustion products ($CO_2$, $H_2O$, any hydrocarbons) may have produced. Only the chlorine species of the combustion gases exerted any significant effects on inorganic scrubber water loads, and their effects were independent of $N_U/N_T$ greater than 1.1.

c. All but three of the correlated inorganic parameters increased directly over the range of $N_U/N_T$=1 to $N_U/N_T$=3. Total iron decreased rapidly to a constant value as $N_U/N_T$ increased from one to two. This was because at $N_U/N_T$ greater than 1.1 enough caustic was available to neutralize the HCl which otherwise reacted with the scrubber tank walls to produce ferric precipitates. Suspended solids responded in the same manner because the ferric precipitates were a large fraction of suspended solids when $N_U/N_T$ was less than 1.29 (Burn VIII). The last exception was hydroxyl alkalinity which was zero at (1) $N_U/N_T$, increased nonlinearly with $N_U/N_T$ from one to two and then increased directly when $N_U/N_T$ was greater than two. Hydroxyl alkalinity approached zero at (1) $N_U/N_T$ because it was depleted via reaction with the HCl in the combustion gases. For $N_U/N_T$ between 1.0 and 2.0, excess hydroxyl ions were present above HCl requirements but they were being reacted with $CO_2$. Excess of hydroxyl ion rose steadily for $N_U/N_T$ values greater than about two because all HCl demands were met and the short water/gas contact time in the scrubber tank precluded any additional reaction with $CO_2$. These relationships of hydroxyl utilization for HCl and $CO_2$ reactions were very correlatable to calculated data; see Figure E-5 which was plotted from the data in Table E-13. It was interesting to note that an average of 10(±4)% of the calculated $CO_2$ in the combustion gas was reacted with NaOH to produce carbonates.

8. SCRUBBER WATER REQUIREMENTS AND RECOVERY

a. Caustic solution and cooling water mass flow rate requirements to cool

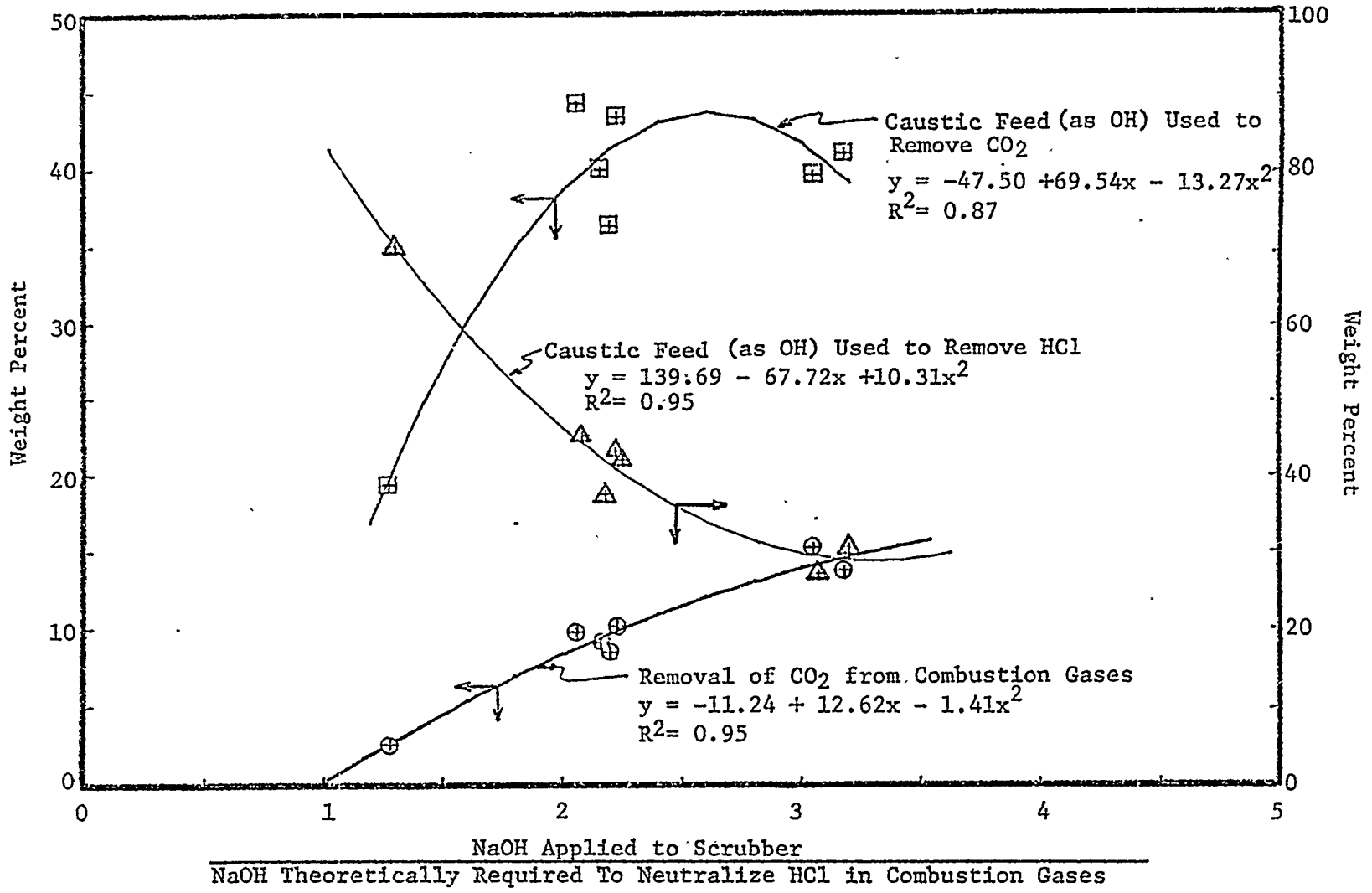



FIGURE E-5: CAUSTIC USED vs PERCENT $CO_2$ REMOVAL AND PERCENT OF CAUSTIC USED TO REMOVE HCl AND $CO_2$

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TABLE E-13: PERCENT OF CAUSTIC FEED USED TO REMOVE $CO_2$ FROM COMBUSTION GASES

| Burn No. | Scrubber Percent Removal of $CO_2$ From Combustion Gases* | Percent Of Caustic Feed Used To Remove $CO_2$* | $\frac{NaOH_{used}}{NaOH_{Theory}}$ |
|---|---|---|---|
| I | 15.3 | 39.6 | 3.05 |
| II | 13.8 | 41.0 | 3.18 |
| III | 9.8 | 44.2 | 2.06 |
| IV | 9.1 | 39.9 | 2.16 |
| V | 10.2 | 43.3 | 2.23 |
| VI/VII | 8.5 | 36.3 | 2.20 |
| VIII | 2.6 | 19.3 | 1.29 |
| Ave | 9.9 | 37.7 | 2.31 |
| Std D. | 4.1 | 8.5 | 0.64 |

*Weight Percent

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and neutralize the combustion gases were based on estimates of combustion gas mass flows, chlorine composition, and temperature. These three parameters were dependent on the fuel to air mass ratios (F/A), see Appendix A. Consistent selection of scrubber water flow rates in relation to F/A were thus expected to produce correlations between scrubber water feed volumes, collected spent scrubber water volumes, and F/A. Excellent correlation of these variables are shown in Figure E-6 as plotted from the data in Table E-14. Even though total water flow into the scrubber was comparable, scrubber water recovery from burns VI and VIII did not correlate to the other burns. The most likely reason for this poorer water recovery in VI and VIII was that the effective caustic strength of the scrubber water into the venturi was lower and thus had a higher vapor pressure than in other burns. This difference of physical property allowed more scrubber water volatilization in burns VI and VIII than in the other burns.

b. Evaluation of Figure E-6 showed that higher strength caustic stock solution (~15% by weight NaOH) was used to minimize total scrubber water requirements to 1200 (±50) gallons/drum of herbicide burned at F/A's of 0.115 (±0.005). Scrubber water recovery averaged about 75% or 1000 gallons/drum of herbicide burned.

9. REMOVAL OF IRON FROM SPENT SCRUBBER WATER: The color of spent scrubber water sediments indicated the presence of particulate iron; particularly burns VI ad VIII. Iron concentrations in well mixed SSW-TBC samples were compared with concentrations in settled holding tank supernatant. The average percent iron removal after settling was 77.5 percent and increased as iron concentration in the SSW-TBC increased. (See Table E-15). Thus conventional settling tanks would effectively reduce the iron to acceptable concentrations for discharge.

10. MASS BALANCE OF SYSTEM CHLORINE, SODIUM, AND HYDROXIDE

a. These mass balances were based upon the inorganic analyses of fresh and spent scrubber water and chlorine's theoretical average composition in the herbicide fuel. Considering the limited number of samples and the calculation errors involved in determining masses for each burn, the average accountability of sodium (104.1%), hydroxide (95.4%), and feed chlorine (96.2%) attested to the overall accuracy of scrubber water collection and analyses.

b. Data presented in Table E-16 denote the fractions of hydroxide used to react with HCl and $CO_2$. Table E-17 shows that scrubber water analyses indicated that about 98.7% of the herbicide chlorine was converted to HCl and monatomic chlorine while 1.3% was formed into diatomic chlorine.

11. EFFECTS OF SPENT SCRUBBER WATER ON INORGANIC QUALITY OF HOLDING POND WATER

a. Inorganic analyses of holding pond water were conducted on samples collected before and after incremental volumes of spent scrubber water were dumped into the 1.4 million gallon concrete wastewater reservoir. No other known industrial wastewaters of any significant detriment were discharged to this reservoir during the sampling period.

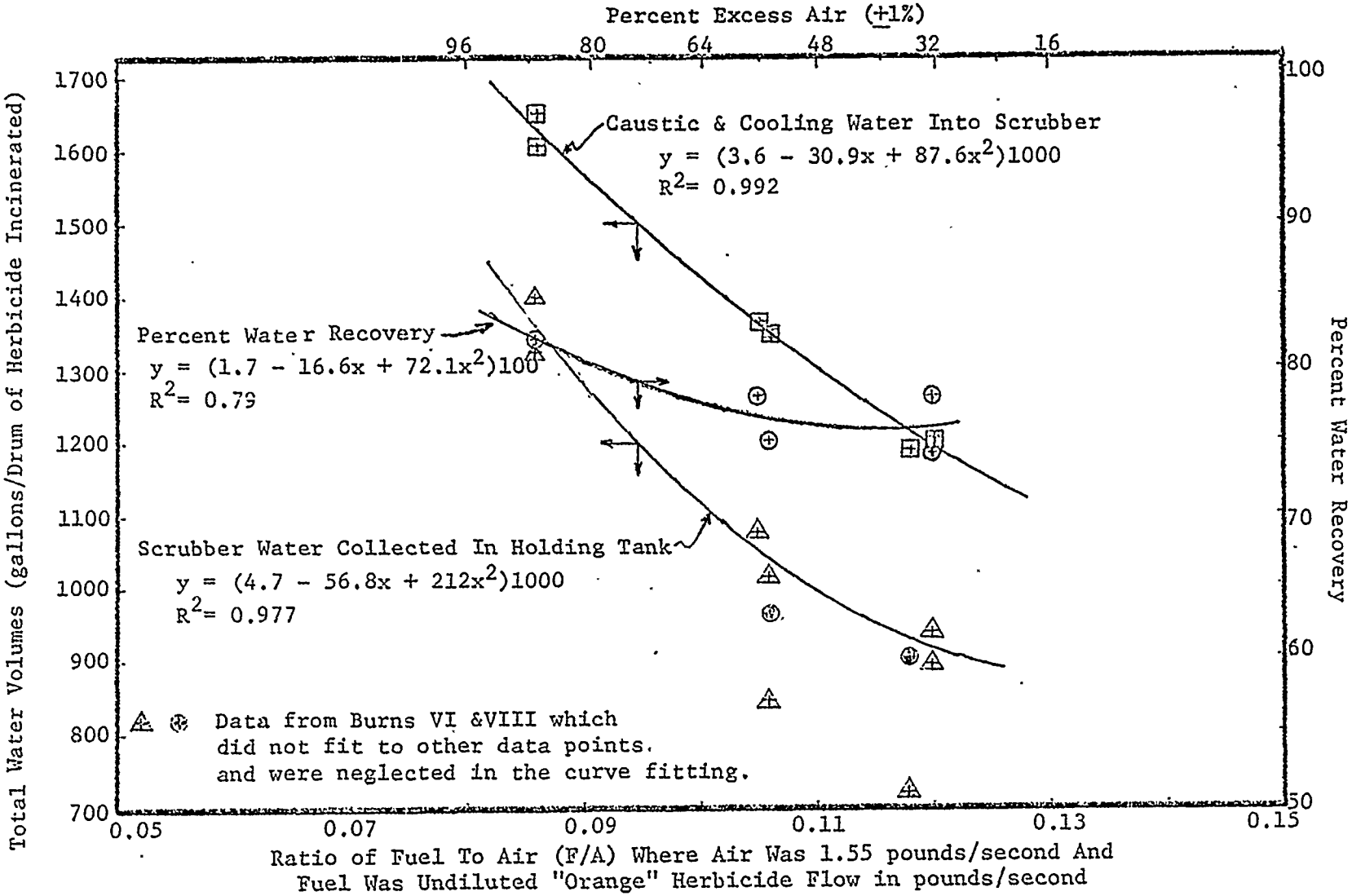



FIGURE E-6: RELATIONSHIP OF WATER USED/DISCHARGED TO FUEL/AIR RATIOS DURING INCINERATION OF ORANGE HERBICIDE

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TABLE E-14: SCRUBBER WATER USED/RECOVERED FOR BURN CONDITIONS

| Burn Number | F/A | Percent Excess Air | $\frac{NaOH_{used}}{NaOH_{Theory}}$ | TOTAL WATER | | |
|---|---|---|---|---|---|---|
| | | | | Into Scrubber (Gallons per Drum of Herbicide Incinerated) | Recovered in Holding Tank (Gallons per Drum of Herbicide Incinerated) | Percent Recovery |
| I | 0.086 | 89. | 3.05 | 1650. | 1397. | 84.7 |
| II | 0.086 | 89. | 3.18 | 1606. | 1322. | 82.3 |
| III | 0.106 | 52. | 2.06 | 1353. | 1013. | 74.9 |
| IV | 0.105 | 53. | 2.16 | 1364. | 1073. | 78.7 |
| V | 0.120 | 34. | 2.23 | 1204. | 892. | 74.1 |
| VI | 0.106 | 52. | 2.11 | 1342. | 841. | 62.7 |
| VII | 0.120 | 34. | 2.26 | 1199. | 934. | 77.9 |
| VIII | 0.118 | 37. | 1.29 | 1214. | 717. | 59.1 |
| Average | 0.106 | 55. | 2.27 | 1366. | 1023. | 74.3 |
| Std. Deviation | 0.014 | 23. | 0.64 | 176. | 234. | 9.0 |

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TABLE E-15: TOTAL IRON REMOVAL FROM SPENT SCRUBBER WATER VIA SETTLING

| Burn No.* | Total Iron Concentration | | Percent Removal (Based on Concentration) |
|---|---|---|---|
| | Into Holding Tank (TBC - mg/l) | Holding Tank Supernatant (mg/l) | |
| I | 4.88 | 0.99 | 79.7 |
| II | 3.29 | 0.73 | 77.8 |
| III | 3.37 | 0.85 | 74.8 |
| IV | 2.86 | 0.74 | 74.1 |
| V | 3.78 | 0.93 | 75.40 |
| VII | 4.53 | 0.77 | 83.00 |
| VIII | 214.29 | 0.74 | 99.7 |
| Average + | 3.79 | 0.84 | 77.5 |

*Burn No. VI data were not evaluated because the holding tank did not fill enough to get a sample from the sampling port.
+Based on Burns I, II, III, IV, V, and VII

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TABLE E-16: CAUSTIC MATERIAL BALANCE FOR SODIUM AND HYDROXIDE FOR THE BURNS

| Burn No. | Sodium | Hydroxide | | | | | |
|---|---|---|---|---|---|---|---|
| | Percent of FSW Feed Accounted For In Holding Tank | Percent of FSW | | | | | |
| | | Used to React With | | Unused and In Holding Tank | Accounted For | Unaccounted For | $\frac{NaOH_{used}}{NaOH_{Theory}}$ |
| | | HCl | $CO_2$ | | | | |
| I | 101.3 | 26.8 | 39.6 | 24.9 | 91.3 | 8.7 | 3.05 |
| II | 112.7 | 30.3 | 41.0 | 29.7 | 100.0 | 0.0 | 3.18 |
| III | 105.2 | 44.8 | 44.2 | 8.9 | 97.9 | 2.1 | 2.06 |
| IV | 109.4 | 37.2 | 39.9 | 16.1 | 92.2 | 7.8 | 2.16 |
| V | 100.5 | 41.7 | 43.3 | 15.6 | 100.6 | 0.0 | 2.23 |
| VI/VII | 102.6 | 42.8 | 36.3 | 17.4 | 96.5 | 3.5 | 2.20 |
| VIII | 96.7 | 69.8 | 19.3 | 0.0 | 89.1 | 10.9 | 1.29 |
| Ave. | 104.1 | 41.9 | 37.7 | 16.1 | 95.4 | 4.7 | 2.31 |
| Std D. | 5.5 | 14.0 | 8.5 | 9.8 | 4.5 | 4.4 | 0.64 |

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TABLE E-17: CHLORINE MATERIAL BALANCE FOR THE BURNS

| Burn No. | Percent of Feed Chlorine (Mass) Converted To * | | Accounted For ** |
|---|---|---|---|
| | HCl & (Cl) | $Cl_2$ | |
| I | 98.46 | 1.54 | 110.09 |
| II | 98.60 | 1.40 | 100.91 |
| III | 98.86 | 1.14 | 94.96 |
| IV | 98.61 | 1.39 | 83.00 |
| V | 98.05 | 1.95 | 94.98 |
| VI†/VII | 98.78 | 1.22 | 96.81 |
| VIII † | 99.48 | 0.52 | 92.77 |
| Ave | 98.69 | 1.31 | 96.22 |
| Std D. | 0.44 | 0.44 | 8.21 |

Based on analytical measurements of spent scrubber water and assuming:

*100% scrubbing efficiency.
** 29.78% weight chlorine in herbicide feed and all settled iron was as $FeCl_3$.

† Stack sampling crew could smell chlorine in scrubbed exhaust gases.

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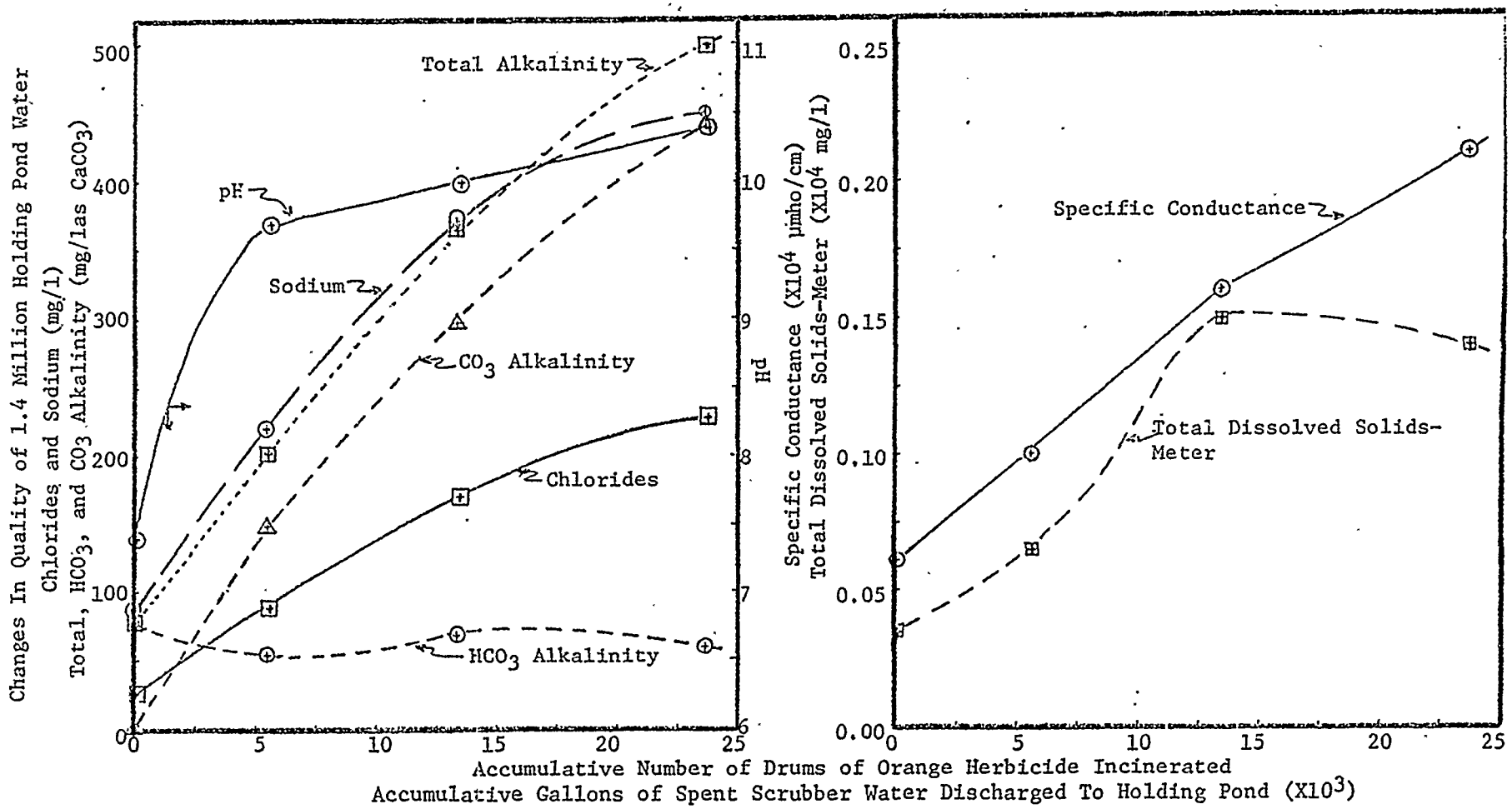
b. Analytical results are presented in Table E-18 and graphed in Figure E-7. The abscissa was double labeled and related the average gallons (1000) of spent scrubber water discharged per drum of herbicide incinerated. The "freshwater" quality of the reservoir changed significantly in rising pH, total and carbonate alkalinity, sodium, chlorides, specific conductance, and total dissolved solids. The rise in pH from 7.4 to 9.7 was the most noticeable and easily measured parameter of change. The pH then slowly increased to the equilibrium value of 10.4 for the bicarbonate-carbonate system. The fluctuating bicarbonate alkalinity indicated the water system's attempt to equilibrate the carbonate alkalinity reactions. Total dissolved solids content stabilized as the pH reached 10.0 -- indicating precipitating reactions had begun. Spent scrubber water caused no significant changes in any other measured parameters of the reservoir's water quality: specific gravity, total solids, chlorine residuals (0.0 mg/l), or hydroxyl alkalinity (0.0 mg/l as $CaCO_3$).

c. The elevated chemical concentrations in the holding pond would begin to decrease as the system slowly adjusts to a more natural equilibrium, with a pH of approximately 8. Exceptions to this natural adjustment would be the conservative sodium and chloride which would increase the reservoir's salinity, but to a level much less than that of sea water.

TABLE E-18: SUMMARY OF EHL/K HOLDING POND WATER ANALYSES

| | Sample No: HP- | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| | Accumulative Holding Tanks Dumped to Holding Pond | NONE | I & II | III & IV | V, VI & VII |
| | Date Holding Tanks were dumped (Nov 73) | N/A | Mon 19<br>Wed 21 | Tue 27<br>Thu 29 | Tue 4 Dec |
| | Date Collected (Nov 73) | Mon 19 | Sat 24 | Sat 1 Dec | Wed 5 Dec |
| | Date Analyzed (Nov 73) | Wed 21 | Mon 26 | Sat 1 Dec | Wed 12 Dec |
| GENERAL | Parameter (mg/l unless noted)<br>Temp ($^0$F) at time:<br>Collected | Mid 60's | | | |
| | Analyzed | 72. | 72. | 73. | 72. |
| | pH | 7.40 | 9.70 | 10.00 | 10.40 |
| | Sp. Gravity | 1.0005 | 1.0010 | 1.0020 | 1.0010 |
| | Sp. Cond. ($x10^4$ μ mho/cm) | 0.06 | 0.10 | 0.16 | 0.21 |
| SOLIDS | TS ($x10^3$) | 0.40 | 1.48 | 0.85 | 1.24 |
| | VTS ($x\ 10^3$) | - | - | - | - |
| | TDS, Mt ($x10^4$) | 0.035 | 0.065 | 0.150 | 0.140 |
| | TDS, Ms ($x10^3$) | - | - | - | - |
| | VTDS ($x\ 10^3$) | - | - | - | - |
| | SS | - | - | - | - |
| | VSS | - | - | - | - |
| IONS/RADICALS | Chlorides | 26.0 | 88.0 | 170. | 228. |
| | Total Chl. Resid. | 0.0 | 0.0 | 0.0 | 0.0 |
| | Free Avail. Chl. | 0.0 | 0.0 | 0.0 | 0.0 |
| | Sodium | 85.0 | 220.0 | 370.0 | 450.0 |
| | Iron, Total | 0.48 | 0.68 | 0.58 | 0.55 |
| ALKALINITY | Total Alk ($CaCO_3$) | 77. | 202. | 365. | 515. |
| | OH-Alk ($CaCO_3$) | 0.0 | 0.0 | 0.0 | 0.0 |
| | $HCO_3$-Alk ($CaCO_3$) | 77. | 53.5 | 68.0 | 59. |
| | $CO_3$-Alk ($CaCO_3$) | 0.0 | 148.5 | 297.0 | 456. |

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NOTE: No significant changes occurred in other measured parameters; specific gravity, total solids, chlorine residuals (0.0 mg/l), or hydroxyl alkalinity (0.0 mg/l as $CaCO_3$).

FIGURE E-7: EFFECTS OF SPENT SCRUBBER WATER DISCHARGE AND ORANGE HERBICIDE INCINERATED ON HOLDING POND WATER QUALITY.

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Kelly AFB, TX 78241

# APPENDIX F

(TO APPENDIX E)

## DRUM CLEANING, DISPOSAL, AND ANALYSES OF DRUM RINSE SAMPLES

E(E-33)

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# APPENDIX F

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# APPENDIX F

## DRUM CLEANING, DISPOSAL, AND ANALYSES OF DRUM RINSE SAMPLES

### 1. Introduction

This task was investigative in nature and was not designed necessarily for future use in any drum cleaning requirements. The objective of this study was to assess the maximal removal of normal butyl esters of 2,4-D and 2,4,5-T from the drums. TCDD removal was not measured but estimates of its removal were made. This appendix describes the equipment and procedures used to clean and dispose of the drums. Methods and results of USAF Environmental Health Laboratory-Kelly AFB (EHL/K) drum rinse analyses are also presented and discussed.

### 2. Drum Cleaning Procedures

a. Drum cleaning operations were performed in the partially enclosed area north of Building 57. This area was curbed and had a sloped concrete floor with a catchment type drain (see Figure 9).

b. Less than two quarts of "Orange" Herbicide were usually left in each drum after the drum's contents had been transferred to the fuel feed tank. Before each drum was rinsed, the contractor upended it and its contents were allowed to "free board" drain until steady dripping stopped. This drain time depended on the herbicide's drip rate, and the drain time ranged from six to nine minutes with an average of 7.3 minutes (s = 0.90). See Table F-1. Herbicide color and drip rate were subjectively observed and no consistent relationship was obtained between herbicide color and drip rate/total drain time.

c. As specified by EHL/K, the contractor used the following procedure to clean the twenty-eight drums that had been drained per paragraph "b" above:

(1) To a first set of seven random drums:

(a) Five gallons of unused JP-4 were poured into a drum and the drum was recapped.

(b) The drum was placed in a barrel rolling device for five minutes.

(c) Drum contents were poured into a "rinse collection" drum as EHL/K personnel collected a 250ml sample of the rinse solution midway through this draining step. The 250ml sample container had been specially cleaned and the cap lined with aluminum foil per the procedure described in paragraph 2a, Appendix E.

TABLE F-1: DRUM DRAINING/DRIPPING DATA

| 3 Dec 73 (1230-1625 hrs) | | | | 4 Dec 73 (0615-0845 hrs) | | | |
|---|---|---|---|---|---|---|---|
| EHL(K) DRUM NO. | DRAIN TIME (MIN) | REMARKS | | EHL(K) DRUM NO. | DRAIN TIME (MIN) | REMARKS | |
| | | HERBICIDE COLOR | DRIP RATE | | | HERBICIDE COLOR | DRIP RATE |
| 83 | 8 | Dark | Slow | 73 | 8 | Light | Slow |
| 88 | 6 | Honey | Fast | 74 | 8 | Light | Slow |
| 90 | 8 | Dark | Slow | 68 | 7 | Light | Slow |
| 82 | 6 | Honey | Fast | 75 | 7 | Light | Slow |
| 71 | 6 | Honey | Fast | 62 | 9 | Dark | Slow |
| 81 | 7 | Dark | Slow | 91 | 8 | Light | Slow |
| 92 | 7 | Honey | Fast | 65 | 8 | Light | Slow |
| 66 | 8 | Dark | Slow | 76 | 8 | Dark | Slow |
| 80 | 6 | Honey | Slow | 63 | 9 | Dark | Slow |
| 84 | 7 | Dark | Slow | 64 | 7 | Light | Slow |
| 70 | 6 | Honey | Fast | 77** | 8 | Light | Slow |
| 86 | 7 | Honey | Fast | | | | |
| 69 | 7 | Honey | Fast | | | | |
| 78 | 6 | Honey | Fast | | | | |
| 87 | 8 | Dark | Slow | | | | |
| 89* | 8 | Dark | Slow | | | | |
| 85 | 7 | Dark | Slow | | | | |

* Drum 89 was a damaged Drum and was manually shaken.

** Drum 77 Was suspected of having $H_2O$ in it. However none was observed.

NOTES: (1) Average drain time for all drums was 7.32 minutes, $\delta = 0.90$
(2) Average ambient air temperature was 60°F during drainings.

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(d) Steps (a) through (c) above were repeated twice.

(e) Drum was then recapped and stored for disposal.

(2) To a second set of seven random drums, (1) above was accomplished except three gallons of unused JP-4 were used for each of the three rinses per drum.

(3) To a third set of seven random drums, (1) above was accomplished except two gallons of unused JP-4 were used for each of the three rinses per drum.

(4) To a fourth set of the seven remaining drums, (1) above was accomplished except that the following volumes of unused JP-4 were used for each rinse: five gallons for the first rinse, three gallons for the second rinse, and two gallons for the third rinse.

3. Drum Disposal

a. EHL/K inquired locally about public landfills which were approved by regulatory agencies for burial of hazardous materials. The Los Angeles County "Class 1" Landfill Number 5 at Calabasas, CA was so approved and selected by EHL/K for the drum disposal. Mr. Robert Van Huet, Los Angeles County Sanitation Office (213-484-1370) and Mr. Jack Johnson, Site Foreman of the Calabasas Landfill (213-889-1430), approved the drum burial after they had been briefed by EHL/K on the following characteristics of the drums:

(1) Quantity and quality of the drums.

(2) Herbicidal content of the drums and the method of drum cleaning that had been accomplished.

(3) Requirement that the drums be crushed and buried to preclude any chance of them being salvaged and recycled for anyone's use.

b. The cleaned drums were loaded onto a flatbed truck, uncapped, and loaded with several cups of laundry detergent and about twenty gallons of tap water. This detergent solution sloshed around in the drums as the truck was driven to the landfill. This action of detergent rinsing was taken to stop any JP-4 vaporization and emulsify any residual JP-4/herbicide that may have been in the drums.

c. The uncapped drums were rolled from the truck bed into a pit freshly dug by the landfill operators. The drums were then immediately crushed, mixed, and compacted with other refuse, and buried while EHL/K personnel observed.

4. EHL/K Procedures/Methods of Analyses of Drum Rinse Samples

a. Equipment and Materials.

(1) Gas Chromatograph - Tracor 220 equipped with flame ionization detector (FID).

(2) Chromatographic column: 4 feet glass "U" tube packed with 3% ov-1 on Chromosorb W, 80/100 mesh.

(3) Chromatographic operating conditions:

(a) Injector temperature - 225°C.

(b) Detector temperature - 175°C.

(c) Column temperature:

1 Programmed initial temperature at 150°C for six minutes rising at 10°C per minute to a final temperature of 200°C.

2 Isothermal condition of 160°C.

(d) Carrier gas - nitrogen.

(e) Gas flow - 70 cc/minute.

b. Standards. Standard solutions of nb 2,4-D and nb 2,4,5-T esters were prepared in JP-4. Standard curves were prepared for the nb 2,4-D and nb 2,4,5-T esters at three different concentrations: 6 µg/µl, 2 µg/µl, and 0.2 µg/µl. Linearity was obtained from 0.2 µg to 24 µg but was lost above 24 µg for both the 2,4-D and 2,4,5-T nb esters. Standard curves were prepared by plotting peak height (cm) vs concentration of ester in micrograms (µg).

c. Procedure.

(1) Samples were injected into the gas chromatograph at an adjusted injection volume so that the concentration would be within the concentration of the prepared standard curves. Sample dilution was therefore unnecessary.

(2) Samples from the first and second rinses were analyzed using the column temperature program. Samples from the third rinse were analyzed using the isothermal column temperature. This was done because samples from the third rinse had the lowest ester concentrations and the solvent interfered with the 2,4-D n-Butyl ester peak when using the temperature program.

(3) Concentration of the samples was calculated using the standard curves. The value obtained was in micrograms per microliter which was then converted to milligrams per liter of sample.

5. Analytical Results and Discussion of Drum Rinse Samples

a. Presentation of Analytical Results.

(1) Analytical results were obtained for each individual nb 2,4-D and nb 2,4,5-T ester in each rinse sample (mg/L). These data were reduced to determine the:

(a) Mass (gm) of each ester and the sum of both esters' masses in each rinse volume,

(b) Accumulated (acc.) mass in grams of each ester and the sum of both esters' masses in the accumulated rinse volume, and

(c) Fraction of accumulated mass of each ester and sum of both esters' masses in the accumulated rinse volume as a percent of the accumulated ester(s) removed in all three rinses.

(2) These reduced data as well as statistical qualities on them are presented in Tables F-2 through F-5. The data points were highly variable with many standard deviations large when compared to a mean value. Whenever possible, statistical comparisons were performed on the data to determine the significance between data sets at or above the 90% confidence level.

(3) TCDD was not analyzed in the rinse samples, but the samples were saved should any need arise. Since TCDD has similar solubility to 2,4-D and 2,4,5-T esters in organic solvents, its removal from the drums was based on the removal efficiencies found for 2,4-D and 2,4,5-T.

b. Relative Removals of Each Ester.

(1) Review of the data in Tables F-2 through F-5 revealed that the 2,4-D mass in a rinse was almost always greater than the 2,4,5-T mass in the rinse. This was expected since the blended herbicide analyses, Table G-1, showed that nb 2,4-D and nb 2,4,5-T esters, respectively, averaged 50.90 and 43.78 percent of the herbicide total weight. Figure F-1 considers the 2,4-D and 2,4,5-T nb esters to be 100 percent of the total herbicide in the rinse and presents the average mass percentage of each of these esters in each rinse for all drums. Also shown is the mass percent of these esters when they are considered to be 100 percent of the herbicide total mass rather than their average 94.68 percent. Similarily,

TABLE F-2: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET A

Drum Set "A" EHL(K) Drum Numbers 63/64/74/75/76/77/91

Rinses: 1 | 2 | 3
Gal/Rinse: 5 | 5 | 5

Date Collected: 3-4 Dec 73
Date Analyzed: 17 ~~Dec 73~~ 8 Jan 74
Collectors: DiLorenzo/Knerl
Chemists: Hodgkinson/Rodriguez

| SAMPLE NO. | Drain or Drip Time (Min) | nb 24D ester gm/rinse 1 | 2 | 3 | nb 24D ester Acc. gm/rinse % Total 1 | 2 | 3 | nb 245T ester gm/rinse 1 | 2 | 3 | nb 245T ester Acc. gm/rinse % Total 1 | 2 | 3 | nb Total Esters gm/rinse 1 | 2 | 3 | nb Total Esters Acc. gm/rinse % Total 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A-63 | 9 | 179.4 | 32.17 | 16.45 | 178.4<br>78.7 | 211.6<br>92.8 | 228.0 | 173.7 | 27.82 | 9.88 | 173.7<br>82.2 | 201.5<br>95.3 | 211.4 | 353.1 | 60.0 | 26.3 | 353.1<br>80.4 | 413.1<br>94.0 | 439.4 |
| A-64 | 7 | 162.4 | 41.07 | 1.10 | 162.4<br>79.4 | 203.5<br>99.5 | 204.6 | 153.3 | 33.50 | 0.62 | 153.3<br>81.8 | 186.8<br>99.7 | 187.4 | 315.7 | 74.6 | 1.7 | 315.7<br>80.5 | 390.3<br>99.6 | 392.0 |
| A-74 | 8 | 176.0 | 19.49 | 6.25 | 176.0<br>87.2 | 195.5<br>96.9 | 201.7 | 166.9 | 10.03 | 2.21 | 166.9<br>93.2 | 176.9<br>98.8 | 179.1 | 342.9 | 29.5 | 8.5 | 342.9<br>90.0 | 372.4<br>97.8 | 380.9 |
| A-75 | 7 | 128.3 | 10.22 | 7.12 | 128.3<br>88.1 | 138.5<br>95.1 | 145.6 | 131.7 | 4.92 | 2.63 | 131.7<br>94.6 | 136.6<br>98.1 | 139.3 | 260.0 | 15.1 | 9.8 | 260.0<br>91.3 | 275.1<br>96.6 | 284.9 |
| A-76 | 8 | 173.7 | 15.52 | 6.66 | 173.7<br>88.7 | 189.2<br>96.6 | 195.9 | 169.2 | 7.38 | 2.42 | 169.2<br>94.5 | 176.6<br>98.6 | 179.0 | 342.9 | 22.9 | 9.1 | 342.9<br>91.5 | 365.8<br>97.6 | 374.9 |
| A-77 | 8 | 156.7 | 43.53 | 27.73 | 156.7<br>68.7 | 200.2<br>87.8 | 228.0 | 151.0 | 30.66 | 15.29 | 151.0<br>76.7 | 181.7<br>92.2 | 197.0 | 307.7 | 74.2 | 43.0 | 307.7<br>72.4 | 381.9<br>89.9 | 424.9 |
| A-91 | 8 | 135.1 | 12.11 | 7.31 | 135.1<br>87.4 | 147.2<br>95.3 | 154.5 | 139.7 | 6.06 | 2.78 | 139.7<br>94.0 | 145.8<br>98.1 | 148.5 | 274.8 | 18.2 | 10.1 | 274.8<br>90.7 | 293.0<br>96.7 | 303.1 |
| Ave ($\bar{x}$)<br>Std D. ($\delta$)<br>Ave ($\bar{x}$)<br>Std D. ($\delta$) | | 158.8<br>20.2 | 24.87<br>13.89 | 10.37<br>8.90 | 158.8<br>20.2<br>82.6<br>7.4 | 183.7<br>28.8<br>94.8<br>3.7 | 194.0<br>32.6 | 155.1<br>15.8 | 17.19<br>12.80 | 5.12<br>5.38 | 155.1<br>15.8<br>88.1<br>7.6 | 172.3<br>23.0<br>97.3<br>2.6 | 177.4<br>25.6 | 313.9<br>35.8 | 42.1<br>26.6 | 15.5<br>14.2 | 313.8<br>35.8<br>85.3<br>7.5 | 355.9<br>51.6<br>96.0<br>3.2 | 371.4<br>58.0 |

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TABLE F-3: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET B

Drum Set "B" EHL(K) Drum Numbers 62/66/68/73/82/85/90

Rinses: 1 2 3 | Gal/Rinse: 3 3 3

Date Collected: 3-4 Dec 73 | Date Analyzed: 17 Dec 73- 8 Jan 74

Collectors: DiLorenzo/Knerl

Chemists: Hodgkinson/Rodriguez

| SAMPLE NO. | Drain or Drip Time (Min) | nb 24D ester gm/rinse 1 | 2 | 3 | nb 24D ester Acc. gm/rinse % Total 1 | 2 | 3 | nb 245T ester gm/rinse 1 | 2 | 3 | nb 245T ester Acc. gm/rinse % Total 1 | 2 | 3 | nb Total Esters gm/rinse 1 | 2 | 3 | nb Total Esters Acc. gm/rinse % Total 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B-62 | 9 | 68.8 | 8.86 | 4.66 | 68.8<br>83.6 | 77.7<br>94.3 | 82.3 | 68.1 | 4.66 | 1.67 | 68.1<br>91.5 | 72.8<br>97.8 | 74.4 | 136.9 | 13.5 | 6.3 | 136.9<br>87.3 | 150.4<br>96.0 | 156.8 |
| B-66 | 8 | 94.0 | 7.04 | 0.90 | 94.0<br>92.2 | 101.0<br>99.1 | 101.9 | 81.8 | 4.20 | 0.49 | 81.8<br>94.6 | 86.0<br>99.4 | 86.5 | 175.8 | 11.2 | 1.4 | 175.8<br>73.3 | 187.0<br>99.3 | 188.4 |
| B-68 | 7 | 158.1 | 36.00 | 5.45 | 158.1<br>79.2 | 194.1<br>97.3 | 199.6 | 149.9 | 22.14 | 2.46 | 149.9<br>85.9 | 172.0<br>98.6 | 174.5 | 308.0 | 58.1 | 7.9 | 308.0<br>82.3 | 366.1<br>97.9 | 374.1 |
| B-73 | 8 | 103.6 | 5.34 | 0.65 | 103.6<br>94.5 | 108.9<br>99.4 | 109.6 | 97.4 | 3.18 | 0.41 | 97.4<br>96.4 | 100.6<br>99.6 | 101.0 | 201.0 | 8.5 | 1.1 | 201.0<br>95.5 | 209.5<br>99.5 | 210.6 |
| B-82 | 6 | 81.8 | 4.20 | 0.78 | 81.8<br>94.3 | 86.0<br>99.1 | 86.8 | 86.5 | 2.73 | 0.39 | 86.5<br>96.5 | 89.2<br>99.6 | 89.6 | 168.3 | 6.9 | 1.2 | 168.3<br>95.4 | 175.2<br>99.3 | 176.4 |
| B-85 | 7 | 62.7 | 15.22 | 3.12 | 62.7<br>77.4 | 77.9<br>96.2 | 81.0 | 65.4 | 8.29 | 1.23 | 65.4<br>87.3 | 73.7<br>98.4 | 74.9 | 128.1 | 23.5 | 4.4 | 128.1<br>82.1 | 151.6<br>97.2 | 156.0 |
| B-90 | 8 | 122.6 | 11.24 | 0.41 | 122.6<br>91.3 | 133.8<br>99.7 | 134.3 | 110.4 | 6.70 | 0.23 | 110.4<br>94.1 | 117.1<br>99.8 | 117.3 | 233.0 | 17.9 | 0.6 | 233.0<br>92.6 | 250.9<br>99.7 | 251.6 |
| Ave ($\bar{x}$) | | 98.8 | 12.56 | 2.28 | 98.8 | 111.4 | 113.6 | 94.2 | 7.41 | 0.98 | 94.2 | 101.6 | 102.6 | 193.0 | 20.0 | 3.3 | 193.0 | 212.9 | 216.3 |
| Std D. ($\delta$) | | 33.2 | 10.99 | 2.11 | 32.2 | 41.6 | 42.3 | 29.1 | 6.78 | 0.84 | 29.2 | 34.7 | 35.1 | 62.1 | 17.8 | 2.7 | 62.1 | 76.0 | 77.2 |
| Ave ($\bar{x}$) | | | | | 87.5 | 97.9 | | | | | 92.3 | 99.0 | | | | | 89.8 | 98.4 | |
| Std D. ($\delta$) | | | | | 7.3 | 2.0 | | | | | 4.3 | 0.8 | | | | | 5.9 | 1.4 | |

TABLE F-4: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET C

Drum Set "C" EHL(K) Drum Numbers 71/81/83/86/88/89/92

| Rinses | 1 | 2 | 3 |
|---|---|---|---|
| Gal/Rinse | 2 | 2 | 2 |

Date Collected: 3-4 Dec 73
Date Analyzed: 17 Dec 73 - 8 Jan 74

Collectors: DiLorenzo/Knerl
Chemists: Hodgkinson/Rodriguez

| SAMPLE NO. | Drain or Drip Time (Min) | nb 24D ester gm/rinse 1 | 2 | 3 | Acc. gm/rinse % Total 1 | 2 | 3 | nb 245T ester gm/rinse 1 | 2 | 3 | Acc. gm/rinse % Total 1 | 2 | 3 | nb Total Esters gm/rinse 1 | 2 | 3 | Acc. gm/rinse % Total 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C-71 | 6 | 82.2 | 6.59 | 0.81 | 82.2<br>91.7 | 88.8<br>99.1 | 89.6 | 75.9 | 3.86 | 0.43 | 75.9<br>94.7 | 79.8<br>99.5 | 80.2 | 158.1 | 10.5 | 1.2 | 158.1<br>93.1 | 168.6<br>99.3 | 169.8 |
| C-81 | 7 | 55.0 | 5.00 | 1.20 | 55.0<br>89.9 | 60.0<br>98.0 | 61.2 | 49.5 | 2.80 | 0.64 | 99.5<br>93.5 | 52.3<br>98.8 | 52.9 | 109.5 | 7.8 | 1.8 | 104.5<br>91.6 | 112.3<br>98.4 | 114.1 |
| C-83 | 8 | 105.4 | 9.84 | 2.45 | 105.4<br>89.6 | 115.2<br>97.9 | 117.7 | 99.0 | 5.83 | 1.26 | 99.0<br>93.3 | 104.8<br>98.8 | 106.1 | 204.4 | 15.7 | 3.7 | 204.4<br>91.3 | 220.1<br>98.3 | 223.8 |
| C-86 | 7 | 104.5 | 15.29 | 1.76 | 104.5<br>86.0 | 119.8<br>98.6 | 121.6 | 97.7 | 9.24 | 0.91 | 97.7<br>90.6 | 106.9<br>99.2 | 107.9 | 202.2 | 24.5 | 2.7 | 202.2<br>88.1 | 226.7<br>98.8 | 229.4 |
| C-88 | 6 | 80.8 | 7.80 | 1.70 | 80.8<br>89.5 | 88.6<br>98.1 | 90.3 | 74.0 | 4.47 | 0.90 | 74.0<br>93.2 | 78.5<br>98.9 | 79.4 | 154.8 | 12.3 | 2.6 | 154.8<br>91.2 | 167.1<br>98.5 | 169.7 |
| C-89 | 8 | 125.8 | 18.17 | 1.42 | 125.8<br>86.5 | 144.0<br>99.0 | 145.4 | 119.9 | 16.35 | 0.74 | 119.9<br>87.5 | 136.3<br>99.5 | 137.0 | 245.7 | 34.5 | 2.2 | 245.7<br>87.0 | 280.2<br>99.2 | 282.4 |
| C-92 | 7 | 107.2 | 13.93 | 1.70 | 107.2<br>87.3 | 121.1<br>98.6 | 122.8 | 102.2 | 8.93 | 0.90 | 102.2<br>91.2 | 111.1<br>99.2 | 112.0 | 209.4 | 22.9 | 2.6 | 209.4<br>89.2 | 232.3<br>98.9 | 234.9 |
| Ave ($\bar{x}$) | | 94.4 | 10.94 | 1.58 | 94.4 | 105.4 | 106.9 | 88.3 | 7.35 | 0.83 | 88.3 | 95.7 | 96.5 | 182.7 | 18.3 | 2.4 | 182.7 | 201.0 | 203.4 |
| Std D. ($\delta$) | | 23.3 | 4.92 | 0.51 | 23.3 | 27.9 | 28.1 | 23.3 | 4.67 | 0.26 | 23.3 | 27.5 | 27.6 | 46.6 | 9.5 | 0.8 | 46.6 | 55.3 | 55.6 |
| Ave ($\bar{x}$) | | | | | 88.6 | 98.5 | | | | | 92.0 | 99.1 | | | | | 90.2 | 98.8 | |
| Std D. ($\delta$) | | | | | 2.1 | 0.5 | | | | | 2.4 | 0.3 | | | | | 2.2 | 0.4 | |

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TABLE F-5: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET D

Drum Set "D" EHL(K) Drum Numbers 65/69/70/78/80/84/87

| Rinses | 1 | 2 | 3 |
|---|---|---|---|
| Gal/Rinse | 5 | 3 | 2 |

Date Collected: 3-4 Dec 73 Collectors: DiLorenzo/Knerl

Date Analyzed: 17 Dec 73 Chemists: Hodgkinson/Rodriguez 8 Jan 74

| SAMPLE NO. | Drain or Drip Time (Min) | nb 24D ester gm/rinse 1 | 2 | 3 | nb 24D ester Acc. gm/rinse % Total 1 | 2 | 3 | nb 245T ester gm/rinse 1 | 2 | 3 | nb 245T ester Acc. gm/rinse % Total 1 | 2 | 3 | nb Total Esters gm/rinse 1 | 2 | 3 | nb Total Esters Acc. gm/rinse % Total 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| D-65 | 8 | 109.0 | 3.97 | 1.20 | 109.0<br>95.5 | 113.0<br>98.9 | 114.2<br>100.0 | 102.2 | 2.38 | 0.63 | 102.2<br>97.1 | 104.6<br>99.4 | 105.2 | 211.2 | 6.4 | 1.8 | 211.2<br>96.3 | 217.6<br>99.2 | 219.4 |
| D-69 | 7 | 138.5 | 8.40 | 0.60 | 138.5<br>93.9 | 146.9<br>99.6 | 147.5 | 127.2 | 4.88 | 0.28 | 127.2<br>96.1 | 132.1<br>99.8 | 132.4 | 265.7 | 13.3 | 0.90 | 265.7<br>94.9 | 279.0<br>99.7 | 279.9 |
| D-70 | 6 | 98.8 | 13.85 | 1.43 | 98.8<br>86.6 | 112.7<br>98.7 | 114.1 | 93.1 | 7.84 | 0.76 | 93.1<br>91.5 | 100.9<br>99.3 | 101.7 | 191.9 | 21.7 | 2.2 | 191.9<br>88.9 | 213.6<br>99.0 | 215.8 |
| D-78 | 6 | 118.1 | 7.04 | 0.89 | 118.1<br>93.7 | 125.1<br>99.3 | 126.0 | 109.0 | 4.20 | 0.48 | 109.0<br>95.9 | 113.2<br>99.6 | 113.7 | 227.1 | 11.2 | 1.4 | 227.1<br>94.7 | 238.3<br>99.4 | 239.7 |
| D-80 | 6 | 163.5 | 11.24 | 1.49 | 163.5<br>92.8 | 174.7<br>99.2 | 176.2 | 156.7 | 6.70 | 0.78 | 156.7<br>95.4 | 163.4<br>99.5 | 164.2 | 320.2 | 17.9 | 2.3 | 320.2<br>94.1 | 338.1<br>99.3 | 340.4 |
| D-84 | 7 | 159.0 | 26.57 | 1.46 | 159.0<br>85.0 | 185.6<br>99.2 | 187.0 | 149.9 | 16.81 | 0.77 | 149.9<br>89.5 | 166.7<br>99.5 | 167.5 | 308.9 | 43.4 | 2.2 | 308.9<br>87.1 | 352.3<br>99.4 | 354.5 |
| D-87 | 8 | 120.4 | 55.64 | 1.45 | 120.4<br>67.8 | 176.0<br>99.2 | 177.5 | 117.0 | 51.32 | 0.79 | 117.0<br>69.2 | 168.3<br>99.5 | 169.1 | 237.4 | 107.0 | 2.2 | 237.4<br>68.5 | 344.4<br>99.4 | 346.6 |
| Ave ($\bar{x}$) | | 129.6 | 18.10 | 1.22 | 129.6 | 147.7 | 149.0 | 122.1 | 13.45 | 0.64 | 122.2 | 135.6 | 136.3 | 251.8 | 31.0 | 1.9 | 251.8 | 283.3 | 285.2 |
| Std D. ($\delta$) | | 24.8 | 18.08 | 0.35 | 24.8 | 31.4 | 31.5 | 23.9 | 17.34 | 0.20 | 23.9 | 30.2 | 30.3 | 48.6 | 35.8 | 0.5 | 48.6 | 61.5 | 61.7 |
| Ave ($\bar{x}$) | | | | | 87.9 | 99.2 | | | | | 90.7 | 99.5 | | | | | 89.2 | 99.3 | |
| Std D. ($\delta$) | | | | | 9.7 | 0.3 | | | | | 9.9 | 0.2 | | | | | 9.7 | 0.2 | |

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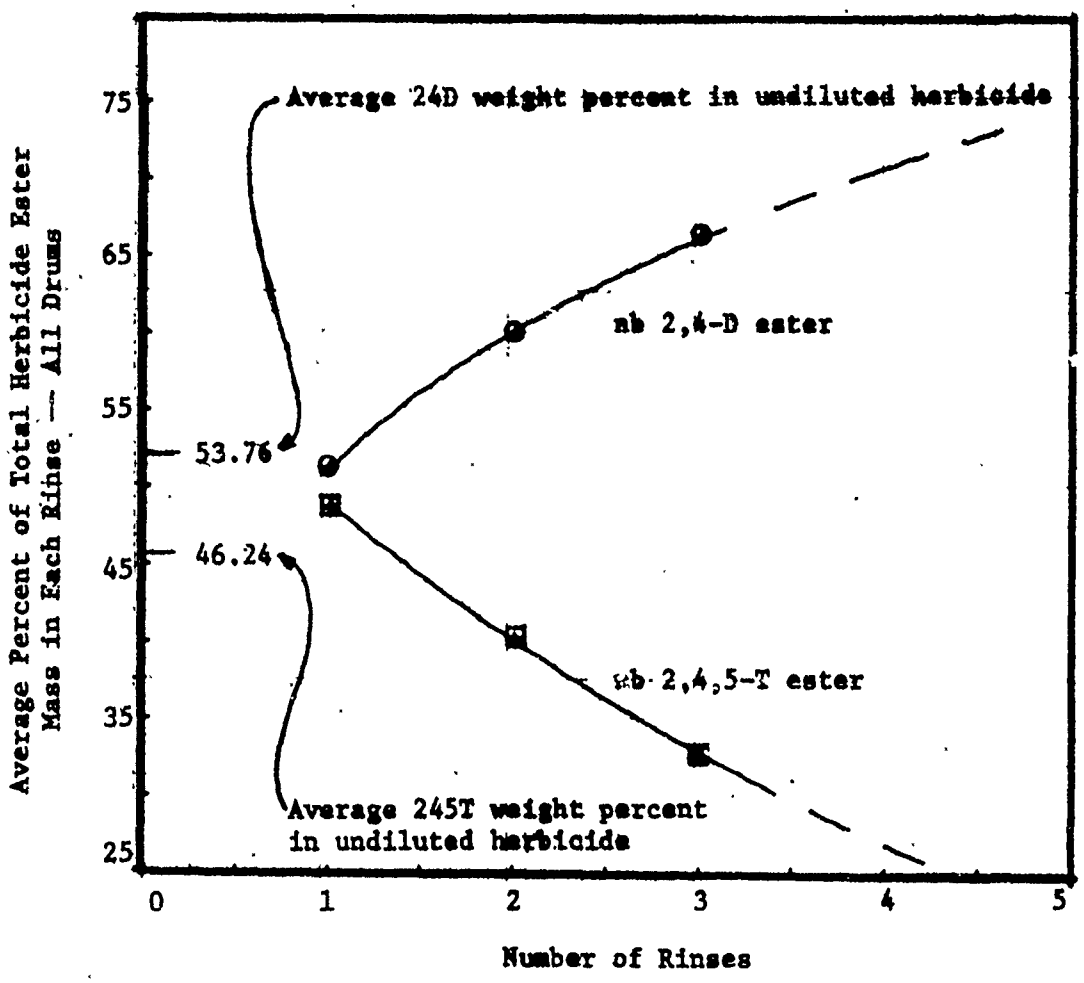



FIGURE F-1: WEIGHT PERCENT OF 2,4-D AND 2,4,5-T ESTERS OF TOTAL HERBICIDE IN EACH RINSE

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Figure F-2 gives, for all drums, the average accumulative mass percentage of each of these esters in the accumulative rinses.

(2) An evaluation of Figures F-1 and F-2 indicated that slightly more of an original mass of nb 2,4,5-T ester was removed from a drum during its first rinse than was the nb 2,4-D ester. This better proportional removal of an original 2,4,5-T mass appeared independent of the solvent volume used in the initial rinse. Apparently, in the competing solubilities, 2,4,5-T was absorbed more rapidly than 2,4-D in an initial rinse of JP-4. The proportion of 2,4,5-T decreased markedly in successive rinses because a larger fraction of it had already been removed. The accumulative three-rinse effect of this phenomenae was less dramatic than the individual rinses but still showed a proportionately higher average removal (106%) of original masses of 2,4,5-T than 2,4-D, respectively, from the drums.

c. Estimate of Herbicide Mass in Drum.

(1) The average accumulative mass of total esters in the accumulative rinses and the average mass of total esters in each rinse are plotted for each drum set in Figures F-3 and F-4, respectively. The curves in both figures were fitted by regression analyses and found to best fit power equations (Figure F-3) and exponential decay equations (Figure F-4). Data in both figures indicated that ester mass removal in the rinses was controlled by a first order absorption isotherm. There was no significant difference in the total herbicide mass in drum set "B" and "C" rinses which was only 70 to 80 percent of the mass in drum set "A" and "D" rinses.

(2) Drum set "A" rinses contained significantly higher amounts of total herbicide mass on a per rinse basis and on an accumulative basis. Drum set "A" rinses removed more herbicide from the drums and this set's data were used to estimate the average total herbicide mass originally in the drums. Applying the principle of first order decay, the seventh rinse or 35th accumulative gallon of rinse should remove an estimated 99 plus percent of the drum's herbicide mass. The equations of best fit were then used for the seventh rinse and 450 ($\pm$ 25) grams of herbicide were concluded to be the best estimate of original mass of herbicide in drum.

d. Herbicide Removal Per Gallon of Rinse Used.

(1) Table F-6 presents the accumulative herbicide mass per gallon of accumulative rinse for each drum in all drum sets. The data in Table F-6 were statistically compared with each other for herbicide mass per accumulated gallon of rinse. At the 95% confidence level, these comparisons showed that:

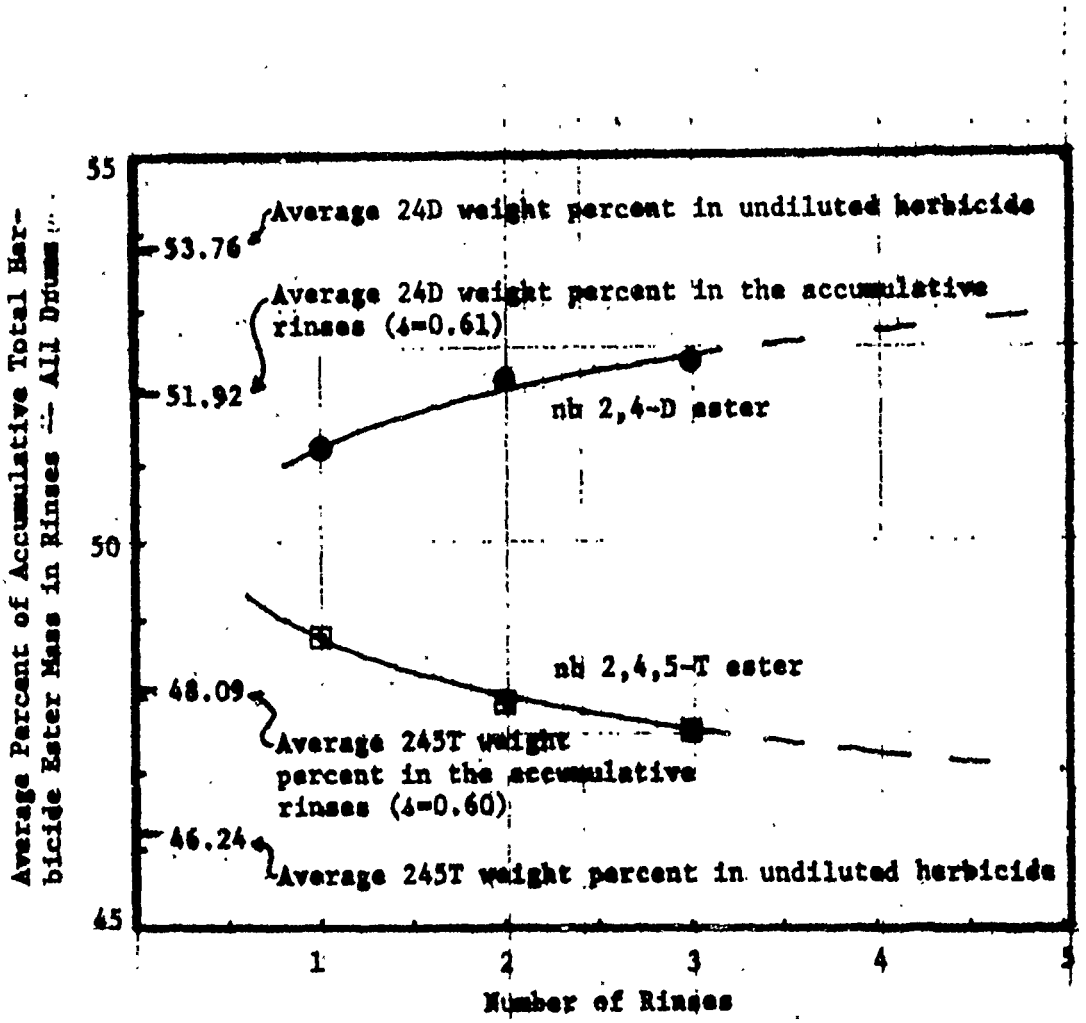



FIGURE F-2: WEIGHT PERCENT OF 2,4-D and 2,4,5-T ESTERS OF TOTAL HERBICIDE IN ACCUMULATED DRUM RINSINGS.

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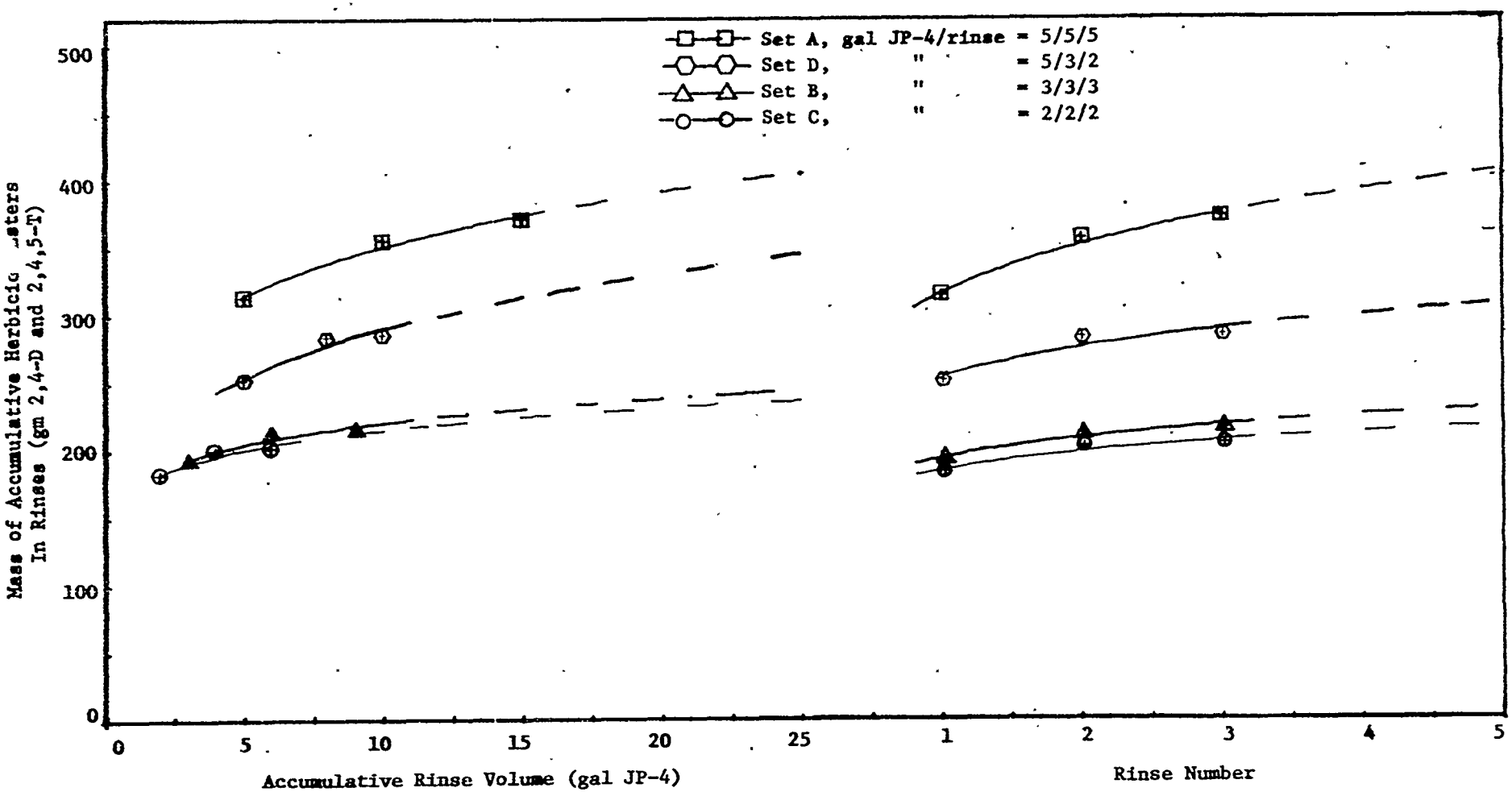



FIGURE F-3: MASS OF ACCUMULATIVE HERBICIDE ESTERS IN RINSES vs ACCUMULATIVE RINSE VOLUMES AND RINSE NUMBERS

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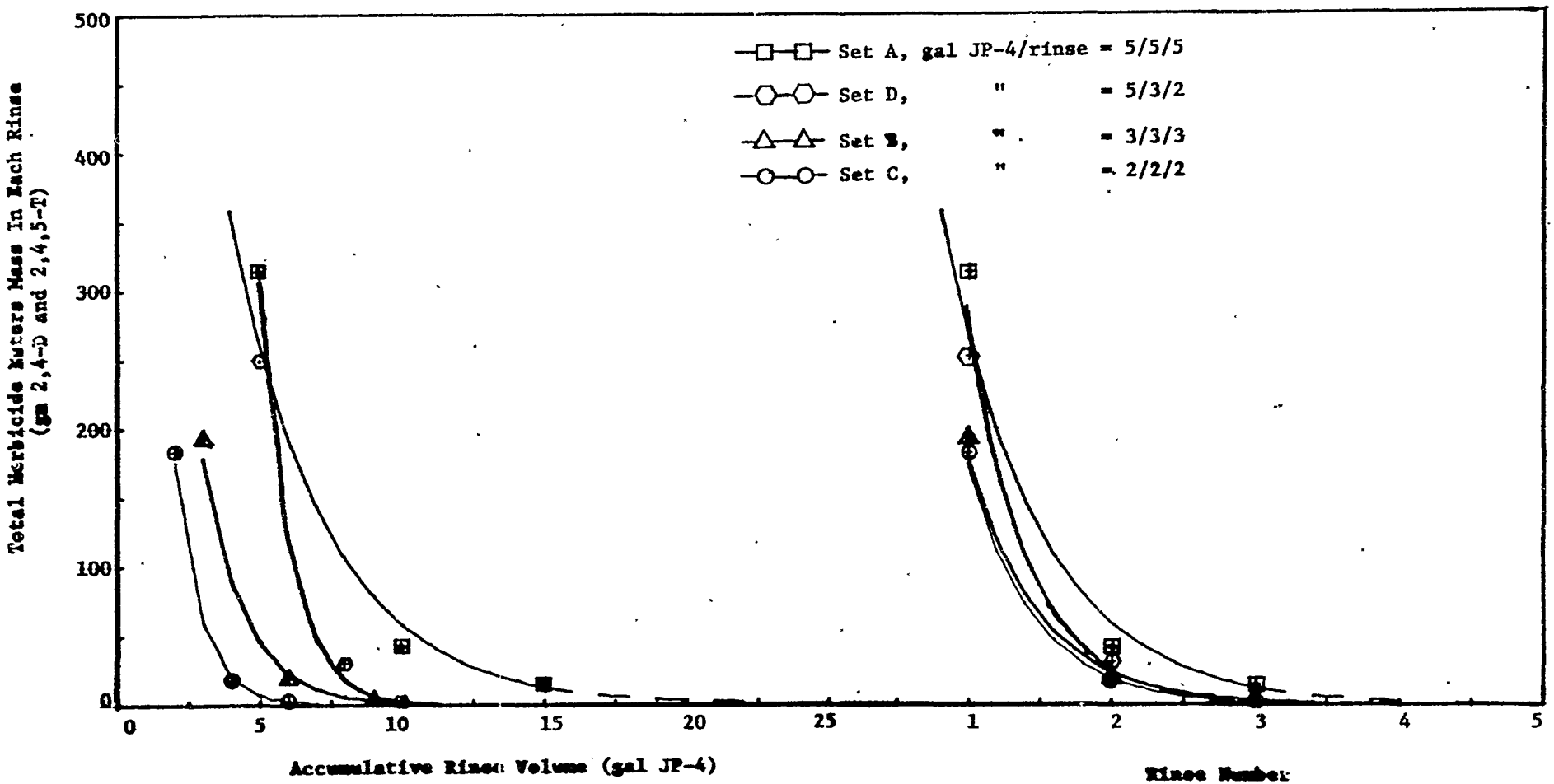



FIGURE F-4: MASS OF TOTAL HERBICIDE ESTERS IN EACH RINSE vs ACCUMULATIVE RINSE VOLUMES AND RINSE NUMBERS

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(a) Variances of herbicide mass per accumulated gallon of rinse for the following cases were:

1 Equal for rinse gallon combinations of 5,3,5, and 2/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 3 to 5 gallons.

2 Equal for rinse gallon combinations of 5/5, 3/3, 5/3, and 2/2/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 6 to 10 gallons.

3 Equal for rinse gallons combinations of 5/5/5, 3/3/3, and 5/3/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 9 to 15 gallons.

4 Unequal for any rinse gallon combinations or their pooled variances when compared to the single rinse of 2 gallons.

(b) Means of herbicide mass per accumulated gallon of rinse for the following cases were:

1 Equal for rinse gallon combinations of 5,3,5, and 2/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled mean. Note range of rinse gallons: 3 to 5 gallons.

2 Equal for rinse gallon combinations of 5/5, 3/3, 5/3, and 2/2/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled means. Note range of rinse gallons: 6 to 10 gallons.

3 Equal for rinse gallon combinations of 5/5/5, 3/3/3, and 5/3/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled means. Note range of rinse gallons: 9 to 15 gallons.

4 Uneq al for any rinse gallon combinations or their pooled means when compared to the single rinse of 2 gallons.

(c) Rinses with smaller volumes caused significantly higher variances in performance. The three gallon rinses had dramatically less variance than the two gallon rinses.

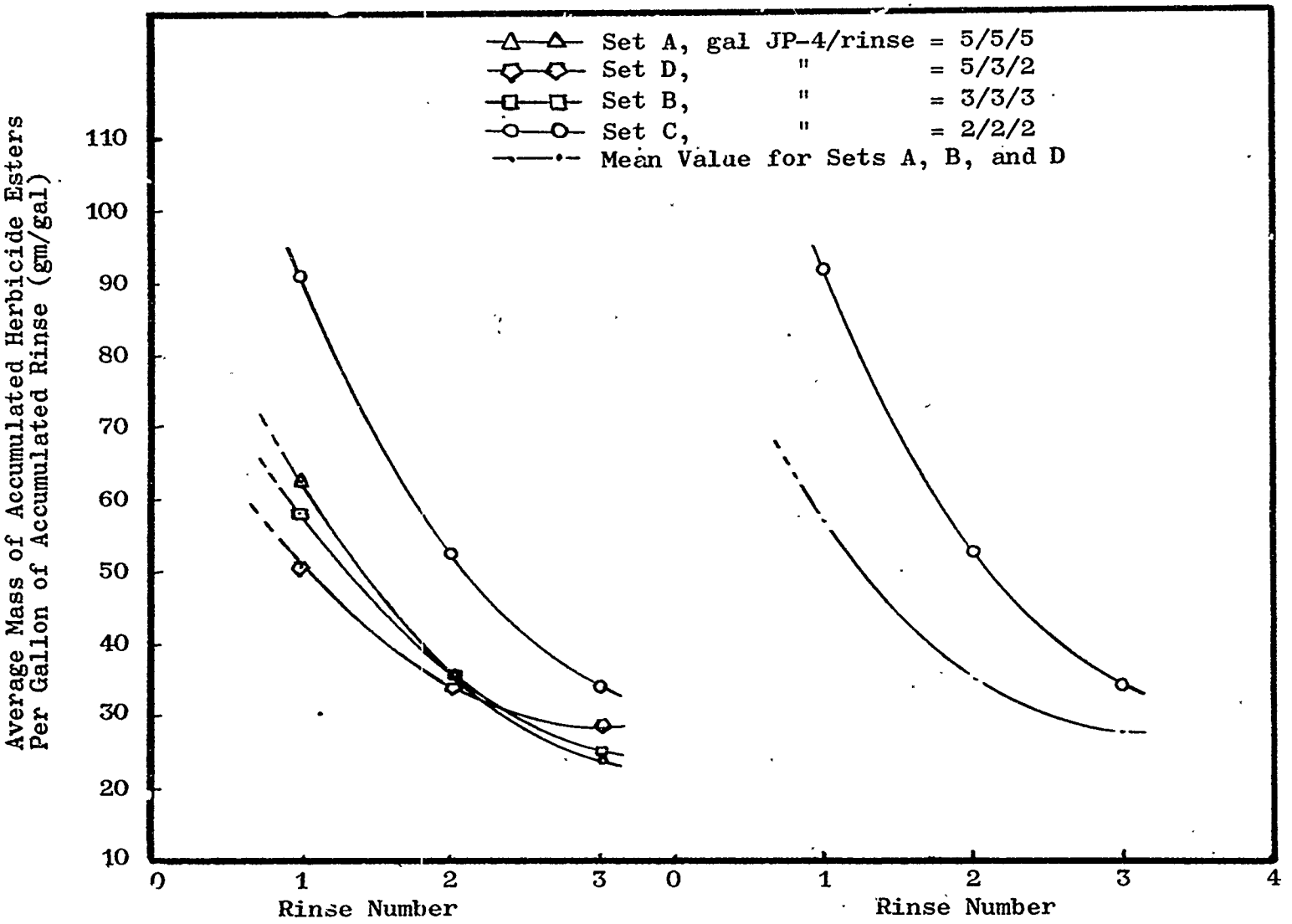
(2) Considering these statistical evaluations, the data of Table F-6 were plotted in Figure F-5 against rinse number and in Figure F-6 against accumulative rinse volume. Interpretation of these figures indicated that:

**TABLE F-6: Accumulative Herbicide Mass Per Gallon of Rinse**

| Drum Set | Acc. Mass of Herbicide Esters Per Acc. Gal. Rinse (gm/gal) Rinse Number/ Acc. Rinse Volume (gal JP-4) | | | Drum Set | Acc. Mass of Herbicide Esters Per Acc. Gal. Rinse (gm/gal) Rinse Number/ Acc. Rinse Volume (gal JP-4) | | |
|---|---|---|---|---|---|---|---|
| A | 1/5 | 2/10 | 3/15 | C | 1/2 | 2/4 | 3/6 |
| | 70.62 | 41.31 | 29.29 | | 79.05 | 42.15 | 28.30 |
| | 63.14 | 39.03 | 26.13 | | 52.25 | 28.08 | 19.02 |
| | 68.58 | 37.24 | 25.39 | | 102.20 | 55.03 | 37.30 |
| | 52.00 | 27.51 | 18.99 | | 101.10 | 56.68 | 38.23 |
| | 68.58 | 36.58 | 24.99 | | 77.40 | 41.78 | 28.28 |
| | 61.54 | 38.19 | 28.33 | | 122.85 | 70.05 | 47.07 |
| | 54.96 | 29.30 | 20.21 | | 104.70 | 58.08 | 39.15 |
| $\bar{x}$ | 62.77 | 35.59 | 24.76 | $\bar{x}$ | 91.36 | 50.26 | 33.91 |
| $s$ | 7.16 | 5.16 | 3.86 | $s$ | 23.30 | 13.82 | 9.27 |
| $s^2$ | 51.30 | 26.64 | 14.93 | $s^2$ | 542.99 | 191.09 | 85.95 |
| B | 1/3 | 2/6 | 3/9 | D | 1/5 | 2/8 | 3/10 |
| | 45.63 | 25.07 | 17.42 | | 42.24 | 27.20 | 21.94 |
| | 58.60 | 31.17 | 20.93 | | 53.14 | 34.88 | 27.99 |
| | 102.67* | 61.02* | 41.57* | | 38.38 | 26.70 | 21.58 |
| | 67.00 | 34.92 | 23.40 | | 45.42 | 29.79 | 23.97 |
| | 56.10 | 29.20 | 18.60 | | 64.04 | 42.26 | 34.04 |
| | 42.70 | 25.27 | 17.33 | | 61.78 | 44.04 | 35.45 |
| | 77.67 | 41.82 | 27.96 | | 47.48 | 43.05 | 34.66 |
| $\bar{x}$ | 57.95 | 31.24 | 21.10 | $\bar{x}$ | 50.35 | 35.42 | 28.52 |
| $s$ | 13.11 | 6.38 | 4.06 | $s$ | 9.72 | 7.69 | 6.17 |
| $s^2$ | 171.79 | 40.67 | 16.48 | $s^2$ | 94.57 | 59.15 | 38.11 |

*Considered to be a possible outlier and not used in statistical calculation.

FIGURE F-5: Average Mass of Accumulated Herbicide Esters Per Gallon of Accumulated Rinse vs Rinse Numbers






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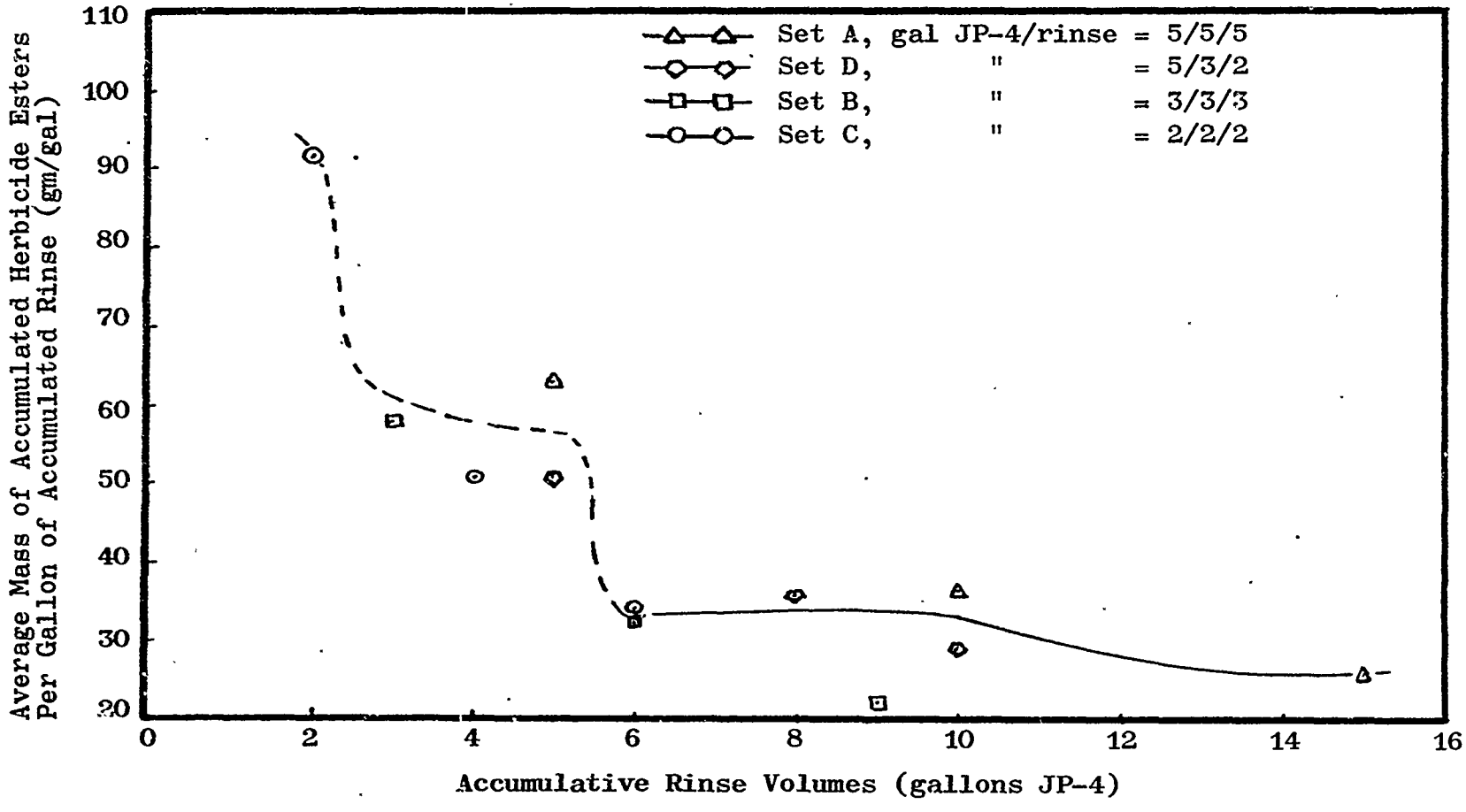



FIGURE F-6: Average Mass of Accumulated Esters Per Gallon of Accumulative Rinse vs Accumulated Rinse Volumes

(a) Herbicide removal per gallon of solvent was essentially independent of any two applied rinse volumes whose accumulative total volume was <5 gallons, 6 to 10 gallons, and 11 to 15 gallons. However, a more consistently average performance could be expected if volume per rinse were maximized within each of these volumetric groupings, i.e., use a single rinse of 5 gallons if total rinse volume is <5 gallons; use two rinse volumes of 3/3, 4/4, or 5/5 gallons if total rinse volume is between 6 and 10 gallons; etc.

(b) The difference in average performance diminished between rinse sets on the third rinse because ≥50% of the herbicide had been removed from the drum and each rinse set had approached its respective plateau for herbicide removal per rinse (see Figures F-3 and F-4).

e. Estimate of Herbicide Removal Efficiency.

(1) The accumulative mass of total herbicide in each rinse volume was compared to the estimated 450 grams of total herbicide in each drum. Percent removal of this estimated amount of herbicide after two rinses was 79.1% for "A", 63.0% for "D", 47.3% for "B", and 44.7% for "C." Regardless of rinse volume used, the third rinse improved the overall herbicide removal efficiency by less than 3%.

(2) Percents of original herbicide remaining in the drum were calculated for each drum set and plotted against accumulative rinse volume in Figure F-7. The five gallon rinses left 15 to 30 percent less herbicide in the drums than did any other rinses. It was thus concluded that given two or three rinses whose total volume was less than 10 gallons, the optimal removal efficiency (79.1% for the total gallons used) was achieved using two rinses of five gallons each.

6. Conclusions and Recommendations

a. Herbicide mass removal from the drums using JP-4 appeared to be dependent upon the applied rinse volume and to follow a first order absorption isotherm.

b. Accumulative mass of herbicide in the accumulative JP-4 rinses were fitted quite well to exponential curves which were used to estimate the original mass of total herbicide in the drained drums: 450 ($\pm$ 25) grams.

c. Based upon the original weights of 2,4-D and 2,4,5-T esters in the herbicide, proportionately more 2,4,5-T ester mass than 2,4-D ester mass was removed in the first JP-4 rinse. These proportions reversed during the following rinses, but the accumulative effect was that about 106 percent more 2,4,5-T ester mass was removed than was the 2,4-D ester mass.

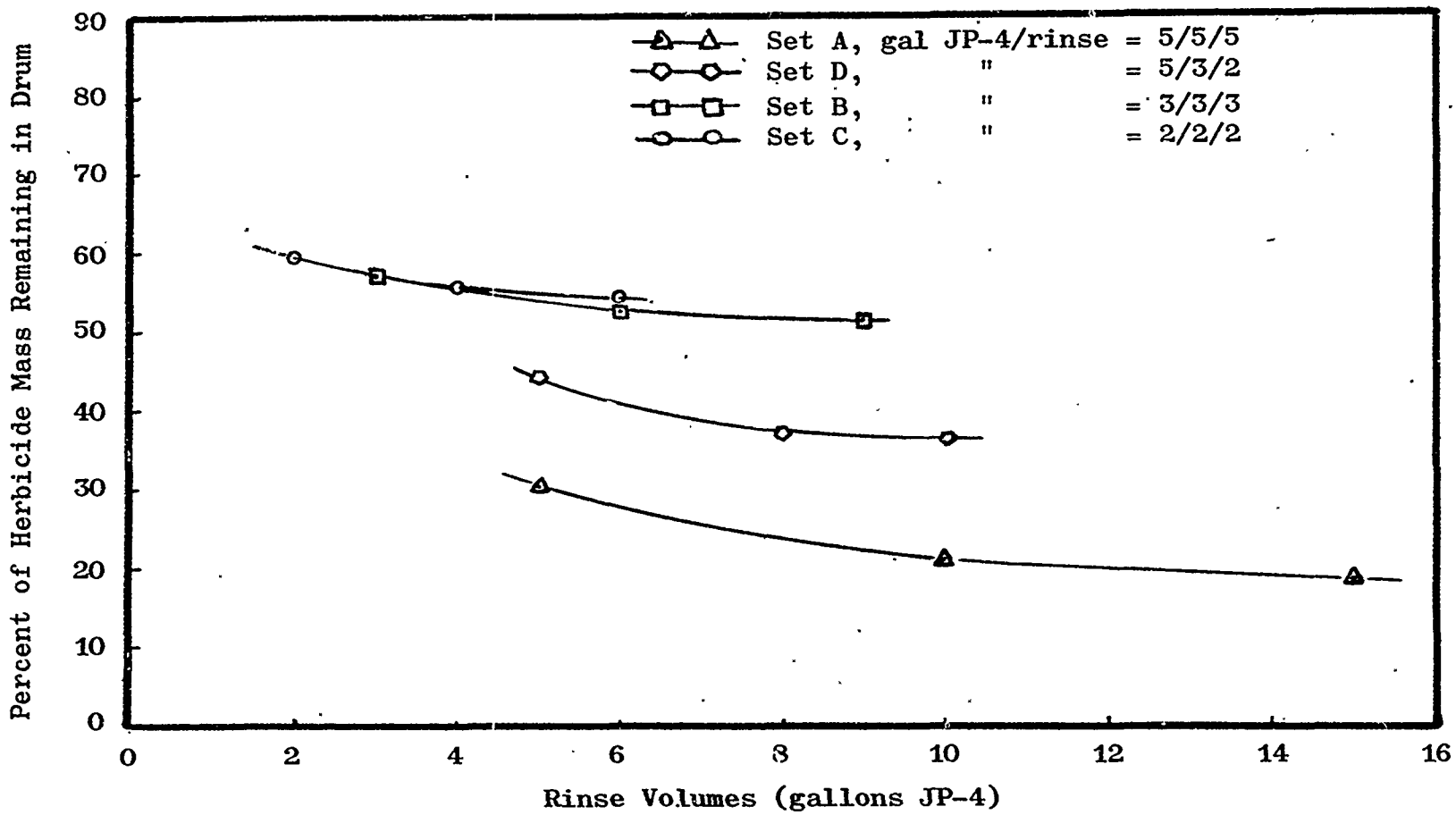



FIGURE F-7: Percent of Herbicide Mass Remaining in Drums vs Applied Rinse Volumes

d. Removing drum ends and spraying the rinse downward through an open drum would provide better herbicide removal efficiency per gallon of rinse used. This is because successive rinses could be thoroughly drained from the drum. Since such draining could not be achieved in this test program, 10 to 25 percent improved results could be expected depending on rinse volumes used.

e. Depending on ultimate drum disposal, desired drum cleanliness, and availability of rinse (JP-4), this program concluded that under the following two constraints, separate rinse procedures could be used to obtain maximum results:

(1) Limited supplies of JP-4 rinse ($\leq$5 gallons per drum) and some cleaning desired. Use the five gallons in a single rinse to obtain minimal variation of drum cleanliness. Any volumetric rinses totaling five gallons per drum would remove about the same herbicide mass but would be more variable in performance.

(2) Up to 10 gallons of JP-4 rinse available per drum and optimal drum cleaning required--use two rinses of 5/5 gallons to remove the most herbicide from the drum, i.e., 79% compared to 45 to 63% for the rinse volumes of 2/2/2, 3/3/3, or 5/3/2 gallons.

(3) A third JP-4 rinse equal to or less than 5 gallons would not improve the overall removal efficiency by more than 3%.

f. No evidence exists to indicate that contaminated JP-4 could not be used to achieve the same drum cleaning performance as unused JP-4.

g. Calculations based on an average TCDD concentration of 13.25 mg/kg of herbicide showed that the mass of TCDD in these drained drums was 5.96 mg. This calculation of TCDD mass in the drum before and after rinses presented the worst case for all herbicide stocks because the TCDD in these 28 drums was 7 times greater than the average TCDD concentration in the Air Force stock (see paragraph 2.2). If TCDD removal efficiency was equal to the herbicide esters, then 1.25 mg of TCDD would have been in the drums after two JP-4 rinses of 5/5 gallons. Rinse samples were not analyzed for TCDD but were saved for analyses should they be needed to select a final drum disposal method.

h. The data of this study can be used to determine the volumetric rinses of unused or contaminated JP-4 needed to meet any prescribed drum cleaning requirements.

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E (F-27)

WEST COAST TECHNICAL SERVICE, INC.

# APPENDIX G

## (TO APPENDIX E)

## ORGANIC ANALYSES OF BLENDED HERBICIDE, COMBUSTION AND SCRUBBED EFFLUENT GASES, SPENT SCRUBBER WATER, AND RESIDUES

E(E-23)

# APPENDIX G

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WEST COAST TECHNICAL SERVICE INC / 17605 FABRICA WAY, SUITE D / CERRITOS, CA 90701

# REPORT

(213) 921-9831
(714) 523-9200

**date/** February 1, 1974 **job no./** 5252

**p.o. no./** 805137-1

**prepared for/**

Dr. R. P. Babbitt

The Marquardt Company
16555 Saticoy Street
Van Nuys, California 91409

The samples from the combustion of liquid herbicide have been analyzed by gas chromatography, combined gas chromatography-mass spectrometry, and/or atomic absorption. The various samples were processed prior to analysis by one of the procedures described below. In addition, extraction efficiency, sensitivity and detection limits for the various compounds were determined. These data are given below:

## I Procedures

### A. Equipment

#### 1. Mass Spectrometer

A DuPont Model 490 Mass Spectrometer was used for identification of the various components. The mass spectrometer was connected to the gas chromatograph through an all glass jet separator. All spectra were taken at an ionization voltage of 70e.v. The spectra were recorded on a recording oscillograph.

#### 2. Gas Chromatograph

A Varian Model 2700 Gas Chromatography equipped with a flame ionization detector was used for separation and quantization of all volatile components. The operating parameters were as follows:

Column -10 ft. x 1/8 inch stainless steel packed with 5% OV-17 on Chromsorb G (AW DMCS)
Detector - 325°C
Injector - 310°C
Flow Rate - 22cc/minute
Column Temperature - 165° - 310°C at 10°C/minute

#### 3. Atomic Absorption

A Perkin-Elmer Model 403 Atomic Absorption Spectrometer was used for determining the iron content of certain samples. The aqueous solutions were run against standard iron solutions. The iron content of the blended herbicide was determined by diluting the sample with xylene and running against an organo-iron standard dissolved in xylene.



This report pertains only to the samples investigated and does not necessarily apply to other apparently identical or similar materials. This report is submitted for the exclusive use of the client to whom it is addressed. Any reproduction of this report or use of this Laboratory's name for advertising or publicity purposes without written authorization is prohibited.

II Calibration

A standard solution containing the following material was prepared in benzene. This solution was used for calibration and determination of recovery efficiency. The solution contains 500 micrograms of the following compounds per milliliter of solution.

2,4-dichlorophenoxy acetic acid
2,4,5-trichlorophenoxy acetic acid
2,4-dichlorophenoxy acetic acid butylester
2,4,5-trichlorophenoxy acetic acid butylester
2,4,5-trichlorophenoxy acetic acid octylester
2,4-dichorophenol

In addition, the standard contained 51 micrograms of 2,3,7,8-tetrachlorodibenzo-p-dioxin per milliliter of solution. The standard solution was treated with diazomethane to convert the acids and phenol to the esters and ether. The sample was then diluted to volume and injected into the gas chromatograph, and the response of the various components determined. The detection limit for these compounds was determined. Since all test samples were taken to a final volume of 25 microliters, the absolute detection limits for the various components were calculated based on this volume. These limits are, therefore, the limit for the quantity present in the total sample.

The detection limits for the components of the standard solution were as follows:

| | Detection Limit Nanograms/Total Sample |
|---|---|
| 2,4-dichlorophenoxy acetic acid (methylester) | 22 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | 21 |
| 2,4-dichlorophenoxy acetic acid butylester | 23 |
| 2,4,5-trichlorophenoxy acetic acid butylester | 21 |
| 2,4,5-trichlorophenoxy acetic acid octylester | 19 |
| 2,4-dichlorophenol (methylether) | 29 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | 22 |

Previous calibration and stability tests show the detection limit to be valid to ± 10% of the value.

III Recovery Efficiency

The efficiency of extraction for the various compounds from a water solution was determined as follows: 1.00ml of the standard solution described in II above was pipetted into a 1 liter beaker. The benzene was removed under a nitrogen stream at 40°C. 500ml of tap water was added and the solution mixed. The water solution was then added to a separating funnel, made acid-pH-2, and extracted four (4) times with 50ml portions of diethylether. The ether extracts were combined, dried over anhydrous sodium sulfate, filtered and evaporated to a volume of 5cc. Excess diazomethane in ether was added and allowed to stand for 15 minutes as the solution evaporated under nitrogen at 40°C. The extract was then diluted to 1.00ml with benzene and analyzed by gas chromatography.

A 1.00ml volume of the standard solution was evaporated to dryness and treated with excess diazomethane for 15 minutes. The ether was then removed and the mixture diluted to 1.00ml with benzene. This solution was then analyzed by gas chromatography.

The recovery efficiency was calculated as the percentage of the standard components extracted from the water solution relative to that from the esterfied standard solution.

The recovery efficiency of the standard components were found to be as follows:

| | Efficiency of Recovery |
|---|---|
| 2,4-dichlorophenoxy acetic acid | 92% |
| 2,4,5-trichlorophenoxy acetic acid | 92% |
| 2,4-dichlorophenoxy acetic acid butylester | 96% |
| 2,4,5-trichlorophenoxy acetic acid butylester | 98% |
| 2,4,5-trichlorophenoxy acetic acid octylester | 97% |
| 2,4,-dichlorophenol | 72% |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | 93% |

IV Work Up and Analysis of Sample

A. Analysis of blended herbicide samples

0.5ml of the blended herbicide was tested with excess diazomethane to convert any acid or phenol present to the more volatile methyl derivation. The ether was removed at 40°C under a stream of nitrogen. The samples were then chromatographed and the composition of the mixture determined. The identity of the various components was determined on the first sample by a use of the combined gas chromatography-mass spectrometry. Subsequent samples were analyzed by gas chromatography only using the retention time from the original gas chromatography-mass spectrometry run for identification.

B. Analysis of combustion, scrubbed effluent, and miscellaneous gas impinger samples

The quantity of the benzene solutions was determined and recorded. The benzene was removed by distillation. The residue was treated with excess diazomethane in ether for 15 minutes and the ether removed at 40°C under a strear of nitrogen. The residue was then diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various compounds in the first sets of samples. Subsequent samples were analyzed by gas chromatography using the retention time data for identification.

The water layer from those samples which contained water were acidified to pH-2 with hydrochloric acid and extracted four (4) times with ether. The ether was dried over anhydrous sodium sulfate. The ether extract was then added to the corresponding benzene solution or treated with diazomethane and processed in a corresponding manner.

C. Analysis of fresh and spent scrubber waters

500ml of the scrubber water sample was acidified (pH-2) with concentrated hydrochloric acid. The water solution was then extracted four (4) times with ether. The ether was than dried and evaporated. The extract was treated with excess diazomethane after which the solvent was evaporated and the residue diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components from the first runs. Subsequent samples were analyzed by gas chromatography using the retention time data for identification. The presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin in sample III SSW TBC was confirmed by gas chromatography-mass spectrometry.

D. Analysis of combustion chamber residues

The hard carbonaceous reside was pulverized. A 100 gram sample was then extracted four (4) times with a boiling mixture of 75% benzene -25% methanol. The extracts were combined and the solvents removed by distillation. The residues were treated with excess diazomethane, concentrated and diluted to 25 microliters with methylenechloride. The residues were analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components. Five grams of the carbon residues were ignited in a platinum crucible. The ash was treated with hydrochloric acid and diluted to 25ml. The acid solution was then analyzed for iron by atomic absorption.

The ash content was determined by thermogravimetric analysis in air. The sample began to lose weight (undergo oxidation) at approximately 525°C. The carbon was completely oxidized by 725°C.

E. Analysis of spent scrubber water sediment

The dark precipitate from the scrubber water sample was separated by filtration through one micron glass filter and washed with 60ml of deionized water. The residue was air dried and weighed. The residue was then treated in the same manner as the combustion chamber deposit.

F. Analysis of particulate filter samples

The filters were extracted four (4) times with hot benzene. The benzene was then removed by distillation. The residue was treated with excess diazomethane and the solvent evaporated. The residue was then diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components.

The benzene insoluable material was then extracted with hot 5% hydrochloric acid. The extract was then diluted to 25ml and analyzed for iron by atomic absorption.

V General Comments

The presence of ionol and didecylphthlate in several of the samples is most probably due to contamination. Since these compounds are used extensively as an anti-oxidant and plasticizer, respectively, in plastics, then presence is quite frequently encountered. These compounds could have been picked up from the sample bottles, screw caps, plastic tubing or from the work area atmosphere.

The absence of biphenyl in the combustion gas and scrubber water while seen in other samples, raises certain questions. It is possible that the biphenyl was not observed in the combustion chamber gases as a result of peak interference. Its absence from the spent scrubber water is most probably due to its being removed by the hot water vapors. Since the biphenyl has a very low solubility in water and the presence of the salt and caustic further reduce this solubility, there is no driving force to retain it in the water phase. The detected biphenyls were unchlorinated.

The presence of butylalcohol was specifically monitored in the spent scrubber water and scrubbed effluent gas since it is a hydrolysis product of the principal herbicides. It was possible that some butylesters of the herbicide would survive the combustion and react with the hot caustic solution. Saponification could then occur producing the acid salt and butylalcohol. The absence of butylalcohol therefore eliminates the possibility of the ester reaching the scrubber and being hydrolyzed.

There was no evidence for the presence of aldehyde in the combustion gases. This was substantiated by the fact that the several peaks identified as aliphatic and aromatic hydrocarbons occurred both in the combustion gas and spent scrubber water samples. If aldehydes had been present in the combustion chamber, they would have undergone further reactions in the presence of hot aqueous caustics and not been detected in the spent scrubber water.

The bulk of the residues on the particulate sampling filters appeared by visual examination to be sodium chloride. The only analysis which was carried out on these residues was for iron and volatile organic compounds.

It is difficult to fully explain the presence of the phenoxyacetic acid in sample III RACC-2, combustion chamber residue. It would appear that it arises directly from the blended herbicide feed since it is present as the butylester in the range of 0.02% to 1.64%. It would therefore appear that the compound exhibits a higher stability than the other products in the zone where the carbon deposit occurs.

No attempt was made to identify the positional isomers of the monochlorophenol or the dichlorophenol. It is reasonable to assume that the monochloro derivitive is a mixture of ortho and para isomers, since these are the normal products from the preparation of chlorophenol. It is also reasonable to assume that the dichlorophenol is 2,4-dichlorophenol since it is a reactant in the preparation of 2,4-dichlorophenoxy acetic acid.

The identity of specific aromatic and aliphatic hydrocarbon was not undertaken. The mass spectrometry of these materials showed them to contain no chlorine. The aromatic hydrocarbons were distributed around the $C_4$ substituted benzene derivation. These compounds also appeared to have saturated sidechain. The amount of these aromatic hydrocarbons was therefore calculated as butylbenzene. The aliphatic hydrocarbons in the system spanned the range of $C_7$ through $C_{15}$. The preponderance of them was centered at $C_{10}$. These compounds were therefore calculated as $C_{10}H_{22}$ even though many of them appear to be unsaturated.

VI Results

The results of the various analyses are given in the following tables.

If we can be of any further assistance, please do not hesitate to contact us.

Respectively submitted,

WEST COAST TECHNICAL SERVICE INC.

H. Dwight Fisher, Ph.D.
Vice President-Technical Director

HDF/lp

P.S.

Reported values were not adjusted for analytical recovery efficiencies but all the reported detection limits were.

TABLE G-1

COMPOSITION OF BLENDED HERBICIDE FEED
(weight percent except as noted)

| | I BH 62/63 64/65 | II BH 76/77/91 | III BH 78/80/ 89/92 | IV BH 86/87/90 | V BH 71/81 82/84 | VI BH 66/83 85/88 | VII BH 69/73 | VIII BH 68/70 74/75 |
|---|---|---|---|---|---|---|---|---|
| Dichlorophenol | 1.86 | .63 | .78 | .82 | .52 | 2.97 | 2.00 | 2.13 |
| Trichlorophenol | .61 | .03 | .08 | .09 | .55 | 1.64 | 1.16 | 1.12 |
| Phenoxy acetic acid - butylester | .02 | .08 | .33 | .38 | .28 | 1.27 | .85 | .79 |
| 2,4-dichlorophenoxy acetic acid | .53 | .44 | .33 | .33 | .14 | 1.47 | 1.64 | .96 |
| 2,4.5-trichlorophenoxy acetic acid | .48 | .37 | .28 | .32 | .24 | .94 | .72 | .82 |
| 2,4-dichlorophenoxy acetic acid-butylester | 50.35 | 52.02 | 53.14 | 52.99 | 52.71 | 47.59 | 49.25 | 49.15 |
| Monochlorophenoxy acetic acid-octylester | .43 | .34 | .27 | .29 | .00 | .76 | .66 | .60 |
| 2,4,5-trichlorophenoxy acetic acid-butylester | 44.46 | 45.30 | 44.41 | 44.29 | 45.21 | 43.21 | 41.23 | 42.15 |
| 2,4,-dichlorophenoxy acetic acid-octylester | .77 | .73 | .32 | .31 | .32 | .06 | 1.24 | 1.13 |
| 2,4,5-trichlorophenoxy acetic acid - octylester | .49 | .06 | .04 | .19 | .00 | .09 | 1.25 | 1.15 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | 12ppm* | 14ppm* | 11ppm* | 16ppm* | 14ppm* | 12ppm* | 13ppm* | 14ppm* |
| Iron | 7.2ppm* | 6.7ppm* | 8.2ppm* | 14.3ppm* | 7.6ppm* | 12.3ppm* | 6.2ppm* | 9.1ppm* |
| Total | 100.00 | 100.00 | 99.98 | 100.01 | 99.97 | 100.00 | 100.00 | 100.00 |

* ppm by weight (mg/kg)



WEST COAST TECHNICAL SERVICE INC.

## TABLE G-2

### COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN
### IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | ICG-1 | ICG-2 | ICG-3 | ICG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 382 | 3.2 | 51.9 | 2.9 | 0.18 |
| Aliphatic hydrocarbons (2) | 83 | 4.1 | 2.1 | 2.7 | 0.18 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.18 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.18 |
| Chlorophenol | 146 | ND | ND | ND | 0.22 |
| Dichlorophenol | ND | ND | ND | ND | 0.22 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.16 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.15 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.17 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.15 |
| Ionol | 1.67 | 3.2 | 4.3 | 4.9 | 0.18 |
| Didecylphthlate | 14 | 1.5 | 1.5 | 0.6 | 0.18 |
| Biphenyl | ND | ND | ND | ND | 0.18 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.16 |
| Total volume of solution (ml) | 647 | 249 | 272 | 213 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

(TABLE G-2 cont'd on following seven pages)

TABLE G-2 (cont'd)

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | IICG-1 | IICG-2 | IICG-3 | IICG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 314 | 8.2 | 6.1 | 0.6 | 0.74 |
| Aliphatic hydrocarbons (2) | 29.3 | 6.2 | 1,2 | 1.0 | 0.74 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.74 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.74 |
| Chlorophenol | ND | ND | ND | ND | 0.88 |
| Dichlorophenol | ND | ND | ND | ND | 0.88 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.65 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.62 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.67 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.62 |
| Ionol | 121.2 | 37.3 | 67.2 | 1.2 | 0.94 |
| Didecylphthlate | 223 | 2.2 | 7.3 | 1.4 | 0.74 |
| Biphenyl | ND | ND | ND | ND | 0.74 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.65 |
| Total volume of solution (ml) | 781 | 368 | 320 | 324 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC

## TABLE G-2 (cont'd)

### COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

| | HCG-1 | HCG-2 | HCG-3 | HCG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 100. | 3.2 | 4.3 | 2.5 | 0.11 |
| Aliphatic hydrocarbons (2) | 201. | 27.1 | 11.2 | 5.9 | 0.11 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.11 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.11 |
| Chlorophenol | ND | ND | ND | ND | 0.13 |
| Dichlorophenol | ND | ND | ND | ND | 0.13 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.10 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.10 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.10 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.10 |
| Ionol | 12.5 | 0.6 | 0.5 | 0.6 | 0.11 |
| Didecylphthlate | 16.2 | 8.3 | 3.1 | 0.2 | 0.11 |
| Biphenyl | ND | ND | ND | ND | 0.11 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.10 |
| Total volume of solution (ml) | 446 | 360 | 352 | 410 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

TABLE G-2 (cont'd)

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | IVCG-1 | IVCG-2 | IVCG-3 | IVCG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 0.7 | 0.4 | 0.3 | 0.2 | 0.10 |
| Aliphatic hydrocarbons (2) | 0.27 | 0.45 | 0.23 | 0.2 | 0.10 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.10 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.10 |
| Chlorophenol | ND | ND | ND | ND | 0.12 |
| Dichlorophenol | ND | ND | ND | ND | 0.12 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.09 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.09 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.09 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.09 |
| Ionol | 0.3 | 0.9 | 36.2 | 1.4 | 0.10 |
| Didecylphthlate | 2.4 | 0.6 | 8.2 | 16.9 | 0.10 |
| Biphenyl | ND | ND | ND | ND | 0.10 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.09 |
| Total volume of solution (ml) | 524 | 286 | 228 | 388 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-2 (cont'd)

### COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

| | VCG-1 | VCG-2 | VCG-3 | VCG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 2.7 | 0.7 | Samples not submitted by EHL/M for analysis. | | 4.2 |
| Aliphatic hydrocarbons (2) | 2.5 | 0.3 | | | 4.2 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | | | 4.2 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | | | 4.2 |
| Chlorophenol | ND | ND | | | 5.0 |
| Dichlorophenol | ND | ND | | | 5.0 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | | | 3.7 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | | | 3.5 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | | | 3.8 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | | | 3.5 |
| Ionol | 5.6 | 1.7 | | | 4.2 |
| Didecylphthlate | 7.2 | 2.9 | | | 4.2 |
| Biphenyl | ND | ND | | | 4.2 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | | | 3.7 |
| Total volume of solution (ml) | 576 | 312 | | | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-2 (cont'd)

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VICG-1 | VICG-2 | VICG-3 | VICG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 29.0 | 0.4 | 0.3 | 0.1 | 0.15 |
| Aliphatic hydrocarbons (2) | 2.6 | 0.3 | 0.3 | 0.2 | 0.15 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.15 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.15 |
| Chlorophenol | ND | ND | ND | ND | 0.18 |
| Dichlorophenol | ND | ND | ND | ND | 0.18 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.13 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.13 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.14 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.13 |
| Ionol | 27.1 | 3.6 | 1.3 | 2.1 | 0.15 |
| Didecylphthlate | 21.7 | 2.9 | 2.2 | 0.8 | 0.15 |
| Biphenyl | ND | ND | ND | ND | 0.15 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.13 |
| Total volume of solution (ml) | 570 | 325 | 315 | 295 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-2 (cont'd)

### COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

| | VECG-1 | VECG-2 | VECG-3 | VECG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 7.0 | 1.3 | 0.6 | 0.3 | 0.22 |
| Aliphatic hydrocarbons (2) | 1.9 | 0.7 | 0.5 | 0.2 | 0.22 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.22 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.22 |
| Chlorophenol | ND | ND | ND | ND | 0.27 |
| Dichlorophenol | ND | ND | ND | ND | 0.27 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.20 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.19 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.21 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.19 |
| Ionol | 19.5 | 1.8 | 1.1 | 0.4 | 0.22 |
| Didecylphthlate | 0.5 | 1.4 | 0.4 | 0.3 | 0.22 |
| Biphenyl | ND | ND | ND | ND | 0.22 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.20 |
| Total volume of solution (ml) | 635 | 315 | 310 | 295 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

TABLE G-2 (cont'd)

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VIIICG-1 | VIIICG-2 | VIIICG-3 | VIIICG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 19.2 | 1.0 | 0.3 | 0.2 | 0.20 |
| Aliphatic hydrocarbons (2) | 10.8 | 2.3 | 0.7 | 0.3 | 0.20 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.20 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.20 |
| Chlorophenol | ND | ND | ND | ND | 0.23 |
| Dichlorophenol | ND | ND | ND | ND | 0.23 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.17 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.16 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.18 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.16 |
| Ionol | 72.8 | 13.6 | 1.3 | 1.8 | 0.20 |
| Didecylphthlate | 495. | 8.6 | 1.0 | 0.3 | 0.20 |
| Biphenyl | ND | ND | ND | ND | 0.20 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.17 |
| Total volume of solution (ml) | 490 | 290 | 285 | 285 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-3

### COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

| | ISG-1 | ISG-2 | ISG-3 | ISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 2.7 | 1.2 | 1.1 | 0.9 | 0.23 |
| Aliphatic hydrocarbons (2) | 1.6 | 1.1 | 0.9 | 0.5 | 0.23 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.23 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.23 |
| Chlorophenol | ND | ND | ND | ND | 0.28 |
| Dichlorophenol | ND | ND | ND | ND | 0.28 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.21 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.20 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.22 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.20 |
| Ionol | 5.4 | 3.0 | 0.6 | 0.6 | 0.23 |
| Didecylphthlate | 35.2 | 2.4 | 0.7 | 0.3 | 0.23 |
| Biphenyl | 0.25 | 0.21 | 0.81 | 0.50 | 0.23 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.21 |
| Total volume of solution (ml) | 448 | 361 | 350 | 276 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

(TABLE G-3 cont'd on following seven pages)

TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | IISG-1 | IISG-2 | IISG-3 | IISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 0.5 | 0.5 | 1.2 | 2.1 | 0.21 |
| Aliphatic hydrocarbons (2) | 1.1 | 0.8 | 1.0 | 1.5 | 0.21 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.21 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.21 |
| Chlorophenol | ND | ND | ND | ND | 0.25 |
| Dichlorophenol | ND | ND | ND | ND | 0.25 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.18 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.17 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.19 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.17 |
| Ionol | 2.8 | 1.5 | 8.2 | 17.9 | 0.21 |
| Didecylphthlate | 5.7 | 6.0 | 3.5 | 2.4 | 0.21 |
| Biphenyl | 0.69 | 0.39 | 0.41 | 0.56 | 0.21 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.18 |
| Total volume of solution (ml) | 626 | 342 | 394 | 380 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | IIISG-1 | IIISG-2 | IIISG-3 | IIISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 9.9 | 1.7 | 2.2 | 1.9 | 0.26 |
| Aliphatic hydrocarbons (2) | 6.7 | 4.1 | 1.2 | 1.1 | 0.26 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.26 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.26 |
| Chlorophenol | ND | ND | ND | ND | 0.31 |
| Dichlorophenol | ND | ND | ND | ND | 0.31 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.23 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.21 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.24 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.21 |
| Ionol | 11.6 | 2.1 | 1.3 | 0.4 | 0.26 |
| Didecylphthlate | 19.5 | 1.5 | 0.4 | 0.3 | 0.26 |
| Biphenyl | 0.63 | 0.10 | 0.07 | 0.12 | 0.26 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.23 |
| Total volume of solution (ml) | 534 | 468 | 362 | 340 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

| | IVSG-1 | IVSG-2 | IVSG-3 | IVSG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 6.1 | 1.7 | 0.3 | 0.2 | 0.19 |
| Aliphatic hydrocarbons (2) | 3.2 | 1.9 | 0.7 | 0.6 | 0.19 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.19 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.19 |
| Chlorophenol | ND | ND | ND | ND | 0.22 |
| Dichlorophenol | ND | ND | ND | ND | 0.22 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.16 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.16 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.17 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.16 |
| Ionol | 53.4 | 3.1 | 2.9 | 3.2 | 0.19 |
| Didecylphthlate | 50.3 | 29.7 | 3.8 | 16.4 | 0.19 |
| Biphenyl | 0.80 | 0:07 | ND | ND | 0.19 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.16 |
| Total volume of solution (ml) | 492 | 406 | 354 | 324 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VSG-1 | VSG-2 | VSG-3 | VSG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 1.1 | 0.4 | 0.6 | 0.6 | 0.23 |
| Aliphatic hydrocarbons (2) | 2.3 | 0.7 | 0.7 | 0.6 | 0.23 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.23 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.23 |
| Chlorophenol | ND | ND | ND | ND | 0.27 |
| Dichlorophenol | ND | ND | ND | ND | 0.27 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.20 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.19 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.21 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.19 |
| Ionol | 2.7 | 5.2 | 4.9 | 5.8 | 0.23 |
| Didecylphthlate | 15.3 | 33.9 | 4.5 | 8.5 | 0.23 |
| Biphenyl | 4.18 | 0.90 | 0.30 | ND | 0.23 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.20 |
| Total volume of solution (ml) | 610 | 250 | 424 | 330 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VISG-1 | VISG-2 | VISG-3 | VISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 2.3 | 1.9 | 0.8 | 0.7 | 0.69 |
| Aliphatic hydrocarbons (2) | 4.2 | 3.7 | 2.0 | 1.2 | 0.69 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.69 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.69 |
| Chlorophenol | ND | ND | ND | ND | 0.83 |
| Dichlorophenol | ND | ND | ND | ND | 0.83 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.61 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.58 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.63 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.58 |
| Ionol | 5.7 | 7.3 | 1.7 | 6.2 | 0.69 |
| Didecylphthlate | 11.0 | 39.4 | 1.5 | 2.9 | 0.69 |
| Biphenyl | 0.98 | 2.17 | 1.67 | 1.29 | 0.69 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.61 |
| Total volume of solution (ml) | 520 | 335 | 335 | 285 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VIISG-1 | VIISG-2 | VIISG-3 | VIISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 1.1 | 1.3 | 1.0 | 0.2 | 0.30 |
| Aliphatic hydrocarbons (2) | 1.1 | 0.8 | 1.1 | 0.7 | 0.30 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.30 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.30 |
| Chlorophenol | ND | ND | ND | ND | 0.36 |
| Dichlorophenol | ND | ND | ND | ND | 0.36 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.27 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.25 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.29 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.25 |
| Ionol | 0.6 | 1.9 | 0.5 | 0.5 | 0.30 |
| Didecylphthlate | 0.4 | 0.8 | 0.5 | 0.1 | 0.30 |
| Biphenyl | 2.05 | 0.42 | 0.04 | 0.03 | 0.30 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.27 |
| Total volume of solution (ml) | 450 | 395 | 410 | 295 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

TABLE G-3 (cont'd)

COMPOSITION OF SCRUBBED EFFLUENT GAS SAMPLING TRAIN
IMPINGER SAMPLES
(micrograms per total sample as compound except as noted)

| | VIIISG-1 | VIIISG-2 | VIIISG-3 | VIIISG-4 | Detection Limits* nanograms/liter |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 7.0 | 1.3 | 0.5 | 0.5 | 0.28 |
| Aliphatic hydrocarbons (2) | 2.2 | 0.7 | 0.2 | 0.2 | 0.28 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.28 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.28 |
| Chlorophenol | ND | ND | ND | ND | 0.33 |
| Dichlorophenol | ND | ND | ND | ND | 0.33 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.24 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.23 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.25 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.23 |
| Ionol | 4.9 | 2.5 | 0.5 | 0.9 | 0.28 |
| Didecylphthlate | 2.2 | 1.1 | 0.4 | 0.4 | 0.28 |
| Biphenyl | 4.37 | 1.21 | 0.87 | 0.02 | 0.28 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.24 |
| Total volume of solution (ml) | 470 | 350 | 400 | 320 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Based on flow data furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-4

### TOTAL QUANTITY OF MATERIAL PRESENT ON PARTICULATE SAMPLING FILTERS

(micrograms per total sample as compound except as noted)

| | I-P | II-P | III-P | IV-P | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | ND | ND | ND | Sample | 0.025 |
| Aliphatic hydrocarbons (2) | 11.3 | 4.2 | 3.1 | lost in transit. | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | | 0.025 |
| Chlorophenol | ND | ND | ND | | 0.030 |
| Dichlorophenol | ND | ND | ND | | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | | 0.021 |
| Ionol | ND | ND | ND | | 0.025 |
| Didecylphthlate | 0.5 | 0.3 | 0.1 | | 0.025 |
| Biphenyl | ND | ND | ND | | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | | 0.022 |
| Iron | 786. | 669. | 1016. | | N/A |
| Total particulate mass ($\times 10^3$) (data furnished by EHL/M) | 79.6 | 44.9 | 51.1 | 92.9 | N/A |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

(TABLE G-4 cont'd next page)

TABLE G-4 (cont'd)

TOTAL QUANTITY OF MATERIAL PRESENT
ON PARTICULATE SAMPLING FILTERS
(micrograms per total sample as compound except as noted)

| | V-P | VI-P | VII-P | VIII-P | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | ND | ND | ND | ND | 0.025 |
| Aliphatic hydrocarbons (2) | 1.3 | 9.3 | 3.7 | 6.2 | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | ND | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | 0.025 |
| Chlorophenol | ND | ND | ND | ND | 0.030 |
| Dichlorophenol | ND | ND | ND | ND | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | 0.021 |
| Ionol | ND | ND | ND | ND | 0.025 |
| Didecylphthlate | 0.1 | 0.6 | 1.1 | 1.2 | 0.025 |
| Biphenyl | ND | ND | ND | ND | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | ND | 0.022 |
| Iron | 1720. | 400. | 659. | 1070. | N/A |
| Total particulate mass ($\times 10^3$) (data furnished by EHL/M) | 167.8 | 88.4 | 114.4 | 191.0 | N/A |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-5

COMPOSITION OF GAS SAMPLING PROBE RINSES
(micrograms per total sample as compound except as noted)

| | ICG-ACP | IICG-ACP | IIICG-ACP | IVCG-ACP | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | | 1.7 | 2.8 | Sample | 0.025 |
| Aliphatic hydrocarbons (2) | 66.7* | 1.3 | 1.7 | rinsed into | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | | ND | ND | IVCG-1. | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | | ND | ND | | 0.025 |
| Chlorophenol | | ND | ND | | 0.030 |
| Dichlorophenol | | 1.38 | 0.7 | | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | | ND | ND | | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | | ND | ND | | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | | ND | ND | | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | | ND | ND | | 0.021 |
| Ionol | | ND | ND | | 0.025 |
| Didecylphthlate | | ND | ND | | 0.025 |
| Biphenyl | | ND | ND | | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | | ND | ND | | 0.022 |
| Total volume of solution (ml) | 265 | 242 | 280 | | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

* Light lubrication oil; material masked other possible compounds present.

WEST COAST TECHNICAL SERVICE INC.

(TABLE G-5 cont'd next page)

TABLE G-5 (cont'd)

COMPOSITION OF GAS SAMPLING PROBE RINSES
(micrograms per total sample as compound except as noted)

| | VCG-ACP | VICG-WCP | VIICG-WCP | VIIICG-WCP | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | Sample | Sample | 0.40 | 1.8 | 0.025 |
| Aliphatic hydrocarbons (2) | not | rinsed into | 0.26 | 0.73 | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | submitted by EHL/M | VICG-1. | ND | ND | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | | | ND | ND | 0.025 |
| Chlorophenol | | | ND | ND | 0.030 |
| Dichlorophenol | | | ND | ND | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | | | ND | ND | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | | | ND | ND | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | | | ND | ND | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | | | ND | ND | 0.021 |
| Ionol | | | ND | ND | 0.025 |
| Didecylphthlate | | | ND | ND | 0.025 |
| Biphenyl | | | ND | ND | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | | | ND | ND | 0.022 |
| Total volume of solution (ml) | | | 118 | 415 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-6

### COMPOSITION OF MISCELLANEOUS SAMPLES RELATED TO GAS SAMPLING

(micrograms per total sample as compound except as noted)

| | IP-1&2 | IIP-1&2 | IIIP-1&2 | IVP-1&2 | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | Samples not | | 72.1 | 51.2 | 0.025 |
| Aliphatic hydrocarbons (2) | submitted | | 7.4 | 45.6 | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | | | ND | ND | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | | | ND | ND | 0.025 |
| Chlorophenol | | | ND | ND | 0.030 |
| Dichlorophenol | | | ND | 1.3 | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | | | ND | ND | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | | | ND | ND | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | | | ND | ND | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | | | ND | ND | 0.021 |
| Ionol | | | ND | ND | 0.025 |
| Didecylphthlate | | | ND | ND | 0.025 |
| Biphenyl | | | ND | ND | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | | | ND | ND | 0.022 |
| Total volume of solution (ml) | | | 65 | 400 | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.



(TABLE G-6 cont'd next two pages)

TABLE G-6 (cont'd)

COMPOSITION OF MISCELLANEOUS SAMPLES RELATED TO GAS SAMPLING
(micrograms per total sample as compound except as noted)

| | VP-1&2 | VIP-1&2 | VIIP-1&2 | VIIIP-1&2 | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 34.7 | 16.2 | Samples not | | 0.025 |
| Aliphatic hydrocarbons (2) | 32.1 | 1.7 | submitted. | | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | | | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | | | 0.025 |
| Chlorophenol | ND | ND | | | 0.030 |
| Dichlorophenol | ND | 0.10 | | | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | | | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | | | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | | | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | | | 0.021 |
| Ionol | ND | ND | | | 0.025 |
| Didecylphthlate | ND | ND | | | 0.025 |
| Biphenyl | ND | ND | | | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | | | 0.022 |
| Total volume of solution (ml) | 475 | 280 | | | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

## TABLE G-6 (cont'd)

### COMPOSITION OF MISCELLANEOUS SAMPLES RELATED TO GAS SAMPLING

(micrograms per total sample as compound except as noted)

| | ICG-CT | IICG-CT | IIICG-CT | IVCG-CT through VIIICG-CT | Detection Limits micrograms |
|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 12.6 | 0.9 | 16.0 | Samples | 0.025 |
| Aliphatic hydrocarbons (2) | 0.3 | 1.8 | 32.0 | not submitted | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | ND | ND | ND | | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | | 0.025 |
| Chlorophenol | ND | ND | ND | | 0.030 |
| Dichlorophenol | 1.2 | 0.1 | 0.1 | | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | 0.70 | ND | ND | | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | 6.5 | ND | ND | | 0.021 |
| Ionol | ND | ND | ND | | 0.025 |
| Didecylphthlate | ND | ND | ND | | 0.025 |
| Biphenyl | ND | ND | ND | | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | ND | | 0.022 |
| Total volume of solution (ml) | 640 | 705 | 637 | | |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

TABLE G-7

EXTRACTABLES FROM FRESH AND SPENT SCRUBBER WATER
(micrograms/liter of compound except as noted)

| | ISSW-TBC | IISSW-TBC | IIISSW-TBC | IVSSW-TBC | VSSW-TBC | VIISSW-TBC | VIIISSW-TBC | Detection Limits µg/l |
|---|---|---|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 191.5 | 121.0 | 56.4 | 5.1 | 1.2 | 7.8 | 6.2 | 0.05 |
| Aliphatic hydrocarbons (2) | 107.6 | 97.2 | 112.5 | 6.2 | 9.6 | 9.7 | 9.8 | 0.05 |
| Chlorinated aromatic hydrocarbons (3) | 524.1 | 465.1 | 32.3 | 7.2 | 3.2 | 1.1 | 2.2 | 0.05 |
| Chlorinated aliphatic hydrocarbons (4) | ND | ND | ND | ND | ND | ND | ND | 0.05 |
| Chlorophenol | 52.7 | 14.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.08 |
| Dichlorophenol | ND | ND | ND | ND | ND | ND | ND | 0.08 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | ND | ND | ND | 0.048 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | ND | ND | ND | ND | ND | ND | 0.046 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | ND | ND | ND | 0.048 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | ND | ND | ND | ND | ND | ND | 0.043 |
| Ionol | 6.3 | 2.6 | 3.8 | 2.2 | 0.5 | 1.2 | 0.3 | 0.05 |
| Didecylphthlate | 16.9 | 7.2 | 7.1 | 6.3 | 4.1 | 3.6 | 7.2 | 0.05 |
| Biphenyl | ND | ND | ND | ND | ND | ND | ND | 0.05 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | ND | 0.25 | ND | ND | ND | ND | 0.047 |
| Butylalcohol | ND | ND | ND | ND | ND | ND | ND | 0.05 |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

NOTE: A VI-SSW-TBC sample was not prepared or submitted by EHL/K.

(TABLE G-7 cont'd next page)

TABLE G-7 (cont'd)

EXTRACTABLES FROM FRESH AND SPENT SCRUBBER WATER
(micrograms/liter of compound except as noted)

| | IFSW-A | IIFSW-A | IIISSW-C1 | IVSSW-C1 | VSSW-C1 | VISSW-C1 | VISSW-C2 | Detection Limits µg/l |
|---|---|---|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 13.5 | * | 1.7 | 0.6 | 15.0 | 5.3 | 1.4 | 0.05 |
| Aliphatic hydrocarbons (2) | 4.0 | | 3.6 | 0.5 | 0.7 | 2.0 | 1.9 | 0.05 |
| Chlorinated aromatic hydrocarbons (3) | ND | | 0.8 | 0.9 | 1.0 | 0.6 | 0.2 | 0.05 |
| Chlorinated aliphatic hydrocarbons (4) | ND | | ND | ND | ND | ND | ND | 0.05 |
| Chlorophenol | ND | | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.08 |
| Dichlorophenol | ND | | ND | ND | ND | ND | ND | 0.08 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | | ND | ND | ND | ND | ND | 0.048 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | | ND | ND | ND | ND | ND | 0.046 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | | ND | ND | ND | ND | ND | 0.048 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | | ND | ND | ND | ND | ND | 0.043 |
| Ionol | ND | | 0.5 | 3.4 | 11.4 | 8.4 | 2.7 | 0.05 |
| Didecylphthlate | ND | | 9.6 | 3.5 | 10.5 | 8.5 | 7.1 | 0.05 |
| Biphenyl | ND | | ND | ND | ND | ND | ND | 0.05 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | | ND | ND | ND | ND | ND | 0.047 |
| Butylalcohol | ND | | ND | ND | ND | ND | ND | 0.05 |

* Sample not analyzed by agreement between WCTS & EHL/K due to aluminum contamination.

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

NOTE: No I/II/VII/ or VIII SSW-C1 samples were submitted by EHL/K.

## TABLE G-8

COMPOSITION OF SEDIMENT FROM SPENT SCRUBBER WATER HOLDING TANK
(micrograms as compound except as noted)

| | ISSW-HT-2 | IISSW-HT-2 | IIISSW-HT-2 | IVSSW-HT-2 | VSSW-HT-2 | VI/VII SSW-HT-2 | VIIISSW-HT-2 | Detection Limit-µg |
|---|---|---|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | Sample apparently lost. | Sample not submitted. | ND | ND | Sample not submitted. | ND | ND | 0.025 |
| Aliphatic hydrocarbons (2) | | | ND | ND | | ND | ND | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | | | ND | ND | | ND | ND | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | | | ND | ND | | ND | ND | 0.025 |
| Chlorophenol | | | ND | ND | | ND | ND | 0.030 |
| Dichlorophenol | | | ND | ND | | ND | ND | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | | | ND | ND | | ND | ND | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | | | ND | ND | | ND | ND | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | | | ND | ND | | ND | ND | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | | | ND | ND | | ND | ND | 0.021 |
| Ionol | | | ND | ND | | ND | ND | 0.025 |
| Didecylphthlate | | | ND | ND | | ND | ND | 0.025 |
| Biphenyl | | | ND | ND | | ND | ND | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | | | ND | ND | | ND | ND | 0.022 |
| Total residue (grams) of sample submitted | | | 11.3 | 8.6 | | 9.6 | 12.2 | N/A |
| Iron (micrograms/gm.of residue) | | | 80600. | 99200. | | 55700. | 44000. | N/A |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

## TABLE G-9

## COMPOSITION OF COMBUSTION CHAMBER RESIDUE

(micrograms of compound per 100 grams of residue)

| | IRACC-2 | IIRACC-1 | IIRACC-2 | IIIRACC-2 | IVRACC-2 | V/VIRACC-2 | Detection Limits micrograms/100gms. |
|---|---|---|---|---|---|---|---|
| Aromatic hydrocarbons (1) | 163.5 | Samples not received at WCTS | | 2.7 | 512.6 | 33.9 | 0.025 |
| Aliphatic hydrocarbons (2) | 86.8 | | | 16.2 | 7.6 | 31.4 | 0.025 |
| Chlorinated aromatic hydrocarbons (3) | ND | | | ND | ND | ND | 0.025 |
| Chlorinated aliphatic hydrocarbons (4) | ND | | | 0.5 | ND | ND | 0.025 |
| Chlorophenol | ND | | | ND | ND | ND | 0.030 |
| Dichlorophenol | ND | | | 6.8 | 5.6 | ND | 0.030 |
| 2,4-dichlorophenoxy acetic acid (methylester) | ND | | | 2.5 | ND | ND | 0.022 |
| 2,4,5-trichlorophenoxy acetic acid (methylester) | ND | | | 2.4 | ND | ND | 0.021 |
| 2,4,-dichlorophenoxy acetic acid - butylester | ND | | | 551 | ND | ND | 0.023 |
| 2,4,5-trichlorophenoxy acetic acid - butylester | ND | | | 542 | ND | ND | 0.021 |
| Ionol | ND | | | ND | ND | ND | 0.025 |
| Didecylphthlate | ND | | | ND | ND | ND | 0.025 |
| Biphenyl | 9.5 | | | 6.2 | 17.1 | 1.6 | 0.025 |
| 2,3,7,8-tetrachlorodibenzo-p-dioxin | ND | | | ND | ND | ND | 0.022 |
| 2,4-dichlorophenoxy acetic acid-octylester | ND | | | 0.2 | ND | ND | 0.020 |
| 2,4,5-trichlorophenoxy acetic acid-octylester | ND | | | 0.6 | ND | ND | 0.020 |
| Iron | 103 | | | 127 | 12.5 | 25.0 | N/A |
| Ash (%) | Not requested | | | 0.05 | 0.04 | 0.06 | N/A |
| Phenoxyacetic acid | ND | | | 1.5 | ND | ND | 0.025 |

(1) calculated as butylbenzene
(2) calculated as decane
(3) calculated as dichlorobenzene
(4) calculated as $C_2H_4Cl_2$

WEST COAST TECHNICAL SERVICE INC.

**NOTE: No VIII RACC-1 sample was submitted by EML/K.**

# APPENDIX H
# (TO APPENDIX E)
# SAFETY AND HANDLING

## 1.0 GENERAL

Due to the potential health hazard related to handling and incineration of "Orange" Herbicide, special safety requirements were established per the contract and TMC safety standards. In general, the items discussed in the following paragraphs were established to insure that:

- Personnel were protected against any contact with the herbicide or its possible hazardous combustion products.
- No herbicide was released to the environment.
- Medical surveillance of applicable personnel was provided.

As applicable, many of these same safety precautions were also observed in the handling of caustic solution.

## 2.0 DRUM MONITORING

An Inspection Log Sheet was established for each drum of "Orange" Herbicide received from the Air Force. This sheet was maintained by a TMC Safety Engineer and all information regarding the drum during its stay was recorded. Information included initial receipt data, receipt condition, results of daily inspection, transfer data, cleaning operations, and final disposal. All drums were received in good condition and no redrumming was required. These records are available at TMC.

## 3.0 PHYSICAL EXAMINATIONS

Complete physical examinations were performed on all TMC personnel directly involved in herbicide operations of unloading, transfer, incineration, operations and drum cleaning. Examinations were performed just prior to TMC receipt of the "Orange" Herbicide, and repeated after the program was completed. Although intermediate examinations were authorized if warranted by exposure problems, none were required. Examinations included a routine history and physical, chext x-ray, and special attention directed to skin and liver. Laboratory procedures included complete hemogram including hematocrit and platelet count, prothrombin time, serium lipids, S-GOT, S-GPT, serium bilirubin, blood glucose, and complete urinalysis. Examinations were conducted at the Van Nuys Medical Clinic, Panorama City, California and the records will be maintained at TMC until at least November, 1976.

## 4.0 EQUIPMENT AND FACILITIES

### 4.1 Personnel Protective Gear

The following gear was worn by personnel during transfer or other operations where direct contact with the herbicide was possible:

- MSA Cyralon Gloves
- MSA Yellow Plastic Suits
- Tingley 10" Neoprene Boots
- MSA Face Shields

Personnel requiring gas masks (including AF) were issued MSA Rocket Propellant Masks No. EF-86847 with Cannisters, Type GMC-S, P/N 05-84908, suitable for use with "Orange" Herbicide, phosgene, or HCl. MSA hard hats were also issued and required in the test area.

### 4.2 Special Equipment

In addition to the normal equipment used in this type of facility operations, the following special items were provided:

- "Orange" Herbicide drums were transported with a fork lift drum handling fixture. This fixture was securely attached around the drum's entire circumference, and allowed the drum to be rotated for draining.
- Barrel pumping was performed with a pneumatic device which forced the fluid through a hose assembly. This device removed all but about two quarts of "Orange" Herbicide from the drum while the drum was in its normal upright position.
- A specially constructed funnel was placed in the run tank for receiving the "Orange" Herbicide from the drum pump hose. This funnel had a closed top to prevent splash or spray and included a filtering screen.
- Steam cleaned 55-gallon drums were available for possible redrumming of any leaking drums.
- Drums of JP-4 were stored in the drum storage area and in the test cell area for use to wash down any spillages.
- Sealable cardboard drums were available for storing any accumulated contaminated materials.
- The Aero Thermo Laboratory and the drum storage area were equipped with fire protection equipment and emergency eye baths and showers.

## 5.0 GENERAL SAFETY PROCEDURES

The following paragraphs present other general safety requirements employed during this program:

- Only authorized personnel (TMC personnel with physical examinations or required AF personnel) were permitted to conduct test program operations and be present in the test area during actual testing.
- The test area was bounded by safety ropes during operations. Access to the area was strictly controlled by the Test Engineer.
- All personnel within the test area during tests were required to have an approved gas mask and cannister attached to their person and available for immediate use.
- Warning signals were prearranged to notify personnel to don gas masks and evacuate the test area during the testing.
- During testing the test area was monitored for the presence of phosgene gas with an MSA Model 1 kit, Universal tester (P/N 08-83500) using MSA phosgene gas sampling tubes (P/N 89890). Monitoring was conducted in the control room, on the scrubber stack sampling platform, and within a 100-foot radius of the test area.
- Visual contact between operators and the test system was maintained at all times.
- All "Orange" Herbicide transfer and cleaning operations were performed within diked areas. Drums were placed on a grounding plate during transfer.
- The protective clothing described in paragraph 4.1 were required to be worn by personnel involved in all operations which directly exposed them to the herbicide or caustic solution.
- All spills or drips were immediately mopped up with JP-4 soaked rags.
- All utensils (funnels, hoses, beakers, etc.) contacted by the herbicide were rinsed in JP-4 after each use and stored in covered containers.
- All materials contaminated with "Orange" Herbicide were stored in sealed containers and disposed of by the Air Force.

## 6.0 INDOCTRINATION

A meeting was held prior to initiating the test program to acquaint all TMC and USAF personnel with the operations to be conducted and the applicable safety requirements and hazards. Facility safety procedures were defined. Gas Masks, face shields, and hard hats were issued and their operations demonstrated.

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USAF ENVIRONMENTAL HEALTH LABORATORIES

Kelly AFB, TX
78241

McClellan AFB, CA
95652

# APPENDIX I

(TO APPENDIX E)

## EVALUATION AND DISCUSSION OF ORGANIC ANALYSES OF BLENDED HERBICIDE, SCRUBBER WATER, COMBUSTION GAS, SCRUBBED EFFLUENT GAS, AND RESIDUES

E(H-5)

# APPENDIX I

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# APPENDIX I

## EVALUATION AND DISCUSSION OF ORGANIC ANALYSES OF BLENDED HERBICIDE, SCRUBBER WATER, COMBUSTION GAS, SCRUBBED EFFLUENT GAS, AND RESIDUES

1. INTRODUCTION: This appendix contains an evaluation and discussion of all organic analyses of EHL samples; see Appendix G for data. Relationships were established between:

a. Measured and theoretical combustion gas volumes.

b. Sample data from replicate burns.

c. Combustion and scrubbed effluent gas hydrocarbon mass concentration.

d. Penetration and collection of hydrocarbon mass in the caustic scrubber.

e. Beckman 109A hydrocarbon data and TCDD sampling train hydrocarbon data.

f. Hydrocarbon mass collected in the TCDD sampling train and hydrocarbon mass incinerated. This relationship was used to calculate relative pyrolysis efficiencies (RPE) for each burn. These RPE's were used in various comparisons.

2. ANALYSES OF "ORANGE" HERBICIDE INCINERATED DURING THIS PROGRAM

a. The twenty-eight 55-gallon drums of "Orange" herbicide incinerated during this program were from the USAF stocks at Gulfport MS. The drums were all from FSN 6840-926-9095, original Air Force Transportation Control Number of FY9461-7165-0001AA, and Air Force Analysis Sequence Number 18.

b. Blended samples of herbicide were taken from the fuel feed tank prior to each burn. WCTS's analyses of each sample are presented in Table G-1, Appendix G, with reference to the EHL/K drums from which the fuel feed tank was filled. Composition of each sample was consistent with no significant variations. The 2,4-D acetic acid-butyl ester content averaged 50.90% by weight and met Air Force procurement specifications for this compound. The 2,4,5-T acetic acid-butyl ester content, however, averaged only 43.78% by weight and was 10% below its Air Force procurement specification. The average weight percent of "contaminant" compounds were, in decending order, as follows:

(1) Dichlorophenol - 1.46% plus trichlorophenol of 0.66% to yield total phenolic contaminants of 2.12%.

(2) 2,4-D, 2,4,5-T, and monochloro octyl esters had a total average of 1.44%.

(3) Acids of 2,4-D and 2,4,5-T were 0.73% and 0.52%, respectively, for total acids of 1.25%.

(4) TCDD concentration averaged 13 mg/kg (ppm) of total herbicide weight (s=2 mg/kg). This composition of TCDD was in very close agreement with other laboratories' TCDD analyses of other herbicide samples taken from drums of Analysis Sequence Number 18.

(5) Iron concentration averaged 9.0 mg/kg of total herbicide weight ($s=2.9$). Iron was considered a minor and insignificant "contaminant" which was slowly leached from the drum walls or from materials during the manufacturing process.

c. Neither ionol nor didecylphthlate was detected in the blended herbicide samples even though these compounds consistently appeared as microgram quantities in nearly all EHL gas and liquid samples. Their presence in these samples is discussed in paragraph 3, this appendix.

3. IONOL AND DIDECYLPHTHLATE IN EHL SAMPLES

a. Ionol (2,6-di-tert-butyl-4-methyl phenol) and didecylphthlate [$C_6H_4(COOC_{10}H_{21})_2$] were not considered products of "Orange" herbicide incineration. Both compounds are associated with tygon tubing and plastics (plasticizers and antioxidants) which had been extensively used in the laboratory areas where gas and water sample containers were prepared for sampling.

b. These compounds were not found in the blended herbicide samples, fresh scrubber water, combustion chamber coke deposits, holding tank sediment samples, the miscellaneous gas sample probe and cold trap rinses, or the "blank" benzene and acetone used in filling or cleaning the impingers. However, the compounds appeared in nearly all the gas sampling impinger liquids and spent scrubber water liquids. Their concentrations were random and could not be related between impingers in a series, applied caustic strength, or incineration parameters.

c. Based upon factors in paragraphs 3a and b and the lack of a likely precursor mechanism for these compounds in the "Orange" herbicide incineration process, it was concluded that these compounds were contaminants not associated with "Orange" herbicide pyrolysis; see Paragraph V, Appendix G.

4. COMBUSTION AND SCRUBBED EFFLUENT GAS VOLUMES PER BURN

a. The scrubbed effluent gas velocity pressures were too low (0.008 to 0.010 inches of water pressure) to be measured accurately. The error in the velocity pressure measurement was estimated by calculating carbon mass balances for burns IV, V, VI, and VII. The calculated carbon masses were 102 to 136% greater than the carbon feed into the system. (See Tables D-6 and I-1.) This carbon imbalance indicated that the measured effluent gas velocity pressures were inaccurate and could not be reliably used to calculate the total effluent gas volumes for each burn.

b. Consequently, an alternative method for determining the total burn combustion gas volumes was to evaluate Marquardt's computer predictions of combustion gas products and gas velocities through the incinerator. In this evaluation, a carbon mass balance could not be used for the combustion or scrubbed effluent gas because neither $CO_2$ nor CO were measured in the combustion gases, the scrubber absorbed various amounts of $CO_2$ per burn depending on the applied mass of NaOH, and the measured $CO_2$ and CO in the scrubbed effluent

TABLE I-1: CARBON MATERIAL BALANCE
"ORANGE" HERBICIDE PROGRAM
12-30 NOV 1973

| Burn No. | INTO SYSTEM: Total In lbs | Into Combustor: Herbicide lbs | Herbicide %T | Air lbs | Air %T | Combustor Coke Deposit lbs | Coke Deposit %T | Holding Tank: Carbonate lbs | Carbonate %T | Particles lbs | Particles %T | OUT OF SYSTEM: Scrubbed Effluent Stack: Per Measurement $CO_2$ lbs | $CO_2$ %T | CO lbs | CO %T | Per Calcul. Balance $CO_2$* lbs | $CO_2$* %T | CO* lbs | CO* %T | Percent of Total Acc'ted For by Measure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 756.74 | 754.33 | 99.68 | 2.41 | 0.32 | 7.9 | 1.04 | 112.8 | 14.9 | 2.49 | 0.33 | - | - | - | - | 589.27 | 77.87 | 44.35 | 5.86 | - |
| † | 289.94 | 289.01 | | 0.92 | | 3.03 | | 43.22 | | 0.94 | | | | | | 225.77 | | 17.00 | | |
| II | 869.95 | 867.18 | 99.68 | 2.77 | 0.32 | 9.02 | 1.04 | 118.51 | 13.6 | 1.98 | 0.23 | - | - | - | - | 688.75 | 79.17 | 51.84 | 5.96 | - |
| † | 289.90 | 289.06 | | 0.92 | | 3.01 | | 39.50 | | 0.66 | | | | | | 229.52 | | 17.28 | | |
| III | 1138.40 | 1135.42 | 99.74 | 2.98 | 0.26 | 12.9 | 1.13 | 109.358 | 9.61 | 2.59 | 0.23 | - | - | - | - | 942.57 | 82.80 | 70.95 | 6.23 | - |
| † | 289.77 | 289.01 | | 0.76 | | 3.28 | | 27.84 | | 0.66 | | | | | | 239.92 | | 18.06 | | |
| IV | 1136.45 | 1133.46 | 99.74 | 2.99 | 0.26 | 11.01 | 0.97 | 100.96 | 8.88 | 2.45 | 0.22 | 1333.4 | 117.33 | 99.12 | 8.72 | 951.29 | 83.71 | 70.72 | 6.22 | 136.1 |
| † | 289.77 | 289.01 | | 0.76 | | 2.81 | | 25.74 | | 0.63 | | 340.00 | | 25.27 | | 242.56 | | 18.03 | | |
| V | 1163.66 | 1160.96 | 99.77 | 2.70 | 0.23 | 3.00 | 0.26 | 117.37 | 10.09 | 2.59 | 0.22 | 1365.33 | 117.33 | 102.24 | 8.79 | 968.13 | 83.20 | 72.53 | 6.23 | 136.7 |
| † | 289.68 | 289.01 | | 0.67 | | 0.74 | | 29.22 | | 0.65 | | 339.89 | | 25.45 | | 241.00 | | 18.06 | | |
| VI/VII | 1824.93 | 1820.51 | 99.76 | 4.43 | 0.24 | 3.50 | 0.19 | 152.53 | 8.36 | 3.70 | 0.20 | 1806.57 | 98.99 | 131.44 | 7.20 | 1552.73 | 85.08 | 112.52 | 6.17 | 115.0 |
| † | 289.68 | 289.01 | | 0.70 | | 0.56 | | 24.22 | | 0.58 | | 286.80 | | 20.87 | | 246.50 | | 17.86 | | |
| VIII | 1293.18 | 1290.12 | 99.76 | 3.06 | 0.24 | 2.59 | 0.20 | 33.33 | 2.58 | 9.23 | 0.71 | - | - | - | - | 1160.68 | 89.75 | 87.35 | 6.76 | - |
| | 289.68 | 289.01 | | 0.69 | | 0.58 | | 7.47 | | 2.07 | | | | | | 260.02 | | 19.57 | | |
| Ave † | 289.77 | 289.02 | 99.73 | 0.77 | 0.27 | 2.00 | 0.69 | 28.17 | 9.72 | 0.89 | 0.31 | 347.38 | 119.90 | 26.89 | 9.28 | 240.76 | 83.08 | 17.98 | 6.20 | - |
| Std. † D. | 0.11 | 0.02 | 0.04 | 0.11 | 0.04 | 1.29 | 0.45 | 11.59 | 3.99 | 0.54 | 0.18 | 62.46 | 21.57 | 2.65 | 0.92 | 11.25 | 3.90 | 0.82 | 0.29 | |

*Based on assumption that 93% of C in effluent gases was as $CO_2$ per Burns IV, V, VI, and VII

†Pounds per drum of herbicide incinerated during Burn.

NOTE: All carbon species expressed in pounds as carbon.

**%T denotes that species carbon as a percent of total carbon into the system.**

USAF EHL(K)

gases could not be conveniently related to what may have been present in the combustion gases. Therefore, this evaluation was based on a chlorine mass balance of the system which considered that no chlorine as HCl, $Cl_2$, or (Cl) escaped in the effluent gases and that these chlorines in the combustion gases were completely absorbed into the scrubber water. This was a reasonable basis of evaluation since none of these chlorines were detected in the effluent gases--except for short periods during burns VI and VIII when slightly less than the required amount of NaOH was applied to the scrubber.

c. The total HCl, $Cl_2$ and (Cl) predicted by Marquardt's theoretical analyses never exceeded 0.03 mole fraction of the combustion gases and these gases had a calculated volume always exceeding a million liters per burn. Thus, if total calculated chlorine mass production per burn from Marquardt's theory was comparable to measured chlorine mass in the scrubber water, then volumes of combustion gas production per burn as calculated from Marquardt theory could be accepted. These volumes could then be used to calculate dry scrubbed effluent gas volumes which would be more accurate than those calculated from measured effluent gas velocity pressures. Table I-2 presents the calculated and measured chlorine mass balance for each burn. The ratio of measured to calculated chlorine mass for each burn averaged 0.947 over the eight burns and had a standard deviation of 0.057. These balances were acceptably close for all burns. Marquardt's theoretical data were therefore used to calculate total dry combustion and dry scrubbed effluent gas volumes for each burn. The mass of $CO_2$ removed in the caustic scrubber was calculated from the mass of carbonate alkalinity measured in the spent scrubber water. The mass of carbonate alkalinity was converted to the equivalent volume of $CO_2$, and this volume plus the volumes of HCl, (Cl), $Cl_2$ and $H_2O$ were subtracted from the combustion gas volume to obtain dry scrubbed effluent gas volume. Table I-3 presents the measured and calculated dry scrubbed effluent gas volume for each burn. Excluding burn VIII, the ratio of measured/calculated dry scrubbed effluent gas volumes per burn averaged 1.15 and had a standard deviation of 0.14.

d. All gas volumes used in this report are dry volumes at standard conditions of 70°F and 29.92" of mercury pressure.

5. COMPARISON OF COLLECTED SAMPLE DATA FOR REPLICATE BURNS

a. A review of Table 2 showed that burns I and II could be considered a set of burns which were conducted with poppet nozzles under nearly identical operating parameters. Similarly, burns V and VII could be considered a different set of near-replicate burns which were conducted with radial slot nozzles under nearly identical operating parameters.

b. Each burn's datum in Table I-4 compared favorably and within accuracies of measurement with its respective replicate burn datum. The only exception to these comparable values was burn V's CGH of 0.90 versus burn VII's CGH of 0.10. This difference was attributed to Burn V's combustion gas sample volume of only six liters versus an average of 150 liters for other burns. This small sample volume was less representative and contained hydrocarbon mass near the analytical detection limit. Since all these burns operated with very minor fluctuations of operating parameters, the comparisons of Table I-4 data lend credence to the replicability of incineration products as determined by reproducible sample collections and analyses.

TABLE I-2 CHLORINE MASS BALANCE - MEASURED VERSUS THEORETICAL VALUES "ORANGE" HERBICIDE PROGRAM 12-30 NOV 1973

| BURN NUMBER | Pounds and Percent of Total | | | | | | | STATISTICS | |
|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI/VII | VIII | MEAN | STD D. |
| EHL(K) Measured | | | | | | | | | |
| Cl as HCl Pounds | 451.7 | 520.1 | 655.6 | 570.5 | 668.5 | 1064.9 | 714.9 | | |
| % of Total | 98.5 | 98.6 | 98.9 | 98.6 | 98.1 | 98.8 | 99.5 | 98.7 | 0.4 |
| Cl as $Cl_2$ Pounds | 7.1 | 7.4 | 35.0 | 116.8 | 35.5 | 39.0 | 67.5 | | |
| % of Total | 1.5 | 1.4 | 1.1 | 1.4 | 2.0 | 1.2 | 0.5 | 1.3 | 0.4 |
| Cl Total Pounds | 458.8 | 527.5 | 690.6 | 687.3 | 704.0 | 1103.9 | 782.4 | | |
| EHL(M) Calculated* | | | | | | | | | |
| Cl as HCl Pounds | 408.5 | 499.2 | 635.9 | 694.2 | 638.8 | 1001.1 | 706.5 | | |
| % of Total | 93.0 | 91.5 | 86.8 | 85.9 | 85.1 | 86.4 | 84.0 | 87.5 | 3.4 |
| Cl as $Cl_2$ & Cl Pounds | 30.9 | 46.3 | 97.0 | 113.7 | 111.8 | 157.2 | 134.1 | | |
| % of Total | 7.0 | 8.5 | 13.2 | 14.1 | 14.9 | 13.6 | 16.0 | 12.5 | 3.4 |
| Cl Total Pounds | 439.4 | 545.5 | 732.9 | 807.9 | 750.6 | 1158.3 | 840.6 | | |
| Measured/ Calculated Totals as Percent | 104.4 | 96.7 | 94.2 | 85.1 | 93.8 | 95.3 | 93.1 | 94.7 | 5.7 |

*EHL(M) calculated based on Marquardt theoretical as predicted by computer program.

USAF EHL(M)
USAF EHL(K)

TABLE I-3

SCRUBBED EFFLUENT GAS ($\times 10^6$ LITERS/BURN)*
MEASURED (M) VERSUS CALCULATED (C)**
"ORANGE" HERBICIDE PROGRAM
12-30 NOV 1973

| BURN NUMBER | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| MEASURED | 8.38 | 9.04 | 9.14 | 10.12 | 10.36 | 4.71 | 8.72 | 16.02 |
| CALCULATED | 6.55 | 7.75 | 8.58 | 9.47 | 7.65 | 5.03 | 7.55 | 8.76 |
| RATIO M/C *** | 1.28 | 1.17 | 1.07 | 1.07 | 1.35 | 0.94 | 1.16 | 1.83 |

* Dry, at 70°F and 29.92" Hg pressure.

** Based on Marquardt's theoretical data.

*** $\bar{x} = 1.23$ $\delta = 0.27$ For burns I thru VIII

$\bar{x} = 1.15$ $\delta = 0.14$ excluding burn VIII

EHL(M)

TABLE I-4

COMPARISONS OF COMBUSTION SYSTEM PARAMETERS AND EHL SAMPLE DATA FOR REPLICATE BURNS "ORANGE" HERBICIDE PROGRAM 12-30 NOV 1973

| BURN NO. | F/A | $TC_{ave}$ (°F) | Stay Time (sec) | Fuel Temp °F (± 2) | CGH | SGH | SGBH | SSWH | SSWC | CCD/D | NOZZLE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 0.086 | 2273 | 0.16 | 65 | 4.02 | 0.081 | 3.5 | 8.59 | 0.89 | 3.03 | Poppet |
| II | 0.086 | 2286 | 0.15 | 97 | 9.59 | 0.063 | 18.6 | 6.38 | 0.68 | 3.01 | Poppet |
| Replicates | | | | | | | | | | | |
| V | 0.120 | 2734 | 0.14 | 99 | 0.90 | 0.055 | 75.7 | 0.13 | 0.62 | 0.74 | Slot |
| VII | 0.120 | 2772 | 0.15 | 105 | 0.10 | 0.076 | 36.5 | 0.22 | 0.60 | 0.75 | Slot |
| Replicates | | | | | | | | | | | |

CGH - Sum of aliphatic and aromatic hydrocarbons as carbon mass per liter (µg/l) in sampled combustion gas, See Table I-6.

SGH - Sum of aliphatic and aromatic hydrocarbons as carbon mass per liter (µg/l) in sampled scrubbed effluent gas, See Table I-7.

SGHB - Beckman 109A hydrocarbon data (ppm) from scrubbed effluent gas, See Table I-9.

SSWH - Total aliphatic, aromatic, and phenolic hydrocarbons as carbon mass (gms) collected in the total volume of spent scrubber water, See Table I-8.

SSWC - Carbon particles in spent scrubber water, pounds per drum of herbicide burned.

CCD/D - Combustion coke deposit in combustion chamber, pounds per drum of herbicide burned.

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6. HYDROCARBON MASS PENETRATION THROUGH THE TCDD, nb-ESTER AND ACID (OF 2,4-D AND 2,4,5-T) SAMPLING TRAINS

a. The TCDD, nb-ester and acid sampling train (TCDD sampling train) was developed and tested specifically for the mass collection of the nb-esters and acids of 2,4-D and 2,4,5-T (See Appendix D.). The collection of TCDD in the sampling trains was not tested in the laboratory. However, TCDD's vapor pressure and solubility similarities to the nb-esters of 2,4-D and 2,4,5-T were sufficient to conclude that TCDD would be collected as effectively in the sampling train as the nb-esters. This same reasoning could not be applied to the mass collection of nonchlorinated aliphatic and nonchlorinated aromatic hydrocarbons. However, sufficient data were collected during the field sampling program so that an assessment of hydrocarbon mass penetration (collection) through the sampling trains could be made.

b. Table I-5 presents, for each burn, the hydrocarbon mass collected in all four impingers, the mass collected only in the last one of the four serial impingers, and the percent of the total mass that was collected in the last impinger. The combustion gas samples and the scrubbed effluent gas samples were grouped respectively as sets because the physical conditions (temperature, pressure, etc.) of these sampled gases were quite different.

(1) The following observations of the data in Table I-5 were made:

(a) The averages of the aliphatic and aromatic hydrocarbon masses collected in the last impinger were nearly equal in both sample sets.

(b) The averages of the total masses collected in all four impingers varied significantly between sample sets.

(c) The total mass collected in all four impingers varied significantly within each sample set.

(d) The mass collected in the last impinger did not vary significantly within each sample set (relative to the variance of mass collected in all four impingers).

(2) From these observations, it was concluded that hydrocarbon mass collection in the last impinger (in the series of four impingers) was independent of:

(a) Mass loading in the first three impingers.

(b) Hydrocarbon mass concentration in the sampled gas.

c. For nonchlorinated aliphatic and aromatic hydrocarbon mass collection in the last impinger of this serial impinger collection system to be independent of mass loading and independent of mass concentration in the sampled gas, the mass collection efficiency in the first three impingers necessarily was good for those hydrocarbons collected or it was near 0% in all impingers. Since collection efficiency was obviously not 0%, collection efficiency in the first three impingers was good (for those hydrocarbons collected). However, since hydrocarbon mass was found in the last impinger, collection efficiency in the impinger sampling train was not 100%.

TABLE I-5 HYDROCARBON MASS COLLECTION IN THE TCDD SAMPLING TRAINS "ORANGE" HERBICIDE PROGRAM 12-30 NOV 1973

| BURN NO. | Total Mass (μ g) Collected in all 4 Impingers | | Mass (μg) Collected in Last Impinger | | % of Total Mass Collected in Last Impinger | |
|---|---|---|---|---|---|---|
| | Aliphatic $C_{10}H_{22}$ | Aromatic $C_6H_5$ $(C_4H_9)$ | Aliphatic $C_{10}H_{22}$ | Aromatic $C_6H_5$ $(C_4H_9)$ | Aliphatic $C_{10}H_{22}$ | Aromatic $C_6H_5$ $(C_4H_9)$ |
| **COMBUSTION GAS SAMPLE SET** | | | | | | |
| I | 91.9 | 440.0 | 2.7 | 2.9 | 3 | 1 |
| II | 37.7 | 329.0 | 1.0 | 0.6 | 3 | 0 |
| III | 245.6 | 110.4 | 5.9 | 2.5 | 2 | 2 |
| IV | 1.2 | 1.6 | 0.2 | 0.2 | 17 | 13 |
| V | 2.8 | 3.4 | 0.3 | 0.7 | 11 | 21 |
| VI | 3.4 | 29.8 | 0.2 | 0.1 | 6 | 0 |
| VII | 3.3 | 9.2 | 0.2 | 0.3 | 6 | 3 |
| VIII | 14.1 | 20.7 | 0.3 | 0.2 | 2 | 1 |
| $\bar{x}$ | 50.0 | 118.0 | 1.3 | 0.9 | 6.2 | 5.1 |
| $\delta$ | 84.9 | 170.7 | 2.0 | 1.1 | 5.3 | 7.7 |
| $\bar{x}$ * | | | | | 3.7 | 1.2 |
| $\delta$ * | *Excluding burns IV and V | | | | 1.9 | 1.2 |
| **SCRUBBED EFFLUENT GAS SAMPLE SET** | | | | | | |
| I | 4.1 | 5.9 | 0.5 | 0.9 | 12 | 15 |
| II | 4.4 | 4.3 | 1.5 | 2.1 | 34 | 49 |
| III | 13.1 | 15.7 | 1.1 | 1.9 | 8 | 12 |
| IV | 6.4 | 8.3 | 0.6 | 0.2 | 9 | 2 |
| V | 4.3 | 2.7 | 0.6 | 0.6 | 14 | 22 |
| VI | 11.1 | 5.7 | 1.2 | 0.7 | 11 | 12 |
| VII | 3.7 | 3.6 | 0.7 | 0.2 | 19 | 6 |
| VIII | 3.3 | 9.3 | 0.2 | 0.5 | 6 | 5 |
| $\bar{x}$ | 6.3 | 6.9 | 0.8 | 0.9 | 14 | 16 |
| $\delta$ | 3.7 | 4.2 | 0.4 | 0.7 | 9 | 15 |
| $\bar{x}$ ** | | | | | 11.3 | 10.6 |
| $\delta$ ** | ** Excluding Burn II | | | | 4.3 | 6.8 |

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d. Two potential causes for penetration of hydrocarbon mass to and through the last impinger were considered:

(1) A specific nonchlorinated aliphatic and aromatic hydrocarbon or a specific group of hydrocarbons was relatively insoluble in the benzene or,

(2) a specific hydrocarbon or group of hydrocarbons was bleeding (movement of the compound down the impinger series) due to high vapor pressure (volatility) and low concentration in the sampled gases.

e. Solubility was dismissed as the potential cause for penetration of hydrocarbons to the last impinger since nonchlorinated aliphatic and aromatic hydrocarbons are generally very soluble in benzene.

f. Bleeding of a specific hydrocarbon or group of specific hydrocarbons was considered the most probable cause of mass penetration to and through the last impinger. Discussion of this consideration is as follows:

(1) Since a gas confined (as in a bubble) in contact with a liquid will dissolve in the liquid (if soluble) until "...its partial pressure above the liquid is in equilibrium with the gas dissolved in the liquid..."[1] any hydrocarbons that existed in the sampled gas and had a significant vapor pressure at ~50°F (benzene temperature during sampling) would not have appreciably dissolved (absorbed) in the benzene at concentrations less than several 1000 ppmv/v and would have bled. Since aromatic hydrocarbons with molecular weights <132.2 have vapor pressures >0.0001 mm of mercury pressure at ~50°F (100 ppm at 760 mm of mercury pressure and at saturation), these hydrocarbons would have bled (penetrated the sampling system) substantially.

(2) However, nonchlorinated aromatic hydrocarbons with molecular weights greater than 200 generally have freezing points near ~50°F (temperature of benzene in the impingers during sampling) and the corresponding vapor pressures are extremely low (<0.00001 mm mercury pressure). Thus, these compounds would have been effectively collected in the TCDD sampling train. An exact number for the collection efficiency of these heavy hydrocarbons (>200) was impossible to determine objectively, however, a subjective evaluation based on previous laboratory work was made and the collection efficiency was considered ≥90% for hydrocarbons with molecular weights >200. For hydrocarbons with mw<200 the collection efficiency becomes a function of their vapor pressure and mass concentration in the sample gas. A similar argument was used for aliphatic hydrocarbons.

(3) At this point, two dependent conclusions were made that the hydrocarbon mass collected in the TCDD sampling trains:

[1]Patty, Frank A., Industrial Hygiene and Toxicology, Volume I, 2nd Edition, page 153.

(a) did not include lightweight hydrocarbons (mw <132) and was thus not representative of a total hydrocarbon mass in the sampled gas, but

(b) was representative of the degree of "Orange" herbicide pyrolytic degradation to unchlorinated hydrocarbon compounds which were considered to have no significant herbicidal or toxic properties even though they were herbicide pyrolyzates.

(4) This latter conclusion, in conjunction with the fact that hydrocarbon collection efficiency in the TCDD sampling train remained equal for all burns, permitted the hydrocarbon mass data from the TCDD sampling systems to be used as an indicator of the relative degree of pyrolysis of Orange herbicide. Thus, relative pyrolysis efficiencies (RPEs) were calculated for each burn. The collection efficiency of specific hydrocarbons in the TCDD sampling trains did not vary between burns since the trains were operated in a consistent manner under similar sampling conditions. An RPE calculation was based on the mass of hydrocarbons as carbon collected in a TCDD sampling train at the reaction tailpipe versus the mass of Orange herbicide as carbon incinerated. Although these calculated efficiencies were relative to hydrocarbon mass collected rather than an absolute quantitation of all potentially existing combustion gas hydrocarbons, they provided a means of evaluating and comparing the different burns.

g. The existence of nearly the same hydrocarbon mass in the last impinger from all sample trains was probable due to a combination of factors:

(1) analytical accuracy decreased as the hydrocarbon mass in the sample volumes approached the detection limit,

(2) hydrocarbon gas chromatographic peaks were more susceptible to interferences, when hydrocarbon mass in the samples was lowest,

(3) potential production of intermediate weight Orange herbicide pyrolysis products (those hydrocarbons having molecular weights between 132 and 200 and being only partially collected) may have been produced in a relatively constant mass concentration during all burns,

h. Essentially the same hydrocarbon mass was collected in each burn's scrubbed effluent gas sampling train. This was probably caused by a relatively consistent mass of light and intermediate weight hydrocarbons (mw <200) which penetrated the scrubber and were collected by the scrubbed effluent gas sampling train.

7. RELATIVE PYROLYSIS EFFICIENCIES OF ORANGE HERBICIDE INCINERATION

a. Relative pyrolysis efficiencies (RPE) of Orange herbicide were calculated for burns I through VIII and are presented in Table I-6. Presented data are described as follows:

(1) Total combustion gas volume per burn (liters) as discussed in paragraph 4, this appendix.

(2) Total hydrocarbons detected in combustion gas samples, divided into two categories: the monochlorophenol and aliphatic hydrocarbons (non-chlorinated) and aromatic hydrocarbons (nonchlorinated), expressed as the:

(a) actual mass of each per liter of sampled combustion gas (µg/l),

(b) carbon mass of each per liter of sampled combustion gas (µg/l),

(c) actual mass as carbon for each in the total burn (g).

(3) Five herbicide compounds (2,4-D and 2,4,5-T nb-esters and acids and TCDD) that were undetected but could have existed without detection in a combustion gas sample -- expressed as the:

(a) mass of each compound as the compound per liter of sampled combustion gas (µg/l),

(b) mass of each compound as carbon per liter of sampled combustion gas (µg/l), and

(c) total masses for all five compounds as carbon for a total burn (g).

The undetected masses of these herbicide compounds were calculated based upon an average detection limit of $22 \times 10^{-9}$ gms per total sample for all five compounds. This detection limit was divided by the burn's combustion gas sample volume to find the minimum combustion gas mass concentration that was necessary for detection of each of these compounds. This value was then multiplied by the total burn combustion gas volume, the average percent carbon content of these compounds, and five in order to determine the total possible undetected mass of these compounds in the combustion gas of each burn. This procedure assumed that the undetected total mass of these compounds and the detected masses of the other hydrocarbons existed evenly throughout the burn.

(4) Herbicide fuel feed mass expressed as carbon mass that was injected into the combustion chamber during a burn period.

(5) Ionol and didecylphthlate were not included in Table I-6 combustion gas sample masses since these compounds were not considered products of Orange herbicide incineration (see paragraph 3, this appendix).

(6) Relative pyrolysis efficiency (RPE) was based upon the analytical values presented for each burn. (See Appendix G for analytical values.)

b. One could double the total combustion gas hydrocarbon masses as carbon per burn and decrease the fuel feed herbicide carbon by 5% to test the significance of the digits of the RPE in Table I-6. These worst case conditions would represent pooling of errors for nonrepresentative sampling, errors of sample analyses, and errors in calculating total burn volumes. This exercise concluded that the second decimal place was significant for all burns and that the third decimal place was significant only for Burns IV through VIII.

8. EFFECTS OF INCINERATOR OPERATING PARAMETERS

a. Effects of various incineration operating parameters on the RPE's

TABLE I-6 RELATIVE "ORANGE" HERBICIDE PYROLYTIC DESTRUCTION
"ORANGE" HERBICIDE PROGRAM
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| BURN NUMBER | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| Combustion Gas Volume (Liters/Burn)[1] | $6.79 \times 10^6$ | $8.02 \times 10^6$ | $8.89 \times 10^6$ | $9.79 \times 10^6$ | $7.98 \times 10^6$ | $5.21 \times 10^6$ | $7.87 \times 10^6$ | $9.03 \times 10^6$ |
| Aliphatic HC[2] (Unchlorinated) | | | | | | | | |
| $\mu$g/l as $C_{10}H_{22}$ | 0.67 | 1.11 | 1.10 | <0.01* | 0.47 | 0.02 | 0.03 | 0.09 |
| $\mu$g/l as C | 0.56 | 0.92 | 0.92 | <0.01 | 0.39 | 0.02 | 0.03 | 0.09 |
| g/Burn as C | 3.80 | 7.38 | 8.18 | <0.01 | 3.11 | 0.10 | 0.24 | 0.81 |
| Aromatic HC[2] (Unchlorinated)** | | | | | | | | |
| $\mu$g/l as $C_6H_5$ ($C_4H_9$) | 4.26 | 9.68 | 0.49 | <0.01 | 0.57 | 0.18 | 0.08 | 0.16 |
| $\mu$g/l as C | 3.46 | 8.67 | 0.44 | <0.01 | 0.51 | 0.16 | 0.07 | 0.14 |
| g/Burn as C | 23.49 | 69.50 | 3.91 | <0.01 | 4.07 | 0.83 | 0.55 | 1.26 |
| Herbicide HC[3] | | | | | | | | |
| $\mu$g/l as HC/compound | 0.00016 | 0.00065 | 0.00009 | 0.00008 | 0.00366 | 0.00013 | 0.00019 | 0.00017 |
| $\mu$g/l as C/compound | 0.00008 | 0.00033 | 0.00005 | 0.00004 | 0.00180 | 0.00006 | 0.00009 | 0.00008 |
| g/Burn as C/5 compounds | 0.003 | 0.013 | 0.002 | 0.002 | 0.072 | 0.000 | 0.004 | 0.004 |
| TOTAL CARBON | | | | | | | | |
| g/Burn Combustion Gas | 27.29 | 76.89 | 12.09 | <0.01* | 7.25 | 0.93 | 0.79 | 2.07 |
| g/Burn Input | 342466. | 393670. | 515480. | 514590. | 527076. | 529992. | 585776. | 585714. |
| % Relative Pyrolysis Efficiency | 99.99 | 99.98 | 99.99 | >99.999 | 99.998 | 99.999 | 99.999 | 99.999 |

1. Based on Marquardt theoretical calculations (See Appendix A )
2. Calculated from hydrocarbon mass found in combustion gas impinger samples.
3. Based on the maximum mass that could have existed in the combustion gas without being detected (Sum of TCDD and the butyl esters and acids of 2,4-D and 2,4,5-T).

*See Discussion of Conflicting Data, page I-25.

**Includes monochlorophenol detected in Burn I.

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of Table I-6 were evaluated by comparing those burns that were replicate except for a change in only one operating parameter. Since the RPE's were almost identical in value, they were not used to assess effects of changed operating parameters. Instead, the following measured/calculated data are defined and were used in the comparisons:

(1) CGH - (See definition on Table I-4)

(2) SSWH - (See definition on Table I-4)

(3) CCD/D - (See definition on Table I-4)

(4) SGHB - (See definition on Table I-4)

(5) Contaminate mass of hydrocarbons found in the combustion coke deposit (CCH) expressed as µg/100 gms, see Table G-9, Appendix G.

b. As selected from Table 2 of this report, the following burns were compared in relation to their one different operating parameter.

(1) "Orange" Herbicide Preheat - Burns III and IV

(a) "Orange" herbicide fuel was preheated to 178°F (±2) in burn IV but only to 91°F(±1) in burn III. The CGH was two orders of magnitude greater in III than IV. The SSWH of III was 2.42 gms or about ten times (on order of magnitude) the SSWH of IV (burn duration of III and IV were about equal.) Additionally, the spent scrubber water of III contained 0.25 µg/l of TCDD which along with any of the other original herbicide compounds were undetected in any scrubber water samples. The CCD/D was 2.81 pounds for burn IV compared to 3.28 pounds for burn III. Burn III's CCH was 1132.6 and contained the methyl and butyl esters of 2,4-D and 2,4,5-T while burn IV's CCH weighed 542 and no methyl/butyl ester of 2,4-D or 2,4,5-T were detected.

(b) A small improvement of effluent quality due to herbicide preheating was also noted between replicate burns I and II, see Table I-6. Although comparisons of Table I-6 values did not show significant improvement, the trend toward better RPE's was evident.

(c) From these comparative observations it was concluded that:

1. Burn IV's RPE appeared at least one order of magnitude better than burn III's, and

2. Preheating of "Orange" herbicide to ~180°F was an important operating parameter which improved burn IV's RPE.

(2) Central Poppet Nozzle Versus Radial Slot Nozzles - Burns III and VI: Burns III and VI were identical in operating parameters except the central poppet nozzle was used in burn III while the radial slot nozzles were used in burn VI. Burn III's CGH was about one order of magnitude greater than burn VI's CGH. The SSWH for burn III was 2.42 while burn VI's SSWH would have been 0.06 for a total burn period equal to III's. Burn III's CCD/D was

3.28 pounds versus 0.85 pounds for burn VI. As previously cited, Burn III's CCH was 1132.6 and herbicidally contaiminated while burn VI's CCH was only 66.9. These data demonstrated that radial slot nozzles produced significantly better incineration results than poppet nozzles when both nozzles were operated under identical parameters and a medium range F/A of 0.106.

(3) Process Flow Rates - Burns VII and VIII: Burns VII and VIII were replicates except that the air and herbicide fuel feed mass flow rates of burn VIII were only 66% of burn VII's: 1.05 pps air/0.123 pps fuel for VIII and 1.55 pps air/0.186 pps fuel for VII. Burn VIII's CGH was about twice that of Burn VII's CGH; however, both concentrations were near the analytical detection limit and thus not sufficiently different to allow a definitive conclusion about which set of process flows was better. Compared to equal burn durations, the SSWH and CCD/D of burns VII and VIII were very nearly equal. Analyses of combustor coke deposit from these burns were not made but there was no reason to believe their qualities differed. These comparisons showed no differences in RPE or effluent quality between these identical burns which had different air and fuel mass flow rates but identical F/A ratios. Thus without any differences, the higher process flow rate could be chosen to minimize incineration time.

(4) Fuel to Air Mass Flow Ratios and Different Nozzles - Burns I and II Versus Burns V and VII

(a) As discussed in paragraph 5, this appendix, burns I and II were replicates of each other as were burns V and VII. As shown in Table I-4, the EHL sample data values of Burns V/VII were all at least ten percent less than those for burns I/II -- particularly noteworthy was that burns V/VII's CGH, SSWH, and CCD/D values were one order of magnitude less than burns I/II's values. The only exception was SBGH, and its inverse relationship to RPE is discussed in paragraph 10, this appendix.

(b) From these comparative observations it was concluded that the radial slot nozzle handled higher mass flow rates than the poppet nozzle and yet produced RPE's and incineration effluent quality generally one order of magnitude better.

(c) Effects of Temperature on RPE

1. The relative degree of "Orange" herbicide destruction in the combustion process was not expected to be a simple function of temperature (heat energy). Other parameters such as burn velocity (stay time), burner pressure, air and fuel preheat, process flow rates, and method of fuel injection were all expected to be interrelated parameters. The following analysis of the relationship of temperature and the relative degree of "Orange" herbicide pyrolysis indicated the complexity of these interrelationships.

2. For example, the average temperature ($TC_{AVE}$ column 16, Table 2 and discussion, paragraph 7.2) for burns I and II was 2280° F and the $TC_{AVE}$ for burns V and VII was 2753° F. The RPE's in burns V and VII were significantly better than in burns I and II, 99.999 vs 99.99%. However, burn VI had an RPE comparable to that in burns V and VII, but the $TC_{AVE}$ was

2454°F, about 300°F less than in burns V and VII and only 174°F greater than the $TC_{AVE}$ in burns I and II. In yet another case, burn IV had the highest RPE of all burns but the $TC_{AVE}$ was only 2508°F, 245°F less than in burns V and VII and only 228°F greater than in burns I and II.

3. From these observations one might have concluded that the RPE was not improved by increasing $TC_{AVE}$ above 2454°F. In these burns and from a temperature standpoint, this conclusion would be correct. However, other combustion parameters were changed in the burns and one could not conclude that destruction efficiency would not have improved with an increase in temperature had different operating parameters existed.

9. HYDROCARBON MASS PENETRATION THROUGH THE CAUSTIC SCRUBBER AND COLLECTION IN THE SCRUBBER

a. Table I-7 presents each burn's CGH and SGH data. Penetration of hydrocarbon mass through the caustic scrubber increased as the burn's RPE improved. Similar to the discussion in paragraph 6 of this appendix, hydrocarbon mass penetration through the caustic scrubber was expected to be a function of hydrocarbon vapor pressure (condensability) since the detected hydrocarbons were only slightly soluble in caustic solution. The hydrocarbon collection mechanism in the caustic scrubber was probably impaction (entrainment) rather than absorption. Heavier, less volatile hydrocarbons were expected to condense from the combustion gases in and downstream of the venturi since the venturi pressure drop and injected caustic solution provided very rapid cooling of the combustion gases. The degree of this rapid cooling was rather consistent between burns, i.e. from an average combustion gas temperature of 1990°F (s=158) exiting the reaction tailpipe, passing through the venturi at 400 ft/sec, and dropping to an average scrubbed effluent gas temperature of 163°F (s=8).

b. Once these condensed hydrocarbons were entrained in the caustic solution, they were either dissolved to their solubility limits and retained or desorbed and entered the scrubbed effluent gas if their vapor pressures were significant in the spent scrubber water's average temperature of 160°F. As the burn's RPE improved, the combustion gas contained less of these heavier hydrocarbon compounds. The hydrocarbon mass collected in the spent scrubber water decreased with the decreasing difference in hydrocarbon mass collected in the combustion and scrubbed effluent gas TCDD sampling trains. Scrubber water "efficiency" of total hydrocarbon collection decreased more rapidly than that of the TCDD sampling trains because of the much higher collection of low vapor pressure hydrocarbons in benzene at ~50°F.

c. Table I-8 presents the detected hydrocarbon (grams) in each burn's total spent scrubber water volume. As discussed in paragraph "b" above, the detected hydrocarbon masses decreased in proportion to increased RPE; i.e. one order of magnitude decrease when the third decimal of the RPE became significant. Except for burns I, II and III, which used poppet nozzles and had the lowest RPE's and $TC_{AVE}$'s, all detected hydrocarbons were less than 20 µg/l in the spent scrubber water . Of this total hydrocarbon mass per liter of SSW, less than 1.5% could have been the total undetectable TCDD and acids/esters of 2,4-D and 2,4,5-T listed in Table I-8.

TABLE I-7: HYDROCARBON MASS PENETRATION THROUGH THE CAUSTIC SCRUBBER (CGH vs SGH)
"ORANGE" HERBICIDE PROGRAM
12-30 NOV 73

| Burn Number | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| Scrubbed Effluent Gas Volume (Liters)* | $6.55 \times 10^6$ | $7.75 \times 10^6$ | $8.58 \times 10^6$ | $9.47 \times 10^6$ | $7.65 \times 10^6$ | $5.03 \times 10^6$ | $7.55 \times 10^6$ | $8.76 \times 10^6$ |
| Aliphatic HC** | | | | | | | | |
| µg/l as $C_{10}H_{22}$ | 0.038 | 0.037 | 0.135 | 0.048 | 0.039 | 0.306 | 0.045 | 0.037 |
| µg/l as C | 0.032 | 0.031 | 0.113 | 0.040 | 0.033 | 0.255 | 0.037 | 0.031 |
| g/burn as C | 0.210 | 0.240 | 0.969 | 0.379 | 0.252 | 1.283 | 0.279 | 0.272 |
| Aromatic HC | | | | | | | | |
| µg/l as $C_6H_5(C_4H_9)$ | 0.055 | 0.036 | 0.162 | 0.062 | 0.024 | 0.157 | 0.044 | 0.103 |
| µg/l as C | 0.049 | 0.032 | 0.145 | 0.056 | 0.022 | 0.141 | 0.039 | 0.092 |
| g/burn as C | 0.321 | 0.248 | 1.244 | 0.530 | 0.168 | 0.709 | 0.294 | 0.806 |
| Biphenyl HC | | | | | | | | |
| µg/l as $C_{12}H_{10}$ | 0.017 | 0.017 | 0.009 | 0.006 | 0.048 | 0.168 | 0.031 | 0.072 |
| µg/l as C | 0.016 | 0.016 | 0.009 | 0.006 | 0.046 | 0.158 | 0.029 | 0.067 |
| g/burn as C | 0.102 | 0.132 | 0.076 | 0.061 | 0.348 | 0.796 | 0.218 | 0.589 |
| Herbicide HC | | | | | | | | |
| µg/l as HC/compound | 0.00021 | 0.00018 | 0.00023 | 0.00016 | 0.00020 | 0.00060 | 0.00026 | 0.00024 |
| µg/l as C/compound | 0.00010 | 0.00009 | 0.00011 | 0.00008 | 0.00010 | 0.00030 | 0.00013 | 0.00011 |
| g/burn as C/5 compounds | 0.003 | 0.004 | 0.005 | 0.004 | 0.004 | 0.007 | 0.004 | 0.005 |
| Total Carbon | | | | | | | | |
| g/burn Scrubbed Gas | 0.636 | 0.624 | 2.289 | 0.974 | 0.772 | 2.795 | 0.79 | 1.672 |
| g/burn Combustion Gas† | 27.29 | 76.89 | 12.09 | <0.01 | 7.25 | 0.93 | 0.79 | 2.07 |
| Penetration, Percent | 2.33 | 0.81 | 18.93 | - | 10.65 | - | 100. | 80.8 |
| Relative Pyrolysis Efficiency, Percent | 99.99 | 99.98 | 99.99 | >99.999 | 99.998 | 99.999 | 99.999 | 99.999 |

*Dry, at 70°F and 29.92" Hg pressure. From Table I-3.

**HC - hydrocarbon

†From Table I-6

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TABLE I-8: SUMMARY OF HYDROCARBON COMPOUNDS COLLECTED IN SPENT SCRUBBER WATER "ORANGE" HERBICIDE PROGRAM 12-30 NOV 1973

| | Spent Scrubber Water Total Volume Per Burn (Liters) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 15693 | 14996 | 15100 | 15916 | 13538 | 7185 | 14267 | 12124 |
| BURN NUMBER → | I | II | III | IV | V | VI | VII | VIII |
| Detected Hydrocarbons (gms) | | | | | | | | |
| Aliphatic Hydrocarbon as $C_{10}H_{22}$ | 1.689 | 1.458 | 1.699 | 0.099 | 0.130 | 0.014 | 0.138 | 0.119 |
| " " as C | 1.407 | 1.215 | 1.415 | 0.082 | 0.108 | 0.012 | 0.115 | 0.099 |
| Aromatic Hydrocarbon as $C_6H_5C_4H_9$ | 3.005 | 1.815 | 0.852 | 0.081 | 0.001 | 0.024 | 0.111 | 0.075 |
| " " as C | 2.692 | 1.626 | 0.763 | 0.073 | 0.001 | 0.022 | 0.099 | 0.067 |
| Dichlorobenzene as $C_6H_4Cl_2$ | 8.225 | 6.975 | 0.488 | 0.115 | 0.043 | 0.003 | 0.016 | 0.027 |
| " " as C | 4.030 | 3.418 | 0.239 | 0.056 | 0.021 | 0.001 | 0.008 | 0.013 |
| Monochlorophenol as $C_6H_4ClOH$ | 0.827 | 0.211 | 0.003 | 0.003 | 0.001 | 0.001 | 0.001 | 0.001 |
| " " as C | 0.463 | 0.118 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Total Weight of Above (gms) | 13.744 | 10.459 | 3.042 | 0.298 | 0.175 | 0.042 | 0.266 | 0.222 |
| " " " " as C (gms) | 8.592 | 6.377 | 2.418 | 0.212 | 0.131 | 0.035 | 0.223 | 0.180 |
| Maximal Undetected Components of Blended Herbicide Feed (mgm) | | | | | | | | |
| TCDD | 0.74 | 0.71 | 3.78* | 0.75 | 0.64 | 0.34 | 0.68 | 0.58 |
| TCDD as C | 0.33 | 0.32 | 1.69 | 0.34 | 0.29 | 0.15 | 0.30 | 0.25 |
| 2,4-D acid (butyl ester) | 0.75 | 0.72 | 0.72 | 0.76 | 0.65 | 0.34 | 0.68 | 0.58 |
| " " " " as C | 0.43 | 0.42 | 0.42 | 0.44 | 0.37 | 0.20 | 0.40 | 0.34 |
| 2,4,5-T acid (butyl ester) | 0.63 | 0.60 | 0.60 | 0.63 | 0.54 | 0.29 | 0.58 | 0.49 |
| " " " " as C | 0.29 | 0.28 | 0.28 | 0.29 | 0.25 | 0.13 | 0.26 | 0.22 |
| 2,4-D acid (methyl ester) | 0.75 | 0.72 | 0.72 | 0.76 | 0.65 | 0.34 | 0.68 | 0.58 |
| " " " " as C | 0.34 | 0.33 | 0.33 | 0.35 | 0.30 | 0.16 | 0.32 | 0.27 |
| 2,4,5-T acid (methyl ester) | 0.67 | 0.64 | 0.64 | 0.67 | 0.57 | 0.30 | 0.60 | 0.51 |
| " " " " as C | 0.27 | 0.26 | 0.26 | 0.27 | 0.23 | 0.12 | 0.24 | 0.20 |
| Total Undetected Weight of Above (mg) | 3.54 | 3.39 | 6.46 | 3.57 | 3.05 | 1.62 | 3.22 | 2.74 |
| " " " " as C (mg) | 1.66 | 1.61 | 2.98 | 1.69 | 1.44 | 0.76 | 1.51 | 1.28 |
| Grand Total of all Hydrocarbons (gms) | 13.748 | 10.462 | 3.048 | 0.302 | 0.178 | 0.044 | 0.269 | 0.225 |
| " " " " " as C (gms) | 8.594 | 6.379 | 2.421 | 0.214 | 0.132 | 0.036 | 0.225 | 0.181 |

*Only one of these compounds detected in any spent scrubber water samples.

d. The unchlorinated aliphatic and aromatic hydrocarbons of Table I-8 were considered as pyrolyzates which were trapped and slightly dissolved in the scrubber water. The detected chlorinated hydrocarbons were considered hydrolyzates formed by reaction of the aromatic hydrocarbons and chlorine species in the combustion gases as they cooled and mixed with the caustic in the scrubber (see paragraph 11, this report). As the RPE's increased (burns IV through VIII), the mass of the chlorinated hydrocarbons in the SSW decreased faster than the mass of the aromatic hydrocarbons. This was because the mass of the former was dependent on the latter, and the latter decreased in the combustion gas as RPE increased.

e. Table I-8 also presents the maximal mass of components of blended herbicide (mgm) that could have existed undetected in each burn's total spent scrubber water volume. These values were based on the detection limits and analytical recovery efficiencies of each compound in 500 ml of collected SSW TBC that was analyzed. These calculated masses were therefore all relative to the total spent scrubber water volume except for TCDD in burn III. This TCDD was the only one of these herbicidal component compounds detected in any SSW-TBC or SSW-Cl samples, see discussion in paragraph 12 of this appendix.

f. Suspended matter in the SSW were analyzed from concentrated sediment samples collected after each burn from the bottom of the SSW holding tank. Analytical results presented in Table G-8, Appendix G, showed that no detectable hydrocarbons were extracted from any of the sediments. These sediments were thus considered as carbon with less than 9.0% iron content. The carbon was a pyrolytic product but the iron came from combustion gas acids leaching the metal of the scrubber tank.

10. BECKMAN 109A DATA COMPARED WITH RPE's

a. Table I-9 was presented to demonstrate that scrubbed effluent gas hydrocarbon data measured with the Beckman 109A total hydrocarbon analyzer (SGBH) was not an indicator of the relative pyrolysis efficiency (RPE) of "Orange" herbicide.

b. Burns I and II had the lowest SGBH of all burns. If SGBH was a good indicator of RPE, burns I and II would have had the best RPE in the set of eight burns. However, the CGH and SSWH was greater in burns I and II than in all other burns and the RPE of burns I and II was less than in all other burns.

c. Burns VII and VIII had a greater RPE than burns I and II, but their SGBH readings were greater than in burns I and II. In burns III through VI, the SGBH had no apparent inverse or direct relationship to RPE.

d. During the incineration of "Orange" herbicide, the CGH and SSWH were related. This was anticipated since the heavier, but not completely combusted hydrocarbons, (pyrolyzates) would be more effectively collected in both the TCDD sampling trains and the caustic scrubber than the light molecular weight pyrolyzates. In burns that had a poorer RPE (burns I and II) the heavy pyrolyzates were more effectively collected in the caustic scrubber and were not

TABLE I-9: COMPARISON OF HYDROCARBON DATA - BECKMAN 109A (SCRUBBED EFFLUENT GAS), CGH, AND SSWH "ORANGE" HERBICIDE PROGRAM 12-30 NOV 73

| BurnNumber | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| SGHB† $\bar{x}$ (ppm) | 3.5 | 18.6 | 395* | 1450.0 | 79.5* | 151.7 | 75.7 | 36.5 |
| s | 2.9 | 5.8 | | 1258.9 | | 22.6 | 23.1 | 17.1 |
| CGH (µg/l) | 4.02 | 9.59 | 1.36 | - | 0.90 | 0.18 | 0.10 | 0.23 |
| SSWH (g/burn) | 8.59 | 6.38 | 2.42 | 0.21 | 0.13 | 0.04 | 0.22 | 0.18 |

*Measured during the same time period of CGH sampling.

†Four (4) values used for $\bar{x}$.

For definition of SGBH, CGH, and SSWH, see Table I-4.

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detected by the Beckman 109A. In burns that had better RPE's (burns IV through VIII) the light pyrolyzates were not collected in the scrubber but were detected by the Beckman 109A, and thus higher SGBH values were observed even though the RPE's were higher.

11. HERBICIDAL COMPOUNDS DETECTED IN GAS SAMPLES AND RELATED EQUIPMENT

a. The nb-esters of 2,4-D and 2,4,5-T were detected in the rinse from the Beckman 109A cold trap used in burn I Monochlorophenol was detected in the first impinger of the combustion gas sampling train from burn I. Dichlorophenol was detected in the rinses from the Beckman 109A cold traps used in burns I, II and III, in the air cooled sampling probe rinses from burns II and III, and in the mixed (one and two impingers) water of the particulate source sampling train impingers from burns IV and VI.

b. The butyl esters found in the cold trap rinse from record burn I could have been deposited during either of two checkout burns made before record burn I (see Marquardt Test 4 and 5). The first attempt at record burn I was aborted 16 minutes into the burn due to fuel injection problems caused by the high viscosity of "Orange" herbicide. Since the incineration of "Orange" herbicide during these checkout burns was not as carefully controlled as during all successful record burns, and since the cold trap was not rinsed after the two checkout burns it was concluded that the cold trap rinse from record burn I was not representative. No butyl esters were found in the cold trap rinses from record burns II and III. The cold traps used in burns IV through VIII were rinsed but not analyzed.

c. The dichlorophenol found in the Beckman 109A cold trap rinse from burn I was considered unrepresentative for reasons given in the previous paragraph.

d. Dichlorophenol was found in the Beckman 109A cold trap rinses from burns II and III and in the combustion gas air cooled sampling probe rinses from burns II and III. However, the compound was not detected in the combustion gas impinger samples that were downstream of the air cooled probes or in the spent scrubber water samples from these burns.

(1) Dichlorophenol has a high melting and boiling point (113$^{o}$F and 403$^{o}$F for 2,4). The caustic scrubber (caustic solution at 160$^{o}$F in collector tank) was expected to collect a significant fraction of compounds as condensable as dichlorophenol (monochlorophenol was collected in the scrubber). Since dichlorophenol was not detected in the combustion gas impinger samples (detection level = 0.88 x10$^{-9}$ grams/liter) downstream from the air cooled probes or in the spent scrubber water (detection level = 0.08 x10$^{-6}$ grams/liter) from these burns, the existence of dichlorophenol in the combustion gas was doubted.

(2) Since no dichlorophenol was detected in the impingers downstream of the air cooled probe, it was supposed that the probe collected all of the dichlorophenol. Based on this conclusion, the apparent combustion gas concentration was 40 x10$^{-9}$ grams per liter (1.38 µg/34 liters). If this

concentration existed throughout the burn, the caustic scrubber was exposed to 320 mg over the total burn. The volume of the spent scrubber water from burn II was 14996 liters. Based on the detection limit of dichlorophenol in the spent scrubber water (0.08 µg/l), 1.2 mg of dichlorophenol in the spent scrubber water would have been detected. The 1.2 mg needed for detection was only 0.37% of the 320 mg available if the 40 $x10^{-9}$ grams/liter existed throughout the burn. The caustic scrubber was expected to collect a significantly greater fraction of dichlorophenol than 0.37% (see Table I-7).

(3) From these observations, the following possibilities were considered. That,

(a) dichlorophenol did not exist at a mass concentration of 40 $x10^{-9}$ grams/liter throughout burn II, and

(b) the dichlorophenol was formed in the air cooled sampling probes and in the Beckman 109A cold traps from reactions of $Cl_2$ and (Cl) with the nonchlorinated aromatic hydrocarbons detected in the combustion gas (these reactions are favorable between 500 and 700°C, slower at <500°C and almost nonexistent >700°C; the combustion gas was cooled from ~1040°C to 150°C rapidly in the air cooled probe; the environment was favorable to formation of dichlorophenol), or

(C) the dichlorophenol was chemically altered to the monochlorophenol in the caustic scrubber. Monochlorophenol and dichlorobenzene were detected in all spent scrubber water samples. The monochlorophenol-dichlorophenol equilibrium could have been shifted to monochlorophenol in the caustic scrubber.

e. The spent scrubber water from burns II and III contained 211 mg and 3 mg of monochlorophenol respectively. The (apparent) total burn production of dichlorophenol was 320 mg and 26.7 mg for burns II and III respectively. There appeared to be a relationship between (apparent) dichlorophenol in the combustion gas and monochlorophenol in the caustic scrubber. However, since dichlorophenol and monochlorophenol could have been formed in the venturi of the caustic scrubber (rapid cooling of combustion gas from ~1040°C to 72°C), to account for the monochlorophenol detected, and the existence of mono and dichlorophenol in the combustion gases was unfavorable (temperature), the conclusion was made that dichlorophenol did not exist in the combustion gas but was generated in the air cooled probe and in the cold trap. This conclusion was supported by the fact that dichlorophenol was not detected in these probes and traps of burns IV through VIII when the mass concentration of unchlorinated aromatic hydrocarbons was low.

f. The dichlorophenol found in the water impingers in the particulate sampling train sample from burns IV and VI was concluded to be contamination not associated with "Orange" herbicide incineration. This conclusion was based upon the following observations:

(1) In burn IV, the dichlorophenol mass concentration in the scrubbed effluent gas that was necessary to produce the mass collected in the particulate sampling train was greater than the detection limit in the TCDD sampling train, i.e., 1.3 µg was collected from a sample volume of 737.2 liters for an apparent mass concentration of 1.76 $x10^{-9}$ grams/liter but the detection limit in the TCDD sampling train was 0.22 $x10^{-9}$ grams/liter. Therefore, dichlorophenol should have been detected in the TCDD sampling train.

(2) In burn VI; 0.1 μg was collected from 444.0 liters for an apparent mass concentration of $0.22 \times 10^{-9}$ grams/liter. However, the detection limit in the TCDD sampling train was only $0.83 \times 10^{-9}$ grams/liter. The apparent mass concentration in the scrubbed effluent gas was below the detection limit of the TCDD sampling train if the collection efficiencies in the particulate and the TCDD sampling trains was assumed to be equal. However, dichlorophenol collection efficiency in the TCDD sampling train was greater than in the particulate train water impingers and dichlorophenol should have been differentially collected in the TCDD sampling train because:

(a) Dichlorophenol is soluble in benzene but only slightly soluble in water.

(b) Fritted impingers, as used in the TCDD system are more effective gas and aerosol collectors than modified impingers used in the particulate train.

(c) A series of four impingers was used in the TCDD sampling train but only two were used in the particulate train.

(3) The water impingers used in the particulate train were packed in sponge rubber and styrofoam for shipment. They had been used in numerous particulate source sampling projects prior to this work. Since it was not anticipated that they would be used for hydrocarbon collection, they were not properly washed for herbicide analysis but merely rinsed with distilled water. Contamination of these impingers with dichlorophenol could have occurred in numerous cases and rinsing with distilled water would not have removed contamination. Also two impinger sets were alternated and the same impinger set (potentially contaminated) was used in burn IV and VI while a different (uncontaminated) set was used in burn III and V.

(4) The water in the impingers and the particulate sampling train from burn III and V did not contain dichlorophenol even though burn III was less efficient in relative pyrolysis of "Orange" herbicide than burn IV and VI. Burn V had a comparable RPE to burn IV and VI. If dichlorophenol was being produced during "Orange" herbicide incineration it would have been produced and detected in burn III and V as well.

(5) Dichlorophenol was not detected in the spent scrubber water (detection limit ≤ equal to $0.08 \times 10^{-6}$ grams/liter) in any of the burns, and as discussed in paragraph 11d(1) the caustic scrubber was expected to collect a significant fraction of dichlorophenol. If dichlorophenol was being produced throughout the burn at the rate indicated by the water impinger samples in burn IV ($1.76 \times 10^{-9}$ grams/liter) then ($1.76 \times 10^{-9}$ grams/liter times $9.47 \times 10^{6}$ liters) 16.67 milligrams would have been produced. If 1.27 milligrams (7.6% of 16.67 milligrams) of dichlorophenol had been collected by the caustic scrubbers it would have been detected.

g. Based upon the fact that dichlorophenol should have been differentially collected in the TCDD sampling train but was not, contamination of the water impingers with dichlorophenol was possible, and no dichlorophenol was detected

in the caustic scrubber, the conclusion was made that dichlorophenol found in the water impingers in burn IV and VI was extraneous contamination.

12. HERBICIDE IN BURN III EHL SAMPLES

a. Only two of all the EHL samples contained any of the following nine herbicide compounds: nb 2,4-D and 2,4,5-T esters and acids, octyl 2,4-D and 2,4,5-T esters and acids, and TCDD. Both of these samples occurred in burn III. First, the combustion chamber coke deposit contained 1100.20 µg of these esters and acids per 100 gms of deposit; of which 551 µg was nb 2,4-D ester and 542 µg was nb 2,4,5-T ester. These esters produced the characteristic "Orange" herbicide odor which was detected in burn III's coke deposit. Neither this odor nor any of the aforementioned nine herbicide compounds were detected in coke deposits from any other burns. Second, the total burn scrubber water composite (SSW-TBC) sample contained 0.25 µg/l of TCDD but none of the other eight herbicide compounds. Suspended matter in burn III's SSW-TBC or from any of the other burns contained none of the nine herbicide compounds. None of these compounds were detected in burn III's first hour spent scrubber water composite (SSW-C1) or any other burn's SSW-TBC or SSW-C1.

b. The total TCDD mass in the spent scrubber water was calculated as 3775 µg for the total burn. If this TCDD mass had been evenly distributed throughout the burn's combustion gas, the sampled combustion gas would have contained about 4.5 times the TCDD mass concentration needed for TCDD detection. However, no TCDD was detected in the combustion gas sample which was initiated 51 minutes into the burn and continued for 64 minutes. Additionally, no TCDD was detected in the SSW-C1 which was initiated 54 minutes into the burn and completed 44 minutes later. Thus, the TCDD must have passed through the incinerator during the last 120 minutes of burn III. The TCDD probably passed through the incinerator in a relatively short period since no noticeable changes in burn III's operational parameters were ever observed.

c. Unlike any other burns, the appearance of burn III's coke deposit indicated very poor combustion and that lower temperatures occurred around the deposit. Although no TCDD was detected in the deposit, it could have been present in concentrations up to about 15 µg/100 grams of deposit. This value was calculated under the assumption that TCDD was present in the 1100.2 µg of esters and acids in the same proportion as it was in the blended herbicide. The 15 µg/100 grams of deposit would have been below the analytical detection limit for that size sample.

d. Earlier comparisons of CGH and SSWH showed no reason to believe that the overall RPE of burn III was significantly less than RPE's in burns I and II. However, burn III's quantity and quality of coke deposit, SGH quality, and TCDD in the SSW-TBC were significantly different than burn I, II, or any other burns. These comparative observations lead to the conclusion that combustor coke chips, 175 grams or more, broke loose from the combustion chamber deposit and, combusted well enough during incinerator dwell time to destruct the herbicide esters and acids but not the TCDD, and then intimately mixed and settled in the scrubber tank. Even though not appreciably soluble in water, enough TCDD must have leached from the coke to produce 250 nanograms per liter of collected SSW-TBC.

13. DISCUSSION OF CONFLICTING DATA

a. Burn IV:

(1) In burn IV, the scrubbed effluent gas hydrocarbon mass concentration (SGH) was greater than the combustion gas hydrocarbon mass concentration (see Table I-7). In all other burns, as expected, the reverse was true.

(2) The mass of hydrocarbons collected in the scrubber (SSWH) during burn IV was comparable to that collected in burns V, VI, VII and VIII. Since caustic scrubber characteristics were not significantly different in burn IV from those in burns V, VI, VII and VIII, one must consider that burn IV combustion gas contained hydrocarbon mass concentrations comparable to burns V, VI, VII, and VIII, or that a combination of two things occurred,

(a) a slug of pyrolyzates occurred during startup (before sampling to account for the hydrocarbon mass in the scrubber) and

(b) the combustion gas and scrubbed effluent gas samples were reversed in the recovery or analytical steps.

(3) Since gas chromatographic peak interferences were possible in the burn IV combustion gas samples, the first consideration was concluded to be the most probable. Therefore, the CGH in burn IV was considered equal to or greater than the CGH in burns V, VI, VII and VIII, but less than the CGH in burns I, II and III.

b. Burn VI: In burn VI, the SGH aliphatics were greater than the CGH aliphatics. This conflict was concluded to be due to:

(1) gas chromatography peak interferences, or

(2) analytical accuracy as the detection limit was being approached.

c. Biphenyls in SGH: Biphenyl (unchlorinated) was not detected in the CGH (Tables G-2 and G-3). Also, it was not detected in the SSWH (Table G-7). The conclusions were made that biphenyl was:

(1) present in the CGH but hidden by gas chromatographic peak interferences (Appendix G, paragraph V),

(2) not collected in the SSWH due to its relatively high vapor pressure (in the scrubber water temperature, 160-170$^{o}$F) and low solubility in the caustic solution,

(3) detected in the SGH because of fewer gas chromatographic peak interferences.

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USAF ENVIRONMENTAL HEALTH LABORATORY

Kelly AFB, TX 78241

# APPENDIX J

(TO APPENDIX E)

# NOISE MONITORING

E(I-27)

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E(I-28)

# APPENDIX J

## NOISE MONITORING

### 1. Introduction

This appendix presents the noise measuring equipment used, octave band analyses of the noise produced by one incinerator, and the location where noise measurements were made. Data are discussed, particularly as regards the occupational hazards of the noise to exposed operators and estimates of noise intensities expected by more than one incinerator.

### 2. Results and Discussion

a. Octave band sound level measurements of the incinerator noise, equipment used, and environmental conditions are presented in Table J-1. Locations where noise measurements were made are shown in Figure J-1.

b. "A" weighted octave band sound levels could not be summed any closer than $\pm$ 2 decibels (db) of the overall dbA. These minor inaccuracies of measurement were acceptable for meeting the objectives of the study. The following unavoidable environmental conditions caused the measurement errors:

(1) Except for location "7", positions of equipment within the area required that all measurements be taken relatively close (10 - 15 feet) to the incinerator in order to get "line-of-sight" measurements. Consequently, the measurements were influenced by "near field" effects.

(2) Many metallic surfaces around the incinerator contributed reverberation noises.

(3) Background noises were present from a commercial airport 100 - 200 yards away as well as industrial noises from within the contractors facility. However, measurements were taken only when these background noises were at a minimum.

c. The incinerator was not considered a point source of noise. The noise was steady state. The overall sound level averaged 91 dbA and 91 dbC at points twelve feet around the incinerator. Such close values of overall dbA and dbC were in agreement because most of the noise level was produced in the higher frequencies, 2000 - 8000 Hertz. At twenty-four feet from the incinerator, overall average noise levels decreased to 85 dbA or 87 dbC because the

TABLE J-1: SUE® Burner Noise Survey-Octave Band Analyses

| Location[1] | Angle | R (ft) | "A" Weighted Slow Response Octave Band Level (dB) Reference 0.0002ubars/M² for Octave-Band Center Frequency in Hertz | | | | | | | | | | "A" All Pass | "C" All Pass |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 31.5 | 63 | 125 | 250 | 500 | 1000 | 2000 | 4000 | 8000 | 16000 | | |
| 1* | -- | 12 | 72 | 79 | 72 | 71 | 74 | 78 | 82 | 88 | 84 | 73 | 92 | 91.5 |
| 2* | -- | 12 | 76 | 80 | 72 | 74 | 79 | 82 | 84 | 89 | 85 | 74 | 93 | 92 |
| 3* | -- | 12 | 78 | 83 | 77 | 77 | 79 | 83 | 84 | 88 | 84 | 71 | 92 | 92 |
| 4* & 5* | -- | 12 | 75 | 85 | 79 | 77 | 80 | 84 | 83 | 86 | 80 | 65 | 91 | 92 |
| 6* | -- | 12 | 74 | 83 | 80 | 84 | 79 | 77 | 79 | 83 | 77 | 62 | 88 | 91 |
| 7* | -- | 24 | 68 | 74 | 69 | 68 | 69 | 76 | 80 | 84 | 78 | 65 | 87 | 86.5 |
| 8* | -- | 15 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 64 | 65 |
| | | | | | | | | | | | | | | |
| 1** | -- | 12 | 71 | 81 | 71 | 73 | 74 | 77 | 81 | 85 | 81 | 72 | 88 | 89 |
| 2** | -- | 12 | 78 | 79 | 77 | 74 | 78 | 83 | 83 | 88 | 84 | 74 | 91 | 91 |
| 6** | -- | 12 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 84 | 87 |
| 7** | -- | 24 | 70 | 75 | 68 | 69 | 70 | 71 | 76 | 80 | 74 | 60 | 83 | 83 |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | $\bar{x}$1,2,3,4,5 | | 91. | 91. |
| | | | | | | | | | | | $\bar{x}$6,7 | | 85. | 87. |

Intstruments Used: General Radio Octave Band Analyzer Type 1558-PB(Serial No. 2473) with General Radio Microphone 1560-P6 with wind shield (Serial No. 2680).Calibrated with General Radio Calibrator Type 1562-A (Serial No. 2579)

Date of Survey: *20Nov **29Nov Surveyor: Capt.C.W. Bullock Operational Mode of Burner: * Burn IV ** Burn VII

Dashed lines indicate that measurements were not taken.

(1) For location of measurement, see Figure J-1.

Wind conditions during survey: * From 120-160°, 9mph, Temp=62°F. **Calm, 0mph, Temp=62°F.

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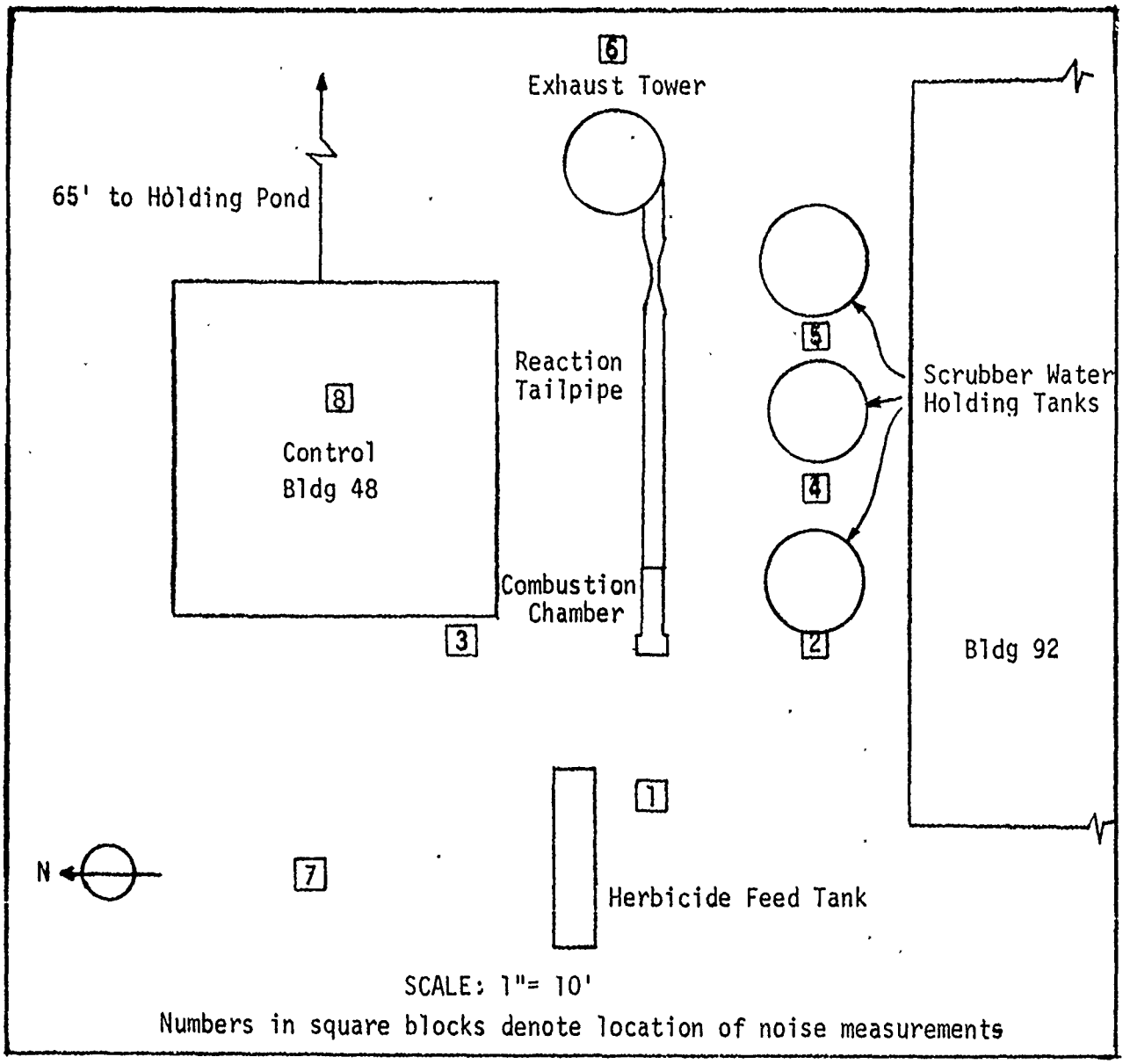



FIGURE J-1: LOCATIONS OF NOISE MEASUREMENTS DURING TEST BURNS

USAF EHL(K)

higher frequency noises had begun to dissipate and the lower frequency components were contributing more significantly to the overall noise level.

d. The control building effectively attenuated exterior incinerator noise to an overall level of 64 dbA. Although octave band analyses were not made, no speech interference was experienced inside the control building.

e. Operators occupationally exposed to the noise within a fifty foot radius of the incinerator should be provided ear muffs and be monitored via a hearing conservation program. The noise data can be used with various hearing protection criteria to determine limited exposure periods in which an unprotected operator could be exposed without risk of developing any hearing loss.

f. Table J-2 below presents estimated overall sound levels with increasing numbers of incinerator units. Appropriate adjustments of hearing conservation protection requirements around the incinerator(s) can be made depending on the number of incinerators and the distance from them to the workers.

TABLE J-2: ESTIMATES OF OVERALL SOUND LEVELS AT VARIOUS DISTANCES FROM ONE TO EIGHT INCINERATORS

| Number of Incinerator Units | Overall Sound Level (Reference 0.0002 μ bars/$M^2$) | | |
|---|---|---|---|
| | At Twelve Feet dbA or dbC | At Twenty-four Feet | |
| | | dbA | dbC |
| 1 | 91 | 85 | 87 |
| 2 | 94 | 88 | 90 |
| 4 | 97 | 91 | 93 |
| 8 | 100 | 94 | 96 |

APPENDIX K

(TO APPENDIX E)

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MAIN REPORT

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(2) INCINERATION OF ORANGE HERBICIDE, USAF Environmental Health Laboratory Technical Report EHL(K) 72-7, USAF EHL(K), Kelly AFB, Texas (July 1972).

(3) REPORT ON THE FEASIBILITY OF DESTROYING HERBICIDE ORANGE BY INCINERATION USING THE MARQUARDT SUE® BURNER, Report S-1224, The Marquardt Company, Van Nuys, California. Prepared under Contract No. F04611-72-C-0087 for Air Force Rocket Propulsion Laboratory (AFRPL), Air Force Systems Command, Edwards, California (August 1972).

APPENDIX B

(4) Private Communication, The Marquardt Company, Van Nuys, California and Air Force Rocket Propulsion Laboratory (AFRPL), Edwards, California (1972).

APPENDIX D

(See References on Page D-27)

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E(K-2)

# APPENDIX F

## THE ECOLOGICAL CONSEQUENCES OF MASSIVE QUANTITIES OF 2,4-D and 2,4,5-T HERBICIDES SUMMARY OF A FIVE YEAR FIELD STUDY

# THE ECOLOGICAL CONSEQUENCES OF MASSIVE QUANTITIES OF 2,4-D and 2,4,5-T HERBICIDES SUMMARY OF A FIVE YEAR FIELD STUDY*

Young, A.L., C.E. Thalken, W.E. Ward and W.J. Cairney
Department of Life and Behavioral Sciences
United States Air Force Academy, Colorado

In support of programs testing aerial dissemination systems, a one square mile test grid on Test Area C-52A, Eglin AFB Reservation, Florida received massive quantities of military herbicides. The purpose of these test programs was to evaluate the capabilities of the equipment systems, not the biological effectiveness of the various herbicides. Hence, it was only after repetitive applications that test personnel began to express concern over the potential ecological and environmental hazards that might be associated with continuance of the Test Program. This concern led to the establishment of a research program in the fall of 1967 to measure the ecological effects produced by the various herbicides on the plant and animal communities of Test Area C-52A. This report documents six years of research (1967 - 1973) on Test Area C-52A and the immediately adjacent streams and forested areas.

This report attempts to answer the major questions concerned with the ecological consequences of applying massive quantities of herbicides (345,117 pounds), via repetitive applications, over a period of eight years, 1962 - 1970, to an area of approximately one square mile. Moreover, the report documents the persistence, degradation, and/or disappearance of the herbicides from the Test Area's soils and drainage waters and their subsequent effects (direct or indirect) upon the vegetative, faunal, and microbial communities.

The active ingredients of the four military herbicides (Orange, Purple, White, and Blue) sprayed on Test Area C-52A were 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-amino-3,5,6-trichloropicolinic acid (picloram), and dimethylarsinic acid (cacodylic acid). It is probable that the 2,4,5-T herbicide contained the highly teratogenic (fetus deforming) contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Ninety-two acres of the test grid received 1,894 pounds 2,4-D, 2,4,5-T per acre in 1962 to 1964, while another 92 acres received 1,168 pounds per acre in 1964 to 1966. In the period from 1966 to 1970, a third distinct area of over 240 acres received 343 pounds per acre of 2,4-D and 2,4,5-T, 6 pounds per acre picloram, and in 1969 to 1970, 53 pounds per acre cacodylic acid (28 pounds per acre of arsenic as the organic pentavalent form; calculated on weight of Blue applied per acre).

From the rates of herbicides that were applied during the years of testing spray equipment, it was obvious that Test Area C-52A offered a unique opportunity to study herbicide persistence and soil leaching. Yet the problem of how best to assess the level of herbicide residue was

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a difficult one. The herbicides could be chemically present but because of soil binding might not be biologically active. Thus, both bioassay techniques and analytical analyses were employed. The first major bioassay experiment was conducted in April 1970. By considering the flightpaths, the water sources, and the terracing effects, it was possible to divide the one-square mile test grid into 16 vegetation areas. These areas formed the basis for the random selection of 48 3-foot soil cores. Soybean bioassays indicated that 27 of the 48 cores were significantly different from control cores (95% probability level). The results indicated that soil leaching or penetration was much more prevalent along the dissemination flight paths than in other areas of the test grid. Efforts to quantitate (chemically) the bioassay were confined to only the top 6-inch increment because of within-core variations. By considering that all phytotoxic effects were from Orange (2,4-D and 2,4,5-T) the average value for the top 6 inches of soil core for the eight cores showing greatest herbicide concentration was 2.82 ppm (parts per million) herbicide. Chemical analyses of soil cores collected from the eight sites showing greatest phytotoxic concentrations were performed in December 1970. Results indicated that the maximum concentration of either 2,4-D or 2,4,5-T was 8.7 ppb (parts per billion). A 1970 analysis of soil cores for arsenic, from areas receiving greatest quantities of Blue, indicated maximum levels of 4.70, 1.30, and 0.90 ppm arsenic for the first three 6-inch increments of the soil profile, respectively. These same increments were again collected and analyzed in 1973: levels of arsenic were 0.85, 0.47, and 0.59 ppm for the three consecutive 6-inch increments. Leaching of the arsenical from the soils may have occurred. Picloram analysis in November 1969 of soil cores from areas receiving greatest quantities of White indicated that maximum levels of 2.8 ppm picloram were present in the 6 to 12-inch depth increment. Analysis of the same sites performed in 1971 indicated the picloram had leached further into the soil profile but concentrations were significantly less (ppb). Analysis of soil cores in 1971 showed no residue of TCDD at a minimum detection limit of less than 1 ppb, even in soil previously treated with 947 pounds 2,4,5-T per acre. However, data from soil analysis (via mass spectrometry) of four total samples collected in June and October 1973 indicated TCDD levels of <10, 11, 30, and 710 parts per trillion (ppt), respectively. These levels were found in the top six inches of soil core. The greatest concentration (710 ppt) was found in a sample from the area that received 947 pounds 2,4,5-T in the 1962 - 1964 test period.

A comparison of vegetative coverage and occurrence of plant species on the one-square mile grid between June 1971 and June 1973 has indicated that areas with 0 to 60% vegetative cover in 1971 had a coverage of 15 to 85% in June 1973. Those areas having 0 to 5% coverage in 1971 (areas adjacent to or under flightpaths used during herbicide-equipment testing) had 15 to 54% coverage. The rate of change in coverage seemed to be dependent upon soil type, soil moisture, and wind. There was no evidence to indicate that the existing vegetative coverage was in any way related to herbicide residue in the soil: dicotyledonous or broadleaf plants that are

normally susceptible to damage from herbicide residues occurred throughout the entire one square mile grid. The square-foot transect method of determining vegetative cover indicated that the most dominant plants on the test area were the grasses, switchgrass (Panicum virgatum), woolly panicum (Panicum lanuginosum), and the broadleaf plants rough buttonweed (Diodia teres), poverty weed (Hypericum gentianoides), and common polypremum (polypremum procumbens). In 1971, 74 dicotyledonous species were collected on the one square mile grid; in 1973, 107 dicotyledonous species were found. All of the plant species collected were pressed, mounted, and placed in the Eglin AFB Herbarium.

An evaluation of the effects of the spray-equipment testing program on faunal communities was conducted from May 1970 to August 1973. The extent of any faunal ecological alterations was measured by assessing data on species variation, distribution patterns, habitat preference and its relationships to vegetative coverage, occurrence and incidence of developmental defects, as well as gross and histologic lesions in post mortem pathological examinations.

A total of 73 species of vertebrate animals (mammals, birds, reptiles, and amphibians) were observed on Test Area C-52A and in the surrounding area. Of these 73 species, 22 species were observed only off the grid, 11 species were observed only on the grid, and 40 species were observed to be common to both areas. During the early studies no attempts were made to quantitate animal populations in the areas surrounding the grid; however, in 1970, preliminary population studies by trap-retrap methods were performed on the beach mouse (Peromyscus polionotus) population for a 60 day period to confirm the hypothesis that it was the most prevalent species on the grid. The hypothesis was supported by the capture of 36 beach mice from widely distributed areas on the grid, except in areas with less than 5% vegetation. Eight pairs of eastern harvest mice were taken to the laboratory and allowed to breed. Six of the eight pairs had litters totalling 24 mice. These progeny were free from any gross external birth defects. During February - May 1971 population densities of the beach mouse were studied at eight different locations on the grid along with two different areas off the grid which served as controls. Populations were estimated on the basis of trap-retrap data. There was no difference in mouse population densitites in herbicide treated and control areas affording comparable habitats. All indications were that any population differences in other animal species between the test area and the surrounding area were due to differences caused by the elimination of certain plants and, therefore, certain ecological niches, rather than being due to any direct detrimental effect of the herbicides on the animal population present on TA C-52A.

During the last day of the 1971 study, 9 mice were captured and taken to the laboratory for post mortem pathological examination. There were no instances of cleft palate or other deformities. Histologically, liver, kidney and gonadal tissues from these animals appeared normal, In the 1973 study several different species of animals were caught, both on and

off the test grid. These included beach mice, (Peromyscus polionotus), cotton mice, (Peromyscus gossypinus), eastern harvest mice, (Reithrodontomys humulis), hispid cotton rats, (Signodon hispidus), six-lined race-runners, (Cnemidophorus sexlineatus), a toad, (Bufo americanus), and a cottonmouth water moccasin, (Ancistrodon piscivorus). A total of 89 animals were submitted to The Armed Forces Institute of Pathology, Washington, D.C. for complete pathological examination including gross and microscopic studies. Liver and fat tissue from 70 rodents were forwarded to the Interpretive Analytical Services, Dow Chemical U.S.A., for TCDD analyses. The sex distribution of the trapped animals was relatively equal. The ages of the animals varied, but adults predominated in the sample. No gross or histological developmental defects were seen in any of the animals. Several of the rats and mice from both groups were pregnant at the time of autopsy. The stage of gestation varied considerably from early pregnancy to near term. The embryos and fetuses were examined grossly and microscopically, but no developmental defects or other lesions were observed. Gross necropsy lesions were relatively infrequent and consisted primarily of lung congestion in those animals that had died from heat exhaustion prior to being brought to the laboratory. The organ weights did not vary significantly between the test and control animals when an animal with lungs and kidneys showing inflammatory pathological lesions was removed from the sample. Histologically, the tissues of 13 of the 26 control animals and 40 of the 63 animals from the test grid, were considered normal. Microscopic lesions were noted in some animals from both groups. For the most part, these were minor changes of a type one expects to find in any animal population. One of the most common findings was parasites. A total of 11 controls and 9 grid animals were affected with one or more classes of parasites. Parasites may be observed in any wild species and those in this population were for the most part incidental findings that were apparently not harmful to the animals. There were exceptions however. Protozoan organisms had produced focal myositis in one rat, and were also responsible for hypertrophy of the bile duct epithelium in a six-lined racerunner.

Moderate to severe pulmonary conjestion and edema were seen in several rats and mice. All of these animals were found dead in the traps before reaching the laboratory, and the lung lesions were probably the results of heat exhaustion. The remainder of the lesions in both groups consisted principally of inflammatory cell infiltrates of various organs and tissues. They were usually mild in extent and although the etiology was not readily apparent, the cause was not interpreted as toxic. The analyses of TCDD from the rodents collected in June and October 1973 indicated that TCDD or a compound chemically similar to TCDD accumulated in the liver and fat of rodents collected from an area receiving massive quantities of 2,4,5-T. However, based on the pathological studies there was no evidence that the herbicides and/or contaminants produced any developmental defects or other specific lesions in the animals sampled or in the progeny of those that were pregnant. The lesions found were interpreted to be of a naturally occurring type and were not considered related to any specific chemical toxicity.

In 1970 beach mice were not found on the more barren sections of the grid (0-5% vegetative cover). There were, however, some areas of the grid which had population densities exceeding those of the species preferred habitat as reported in the literature. In an attempt to correlate distribution of the beach mouse with vegetative cover (i.e., habitat preferance) a trapping-retrapping program of 8 days duration was conducted in 1973. The majority of animals (63) were found in areas with 5% to 60% vegetative cover: Within this range, the greatest number of animals trapped (28) was from an area with 40% to 60% cover. A similar habitat preference has been observed along the beaches of the Gulf Coast. In this study, it appeared that the beach mouse used the seeds of switchgrass (Panicum virgatum) and wooly panicum (Panicum lanuginosum) as a food source.

Trapping data from 1971 was compared to trapping data collected in 1973 to determine whether an increase in the population of beach mice had occurred. The statistical evidence derived from that study showed that the 1.64 beach mice per acre population (based on the Lincoln Index for 1973) was slightly higher than the 0.8 and 1.4 mice per acre reported for a similar habitat. The population of beach mice was also higher in 1973 than in 1971 in the area of the test grid. The apparent increase in beach mouse population on the grid in 1973 over 1971 was probably due to the natural recovery phenomenon of a previously disturbed area (i.e., ecological succession). Some areas of the test grid have currently exceeded that preferred percentage of vegetative coverage of the beach mouse habitat, and other areas were either ideal or fast developing into an ideal habitat. If the test grid remains undisturbed and continues toward the climax species, a reduction in the number of beach mice will probably occur simply due to decline of preferred habitat.

A 1973 sweep net survey of the Arthropods of Test Area C-52A resulted in the collection of over 1,700 specimens belonging to 66 insect families and Arachnid orders. These totals represented only one of five paired sweeps taken over a one-mile section of the test grid. A similar study performed in 1971 produced 1,803 specimens and 74 families from five paired sweeps of the same area using the same basic sampling techniques. A much greater number of small to minute insects were taken in the 1973 survey. Vegetative coverage of the test area had increased since 1971. The two studies showed similarities in pattern of distribution of Arthropods in relation to the vegetation, number of Arthropod species, and Arthropod diversity. Generally, the 1973 study showed a reduction of the extremes found in the above parameters in the 1971 study. This trend was expected to continue as the test area stabilizes and develops further plant cover, thus allowing a succession of insect populations to invade the recovering habitat.

There are two classes of aquatic areas associated with the Test Area; ponds actually on the square mile area and streams which drain the area. Most of the ponds are primarily of the "wet weather" type, drying up once in the last five years, although one of the ponds is spring fed. Three major streams and two minor streams drain the test area. The combined

annual flow of the five streams exceeds 24 billion gallons of water. Seventeen different species of fishes have been collected from the major streams while three species have been collected from the spring-fed pond on the grid. Statistical comparisons of 1969 and 1973 data of fish populations in the three major streams confirm a chronologically higher diversity in fish populations. However, the two control streams confirm a similar trend in diversity. Nevertheless, from examining all of the aquatic data, certain observations support the idea that a "recovery" phenomenon is occurring in the streams draining TA C-52A. These observations are difficult to document because of insufficient data. For example, in 1969, the Southern Brook Lamprey (Ichthyomyzon gagei) was never collected in one of the streams immediately adjacent to the area of the grid receiving the heaviest applications of herbicides; however, in 1973 it was taken in relatively large numbers. These observations may or may not reflect a change in habitat due to recovery from herbicide exposure. Residue analyses (1969 to 1971) of 558 water samples, 68 silt samples and 73 oyster samples from aquatic communitites associated with drainage of water from Test Area C-52A showed negligible arsenic levels. However, a maximum concentration of 11 ppb picloram was detected in one of the streams in June 1971 but dropped to less than 1 ppb when sampled in December 1971. TCDD analysis of biological organisms from streams draining Test Area C-52A or in the ponds on the test area were free from contamination at a detection limit of less than 10 parts per trillion.

In analyses performed 3 years after the last application of 2,4-D and 2,4,5-T herbicide the test grid exhibited population levels of soil microorganisms identical to that in adjacent control areas of similar soil and vegetative characteristics not exposed to herbicides. There were increases in Actinomycete and bacterial populations in some test site areas over levels recorded in 1970. This was possibly due to a general increase in vegetative cover for those sampling sites and for the entire test grid. No significant permanent effects could be attributed to exposure to herbicides.

Data on aquatic algal populations from ponds on the one square mile grid (previously exposed to repetitive applications of herbicides) indicated that the genera present were those expected in warm, acid (pH 5.5), seepage, or standing waters.

# APPENDIX G

## FIELD STUDIES ON THE SOIL PERSISTENCE AND MOVEMENT OF 2,4-D, 2,4,5-T, AND TCDD

# FIELD STUDIES ON THE SOIL PERSISTENCE AND MOVEMENT OF 2,4-D, 2,4,5-T, and TCDD*

A.L. Young, E.L. Arnold and A.M. Wachinski
Department of Life and Behavioral Sciences
USAF ACADEMY, COLORADO 80840

## INTRODUCTION

Concern over the level of contamination of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) herbicide by the teratogen 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) may result in the disposal of selected inventories of this herbicide. A potential disposal method is that of soil incorporation. The soil incorporation method is based on the premise that high concentrations of phenoxy herbicide and TCDD will be degraded to innocuous products by the combined action of soil microorganisms and soil chemical hydrolysis.

It has been known for several years that the rate at which herbicides disappear from the soil is largely dependent upon their susceptibility to metabolism by soil microorganisms. Much of the information available on the biological breakdown of the phenoxy herbicides comes from laboratory studies and is very useful for predicting what might happen when relatively high concentrations of phenoxy herbicides are applied to a soil incorporation site. Conversely, a certain amount of caution must always be used when extrapolating laboratory data to a field situation. Data on the field persistence of TCDD is extremely limited primarily due to the low levels of contamination in commercial formulations, the rate of application of such formulation, and the lack of a sensitive analytical method for the detection of TCDD. This report documents current field research on the soil degradation of a TCDD-contaminated phenoxy formulation when incorporated in the soil at massive rates of application.

## METHODS AND MATERIALS

In August 1972, a site for the soil incorporation of phenoxy herbicides was selected on the Air Force Logistics Command Test Range Complex, Hill Air Force Base, Utah. The potential site was characterized as being relatively flat and having a uniform surface without rock outcrops or areas of marked deflation or dunes. Sediments in this area are lacustrine in origin and were deposited when ancient Lake Bonneville covered this region of the Great Basin. Sediments consist of clays interlaced irregularly with sand lenses and remnant stream sands; the clays predominanting. The undifferentiated clays contain various amounts of dissolved salts. Table 1 shows an analysis of the top two

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TABLE 1. Soil analysis of the top two six-inch soil increments from the soil incorporated plots, Air Force Logistics Command Test Range Complex, Hill Air Force Base, Utah[a]

| Inches | pH | Organic Carbon (%) | Electrical Conductivity (EC x $10^3$)[b] | Ca/Mg | K | Na | Sand (%) | Silt (%) | Clay (%) | Moisture at Saturation (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g soil) | | | | | | |
| 0-6 | 7.8 | 0.82 | 28.0 | 23.7 | 3.9 | 13.4 | 27 | 53 | 20 | 31.1 |
| 6-12 | 7.9 | 0.95 | 31.0 | 23.8 | 3.9 | 13.2 | 26 | 52 | 22 | 34.2 |

[a] Determined by Soils Laboratory, Utah State University, Logan, Utah, and the Soils Laboratory, Kansas Agricultural Experiment Station, Garden City, Kansas.

[b] Electrical conductivity in millimhos per cm at 25 C.

six-inch increments (0-6, 6-12 inches) of the soil profile. The annual rainfall of the area is less than ten inches taking into consideration the water equivalent of snowfall. Ground water of the area varies from 16 to 20 feet below the surface. It is supplied primarily by the precipitation falling on the nearby mountains. The small amount of water which percolates through the existing clays moves laterally westward towards the salt flats, picking up chemical matter from these clays. As a result, the ground water contains up to 1,000 parts per million (ppm) sodium chloride. The annual mean daily minimum temperature is 38.5 F and the annual mean daily maximum temperature is 64.7 F. The experimental area has a vegetative cover of 15 percent and is dominated by fourwing saltbush, Atriplex canescens (Pursh) Nutt,; halogeton, Halogeton glomeratus (M. Bieb.) C.A. Mey; and graymolly, Kochia vestita.

Six field plots, each 10 x 15 feet, were established on the Air Force Logistics Command Test Range Complex on 6 October 1972. To simulate subsurface injection (incorporation), three equally-spaced trenches, 6 inches wide and 10 feet in length were dug to a depth of 4-6 inches in each plot. The rates of herbicide selected for incorporation were 1,000, 2,000, and 4,000 pounds active ingredient per acre (lb ai/A) 2,4-D plus 2,4,5-T. Two replications (plots) per rate were included in the experiment. The quantity of herbicide required for each rate was divided into three equal parts and sprayed, as the concentrate, into each of the three trenches per plot, respectively. A hand sprayer with the nozzle removed was used to spray as uniformly as possible an approximate two-to-three-inch band of herbicide in the center of the 6-inch by 10-foot trench. The trenches in each plot were then covered by use of a handshovel, tamped, and levelled using a handrake.

The herbicide formulation used for these simulated incorporation experiments was an approximate 50:50 mixture of the n-butyl esters of 2,4-D and 2,4,5-T. One gallon of this formulation contains 4.21 pounds of the active ingredient of 2,4-D and 4.41 pounds of the active ingredient of 2,4,5-T. The formulation was originally specified to contain:

| | |
|---|---|
| n-butyl ester of 2,4-D | 49.40% |
| free acid of 2,4-D | 0.13% |
| n-butyl ester of 2,4,5-T | 48.75% |
| free acid of 2,4,5-T | 1.00% |
| inert ingredients (e.g., butyl alcohol and ester moieties) | 0.62% |

Some of the physical, chemical, and toxicological properties of the herbicide formulation are:

| | |
|---|---|
| Specific Density (25 C) | 1.282 |
| Viscosity, centipoise (23 C) | 43 |
| Molecular mass | 618 |
| Weight of Formulation (lbs/gal) | 8.63 |
| Soluble in water | no |
| Specific toxicity for female white rats (mg formulation/ kg body weight) | 566 |

A 200 ml sample of the formulation was removed from the container of herbicide used on these plots, placed in a hexane-acetone-rinsed glass jar and shipped to the Interpretive Analytical Services Laboratory, Dow Chemical U.S.A., Midland, Michigan, for analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The results of the analysis indicated a concentration of 3.7 parts per million (ppm) TCDD.

The first initial soil samples were to be taken the following day after incorporation of the herbicide. However, because of adverse weather initial samples were not obtained. Beginning in January 1973 soil samples were collected routinely every 2-3 months. Sampling was done by using a 3-inch by 6-inch hand auger. Each row (trench) in each plot was sampled once by removing 6-inch increments to a depth of 36 inches. Each depth was uniformly mixed per plot (i.e., the three rows per plot were mixed for each depth), placed in sample containers, and shipped under dry ice to the laboratory for herbicide analysis. In all cases, the soil cores were obtained as accurately as possible from the center of the 6-inch wide row (trench). In the laboratory, each sample was analyzed for 2,4-D acid, 2,4,5-T acid, 2,4-D n-butyl ester, and 2,4,5-T n-butyl ester by the gas chromatographic procedure of Arnold and Young (in press, Analytical Chemistry, 1974).

## RESULTS AND DISCUSSION

The results of the analysis of soil samples taken from the test plots are displayed in Tables 2-4. Table 2 illustrates the loss of total active herbicide from the upper 12 inches of soil increment over a period of 440 days (6 Oct 1972 - 14 Dec 1973). Assuming normal climatological conditions this period represents 7 months of relatively cold temperatures and 7 months of relative warmth. The percent loss of herbicide over just the 330 day sampling period (from 110 to 440 days) was 78.2%, 75.2% and 60.8% for the 1,000, 2,000, and 4,000 lb ai/A plots, respectively. If the theoretical values for herbicide concentration at day 0 are used, percent loss of herbicide during the entire experiment was 87.8%, 85.3% and 82.6%, respectively. These data tend to indicate a decreased degradation of herbicide with increased application rate. However, the unusually low rate calculated for 4,000 lb ai/A application over the 330-day period is likely a result of low value of herbicide measured in the first sample (110 days) rather than a difference in degradation rate. If a strict exponential decay curve is assumed, the half life for the total herbicide ranges from 146 to 155 days depending on application rate.

Tables 3 and 4 illustrate the individual loss of each of the herbicides (2,4-D and 2,4,5-T) contained in the original formulation. Except at the lowest rate of applicaton, no significant difference was seen in the rate of degradation of the individual components in this formulation. At the application rate of 1000 lbs/A, there was a 7.5% difference (rate, 2,4-D = 81.2%; 2,4,5-T = 73.7%) in degradation rates. It was originally thought that this was due to laboratory error, however, further sampling has tended to confirm this difference. It should be noted at this

TABLE 2. Soil concentration, part per million, of 2,4-D and 2,4,5-T herbicide at selected sampling periods, days, following soil incorporation.

| Application Rate of Formulation (lb ai/A)[b] | Sampling Time After Incorporation (Days)[a] | | | | |
|---|---|---|---|---|---|
| | 0[c] | 110 | 220 | 282 | 440 |
| 1,000 | 10,000 | 5,580 | 1,876 | ---- | 1,216 |
| 2,000 | 20,000 | 11,877 | ---- | 4,670 | 2,944 |
| 4,000 | 40,000 | 17,729 | ---- | 8,489 | 6,944 |

[a] Data represent an average of two replications with the duplicate samples of each replication: the total value for depths 0-6 and 6-12 inches of soil increment.

[b] Pounds active ingredient per acre.

[c] Theoretical concentration at time of application based on a two-inch spray swath at a depth of 4-6 inches within the soil profile.

TABLE 3. Soil concentration, parts per million, of 2,4-D herbicide at selected sampling periods, days, following soil incorporation.

| Approximate[a] rate of 2,4-D. (lb ai/A) | Sampling Time After Incorporation (Days)[b] | | | | |
|---|---|---|---|---|---|
| | 0[c] | 110 | 220 | 282 | 440 |
| 500 | 5,000 | 3,280 | 976 | ---- | 616 |
| 1,000 | 10,000 | 7,261 | ---- | 2,370 | 1,844 |
| 2,000 | 20,000 | 10,545 | 4,829 | ---- | 4,112 |

[a] Rate of herbicide per acre was based on the original specification of the formulation (i.e., a 50:50 n-butyl formulation containing 8.63 pounds active ingredient per gallon).

[b] Data represent an average of two replications with two duplicate samples of each replication: the total for depths 0-6 and 6-12 inches of soil increment.

[c] Theoretical concentration at time of application based on two-inch spray swath at a depth of 4-6 inches within the soil profile.

TABLE 4. Soil concentration, parts per million, of 2,4,5-T herbicide at selected sampling periods, days, following soil incorporation.

| Approximate[a] Rate of 2,4,5-T (lb ai/A) | Sampling Time After Incorporation (Days)[b] | | | | |
|---|---|---|---|---|---|
| | 0[c] | 110 | 220 | 282 | 440 |
| 500 | 5,000 | 2,300 | 900 | ---- | 604 |
| 1,000 | 10,000 | 4,616 | ---- | 2,300 | 1,100 |
| 2,000 | 20,000 | 7,184 | ---- | 3,734 | 2,832 |

[a] Rate of herbicide per acre was based on the original specification of the formulation (i.e., a 50:50 n-butyl formulation containing 8.63 pounds active ingredient per gallon).

[b] Data represent an average of two replications with two duplicate samples of each replication: the total for depths 0-6 and 6-12 inches of soil increment.

[c] Theoretical concentration at time of application based on two-inch spray swath at a depth of 4-6 inches within the soil profile.

point that while it was originally assumed that the formulation which was applied contained equal amounts of each herbicide, data obtained from soil analysis tended to contradict this assumption. On the first sampling date the soils contained an average of 66.9% 2,4-D and only 33.1% 2,4,5-T. This ratio was approximately maintained throughout the study. A sample of the herbicide formulation was analyzed by gas chromatographic-mass spectrometry techniques and found to contain approximately 60% 2,4-D and 40% 2,4,5-T In addition to the butyl esters, the formulation also contained relatively large amounts of octyl and iso-octyl esters of both components.

A great deal of difficulty was encountered in our attempt to accurately measure the rate of herbicide loss in these field samples. Without averaging, loss rates calculated varied over a rather large range from sample to sample. Even with averaging a few samples which were analyzed were not included in the data due to extreme variations in herbicide concentration, i.e. much higher or lower than previous samples. We attribute these variations to a number of uncontrollable variables, the most significant of which was a variation in application rates within the test rows. When the test plots were established, the herbicide was sprayed into the rows with a hand sprayer and it appears likely that there were originally concentration differences at various points due to this method of application. A second source of error is attributable to the moisture content of the soil samples. On some of the sampling dates, the samples received were extremely wet due to snow drifts over the plots while others were relatively dry. This variation in moisture tended to change the consistency of the soil and in many cases made the obtaining of a uniform sample impossible. A third source of variation occurred due to the composition of the herbicide sample which was originally applied. As was previously mentioned in addition to the expected n-butyl esters of 2,4-D and 2,4,5-T, a portion of the formulation of the sample was made up of n-octyl and iso-octyl esters of the two herbicides. No attempt was made to analyze for these esters in the soil samples; consequently, the effect of these compounds on the overall degradation pattern would only be noted after they had been hydrolyzed to the free acid. Since the rates of hydrolysis of these compounds may be different than that of n-butyl esters, this is another possible source of variation in the data obtained on early sampling dates.

In order to minimize variations in the data, on February 1, 1973, small amounts of soil (200 g) from the field plots were analyzed and placed in glass stoppered bottles. These bottles were then placed in a constant temperature incubator at 83 F to be analyzed periodically at later dates. The analytical data from these samples are presented in Table 5. Average percent loss/day values calculated from these samples were 0.42%/day for 2,4-D and 0.48%/day for 2,4,5-T. Half lives for 2,4-D and 2,4,5-T calculated from these data are 119 days and 104 days, respectively. In these samples it appears that the rate of degradation decreases with time since, in most samples, the loss of herbicide was greater from day 0 to 82 than between days 82-156. Apparently initial concentration had little effect on the degradation rate. The average rates of loss for the 6 samples with the highest initial concentrations were .43 and .48 while those for the 6

TABLE 5. Loss of herbicide (ppm) from field samples incubated in the laboratory at 83 F.

| Sample Number | 0 Days | | 82 Days | | 156 Days | | Total loss/ day (percent) | |
|---|---|---|---|---|---|---|---|---|
| | 2,4-D[a] | 2,4,5-T[b] | 2,4-D | 2,4,5-T | 2,4-D | 2,4,5-T | 2,4-D | 2,4,5-T |
| 1 | 2740 | 1980 | 2300 | 1178 | 868 | 480 | .44 | .44 |
| 2 | 2440 | 1500 | 1412 | 695 | 680 | 320 | .46 | .50 |
| 3 | 3220 | 2380 | 1340 | 820 | 840 | 488 | .47 | .51 |
| 4 | 2360 | 1500 | 1260 | 750 | 784 | 440 | .43 | .45 |
| 5 | 5704 | 4220 | 3148 | 1640 | 2000 | 1124 | .42 | .47 |
| 6 | 5484 | 3388 | 2408 | 1350 | 1852 | 920 | .43 | .47 |
| 7 | 3260 | 2100 | 1540 | 760 | 1164 | 632 | .41 | .45 |
| 8 | 2980 | 2200 | 1162 | 547 | 1300 | 720 | .36 | .43 |
| 9 | 9680 | 7080 | 4584 | 2408 | 3552 | 1740 | .41 | .48 |
| 10 | 11000 | 7720 | 4644 | 2388 | 3590 | 1902 | .43 | .48 |
| 11 | 2820 | 1820 | 1500 | 700 | 1032 | 608 | .41 | .43 |
| 12 | 3320 | 2440 | 1448 | 895 | 1028 | 500 | .44 | .51 |
| AVG. | 4584 | 3194 | 2229 | 1178 | 1558 | 823 | .42 | .43 |
| TOTAL | 55,008 | 38,328 | 26,746 | 14,131 | 18,690 | 9,879 | | |

[a] Total value for esters and acids of 2,4-D.

[b] Total value for esters and acids of 2,4,5-T.

samples of lowest concentration were .42 and .46, respectively, and are therefore not significantly different.

One observation that was apparent in all degradation studies which have been performed is the relatively rapid hydrolysis of the n-butyl esters of the herbicide due to contact with the alkaline Utah soils. Table 6 gives the percentage saponification of the n-butyl esters of 2,4-D and 2,4,5-T to the acids over a period of 282 days for two different application rates. It was found that in all samples, the rate of hydrolysis of n-butyl 2,4-D was greater than that of n-butyl 2,4,5-T. Moreover, it is likely that at the higher concentrations (e.g., 4,000 lb ai/A), the acid salts formed could not be removed at a sufficiently rapid rate (via degradation and/or penetration), causing the chemical equilibrium to shift to the left.

Data concerning herbicide penetration in Utah soils are shown in Table 7. Samples from lower soil increments were taken from those plots where it was expected that herbicide concentrations would be most likely to penetrate into the soils. With one exception, both 2,4-D and 2,4,5-T residues were found at all levels sampled. In all cases the total herbicide concentration in levels greater than 18 inches was made up entirely of the free acids. Butyl esters were not detected at depths greater than 12 inches for 2,4-D or 18 inches for 2,4,5-T. It is also interesting to note that the penetration of 2,4-D is greater than that of 2,4,5-T. Apparently this is due to the greater water solubility of the free acid of 2,4-D. This may also explain why 2,4-D appeared to degrade more slowly in laboratory samples where there was no loss from the sample due to penetration.

In June 1973, a composite soil core from one of the 4,000 lb ai/A plots was selected for TCDD analysis. The Interpretive Analytical Services Laboratory, Dow Chemical U.S.A. performed the analysis using a modification of the method developed by Baughman and Meselson (published in Environmental Health Perspectives, Experimental Issue No. 5, September 1973). The following data were obtained:

| Sample | 2,3,7,8-tetrachlorodibenzo-p-dioxin | |
|---|---|---|
| | parts per trillion | parts per billion |
| Control (0-6 inches) | <10 | <10 |
| Plot 5 (0-6 inches) | 15,000 | 15.00 |
| Plot 5 (6-12 inches) | 3,000 | 3.00 |
| Plot 5 (12-18 inches) | 90 | 0.09 |
| Plot 5 (18-24 inches) | 120 | 0.12 |

Thus, within the four samples from the plot 5 core (4,000 lb ai/A) a total concentration of 18,210 ppt (18.21 parts per billion - ppb) was found. Undoubtedly the lower two depths (12-18 and 18-24 inches) represent contamination from the upper two increments, via the use of the hand auger.

TABLE 6. Percentage saponification of the n-butyl esters of 2,4-D and 2,4,5-T at selected time periods, days, following soil incorporation in alkaline soils.

| Application Rate of Formulation | Days After Incorporation[a] | | | |
|---|---|---|---|---|
| | 0 | 110 | 220 | 282 |
| 1,000 lb ai/A[b] | | | | |
| Esters | 100 | 24 | 13 | 3 |
| Acids | 0 | 76 | 87 | 97 |
| 4,000 lb ai/A | | | | |
| Esters | 100 | 77 | 40 | 32 |
| Acid | 0 | 23 | 60 | 68 |

[a] Data are the percent acid and esters of herbicides found in top 0-6 of soil profile.

[b] lb ai/A = pounds active ingredient per acre.

TABLE 7. Herbicide (2,4-D and 2,4,5-T) penetration (ppm) in the 4,000 lb ai/A plots 282 days after soil incorporation.

| Depth (inches) | 2,4-D[a] (ppm) | 2,4,5-T[a] (ppm) | Percent of total Herbicide |
|---|---|---|---|
| 0-6 | 4262 | 2982 | 72.4 |
| 6-12 | 1093 | 752 | 18.4 |
| 12-18 | 126 | 101 | 2.3 |
| 18-24 | 158 | 70 | 2.7 |
| 25-30 | 230 | 50 | 2.9 |
| 30-36 | 161 | 21 | 1.8 |

[a] Data are an average of two analyses and represents the total of both the ester and acid components.

Since the TCDD concentration of the formulation was known (see Methods), and since its determination in the soil core was performed by the same laboratory and instrumentation, an estimation of the degradation of TCDD can be obtained by comparison to the expected value based on the known concentration of herbicide at time of sampling. Subsamples of the soil core analyzed for TCDD were also analyzed for 2,4-D and 2,4,5-T. The total concentration of herbicide in the 0-6 and 6-12 inch increments was approximately 14,000 ppm. Therefore, the actual concentration should have been approximately 51.8 ppb TCDD ($14,000 \times 3.7 \times 10^{-3} = 51.8$) if degradation of the TCDD was at the same rate as 2,4-D and 2,4,5-T. If the theoretical values for herbicide concentration at day 0 (time of incorporation) are used, then the initial concentration of TCDD would have been 148 ppb ($40,000 \times 3.7 \times 10^{-3} = 148$ ppb). The percent loss of TCDD over a period of 265 days was 87.7% (18.21/148 = 12.3%; 100% - 12.3% = 87.7%). The value 87.7% would represent 3 half-lives for TCDD persistence. Therefore a rough estimate for the half-life of TCDD would be 88 days in these alkaline soils, under desert conditions, and in the presence of massive quantities of 2,4-D and 2,4,5-T.

These preliminary data suggest that TCDD degrades at a more rapid rate than 2,4-D or 2,4,5-T. Moreover, the movement of the TCDD to the 6-12 inch depth probably represents co-movement with the massive amounts of esterified herbicide, rather than independent penetration into the soil profile.

# APPENDIX H

# JOHNSTON ISLAND DATA

# APPENDIX H - JOHNSTON ISLAND DATA


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1. BACKGROUND INFORMATION

a. History of Johnston Island

(1) Johnston Atoll has had a varied history. It is one of the most isolated atolls in the entire Pacific Ocean. Originally it consisted of two small, insignificant islands, a partial coral reef to the west and northwest and a rather large, shallow lagoon to the east and south. This lagoon is dotted by numerous patch reefs and coral heads. It is now a large Department of Defense (DoD) complex. Johnston Atoll was originally discovered by the American brig "Sally" out of Boston on September 2, 1796 (Bryan, 1942)(Wetmore, 1963). However, no landing was made. On December 1, 1807 the HMS "Cornwallis" under the command of Captain Charles James Johnston visited the atoll (Marshall, 1825). Today the atoll bears this discoverer's name. Since 1858, Johnston Atoll has been the undisputed possession of the United States. Prior to that date it was claimed for short periods of time by the Kingdom of Hawaii (Bryan, 1942). In 1892, Great Britain filed a claim that Johnston Atoll was being considered as a possible relay station for a transoceanic communications cable (Bauer, 1973). Johnston Atoll is not now and never has been a part of the State of Hawaii. It is presently an unincorporated territory which is distinguished from an incorporated territory, i.e., it is a territory to which the constitution of the United States has not been fully and expressly extended (U.S. Department of State, 1965). Birds have in the past and continue at present to play an important part in the history of the atoll. Following passage of the Guano Act of 1856 by the United States Congress there were transient guano mining efforts in 1858-1860. The first scientific visit in July 1923 resulted largely from interest in the bird population (Wetmore, 1963). As a result of this visit, the atoll was made a Federal bird refuge on July 29, 1926 by Executive Order No. 4467 signed by President Calvin Coolidge. Initially the atoll was under the jurisdiction of the Department of Agriculture but in 1940 this responsibility was transferred to the Department of the Interior. This executive order remains in force although subsequent executive orders have given jurisdiction over the atoll to the Department of Defense, see Appendix B.

(2) Because of its strategic military location, President Franklin D. Roosevelt, on December 29, 1934, by Executive Order No. 6935, placed the atoll under the Department of the Navy. From 1934 to 1939 infrequent visits were made to Johnston Atoll by Pacific Fleet units. In the fall of 1939 the Navy awarded a contract for construction of a small naval base. A lagoon seaplane landing area with headquarters on Sand Island was initially constructed (Bauer, 1973). In February 1941, by Executive Order No. 8682, the airspace above and the water within the 3-mile marine boundary were designated as the Johnston Island Naval Airspace Reservation and the Johnston Island Naval Defense Sea Area, respectively, see Appendix B. On August 15, 1941, the Naval Air Station was commissioned. On December 15, 1941, eight days after the attack on Pearl Harbor, Johnston Island was shelled for a short time by Japanese surface vessels. Again on December 21, 22, and 29, 1941 both Johnston and Sand Islands were shelled; one Japanese submarine was reported sunk by American gunfire. There were no injuries to personnel but the shelling caused considerable damage to various facilities. Construction continued until April 1942. Channel approaches and a seaplane landing area were dredged. Other construction included bomb shelters, living quarters, runways, parking aprons, storage sheds and gun emplacements (Bauer, 1973).

(3) During early World War II, patrol submarines used the atoll as a refueling station. By 1944, and throughout the rest of the war, it became a major transport terminal for the Pacific area, servicing aircraft going to and from the Pacific battle fronts (Abend, 1942). After World War II, the Navy continued to operate the Naval Air Station at reduced strength. The status was later reduced to that of a Naval Air Facility. Sand Island was abandoned in 1946. By order of the Secretary of the Navy, operational control of Johnston Atoll was transferred to the U.S. Air Force on July 1, 1948. The Navy retained technical jurisdictic During the Korean airlift in 1951 and 1952, Johnston Island again assumed ajor military importance. The airstrip was enlarged by dredging and new buildings and improved utilities were added (Bauer, 1973).

(4) On January 25, 1957, the Treasury Department was granted a permit for the U.S. Coast Guard to operate a LORAN (Long Range Air to Navigation) transmitter on Johnston Island. On September 13, 1957, the Department of Commerce began operation of a Weather Bureau facility on the island. On April 22, 1958 operational control of Johnston Atoll was assumed by the commander of Joint Task Force Seven. As part of Operation Hardtack, two missiles carrying thermonuclear devices were fired from Johnston Island into the stratosphere to obtain information on the effects of nuclear detonations at high altitudes. These were the first megaton devices detonated in the stratosphere by the United States. The Pacific phase of Operation Hardtack lasted until August 19, 1958. Operational control of Johnston was assumed by Joint Task Force Eight and the Atomic Energy Commission on January 17, 1962 for the purpose of conducting additional high-altitude nuclear tests. The Secretary of Defense granted permission on December 10, 1959 to relocate the U.S. Coast Guard LORAN-A and -C Station to Sand Island. Completed in 1961, the U.S. Coast Guard facility presently maintains a staff of approximately 25 men. Sand Island is still a bird sanctuary under the jurisdicition of the Department of Interior (Bauer, 1973).

(5) By August 1960, Air Force retention of Johnston Island seemed assured, and a survey was made to ascertain the scope of work required to restore base facilities to minimum operational condition. Extensive engineering activity continued throughout 1961. Also, during this period the LORAN station on Sand Island and the U.S. Weather Station authorized by JCS Document 1910/10 were finished. Important contracts were let for modification and alteration, airfield pavement repair and emergency runway lighting. Repair of the old distillation system and installation of new equipment was accomplished. Several construction projects continued with a deadline of 15 March 1962, necessitated by 1962 Pacific Atomic Tests (USAF Hist, 1959-1963). Joint Task Force Eight and the Atomic Energy Commission entered into an operational agreement with the Department of the Air Force on 17 January 1962 to take control of Johnston Island. Additionally a memorandum of understanding was executed between Commander, Joint Task Force Eight and Commander in Chief, Pacific Air Forces on 18 January 1962. As part of this agreement, support of both the Coast Guard LORAN Station and the Weather Bureau Station, previously a commitment of Pacific Air Force Base Command, was undertaken by Commander, Joint Task Force Eight. Major construction projects in support of the test series were completed in May 1962; however, numerous minor projects continued throughout the test period. All existing facilities were augmented to the fullest extent possible, but were subject to the limitations imposed by useable estate and available time (Bauer, 1973).

(6) Commander, Joint Task Force Eight proposed in his message 26030Z of October 1962 to the Chairman, JCS, that steps be taken for preservation on the island of certain test assets there and to return operational control of the island to Commander in Chief, Pacific Air Forces providing there were no plans for additional nuclear tests prior to mid-1964. The JCS generally concurred; however, because of plans for possible use of Johnston Island during calendar year 1963, by their message 071837Z of November 1962, requested that the plan be reviewed in light of this development. While this review was being conducted, further direction by JCS message JCS 7654 011648Z of December 1962 was received. It directed Commander, Joint Task Force Eight to retain control of Johnston Island pending further guidance. On 16 January 1963, Commander, Joint Task Force Eight, proposed that the control and support arrangements for Johnston Island be maintained until at least 1 April 1963. Additional plans and guidance for the Task Force were received from the JCS through their Paper SM-373-63 of 19 March 1963. It was clear at this time that the most efficient procedure would be for Commander, Joint Task Force Eight to retain operational control of Johnston Island at least through the completion of the 1964 test plans. The proposal was affirmed by JCS Paper SM-758-63 of 11 June 1963. Later in 1963 the mission and the future of Johnston Atoll were to be guided by the national requirements for possible continuation of nuclear testing in the atmosphere. The significant influence for ratification of the Limited Test Ban Treaty of 1963 was President Kennedy's assurance to Congress that four safeguards would be established and maintained to keep the U.S. from falling behind in nuclear technology. One of the safeguards, Safeguard III, was the development of the ability to resume testing promptly in those environments prohibited by the treaty in the event of Russia's abrogating the treaty or if such test should be deemed essential to national security. Thus, by Safeguard III, the future of Johnston Atoll was established as an overseas nuclear test base. Plans for the 1964 tests were later cancelled; however, CJTF-8 continued to maintain Operations control of Johnston Atoll (until 1970) under the direction of the Director, Defense Atomic Support Agency (DASA), now the Defense Nuclear Agency (DNA) (Bauer, 1973).

(7) During the latter part of 1964 and early 1965, an advanced state of readiness was developed at Johnston Atoll in support of the National Nuclear Test Readiness Program (NNTRP), a prompt response testing program, prepared by both the Atomic Energy Commission (AEC) and DoD (DoD-AEC a., 1965) (DoD-AEC b., 1965) to satisfy the Safeguard III requirement. This readiness posture, which included an extensive building program on Johnston Atoll, was maintained until 1970. Annual exercises conducted by JTF-8, commencing in 1964, evaluated the capability of the AEC and DOD agencies to initiate nuclear testing within specified reaction times. These full scale exercises at Johnston Atoll commenced with Operation Crosscheck in 1964 and continued with Operation Roundup in 1965. Operation Windlass in 1966 and Operation Paddlewheel in 1967 (the last JTF-8 readiness-to-test exercise) included in addition to the previous years activities, a series of coordinated rocket firings from Johnston Atoll. The Department of the Interior approved the title "Johnston Atoll" to be used henceforth and forevermore as a fitting recognition of the importance of the Johnston Island complex and its environs. Further, it was proposed that the two man-made island, created within the surrounding barrier reef, be named Akau and Hikina, Hawaiian words meaning north and east. On 20 May 1965, these names were officially assigned to the two islands. Extensive building of testing and support facilities, including airfield improvements and the installation of the Pacific Missile Range tracking complex, continued during 1965 to 1967. An Air

Force Baker-Nunn space camera station was constructed on Sand Island and was functioning in 1965. It has continued to remain in full operational status. An agreement between AEC and DoD (AEC-DoD, 1971) in 1965 provided the basis for the necessary contractual arrangements for engineering, construction, maintenance, and operations services. The build-up program consisted of laboratories, shops, rocket launch pads, rocket assembly buildings, storage bunkers, control and monitoring facilities, sampling and tracking facilities, photo and optical stations, and weather facilities (AEC-DoD, n.d). A significant portion of the readiness-to-test capability is the THOR launch complex developed by the USAF which was used for launching nuclear payloads during the test series (Dominic/Fishbowl) of 1962. Since then this complex operated by Program 437, a USAF R&D space program, made 15 scheduled THOR launches from 1965 to 1970. Since that time only crew training (operations terminated short of actual launch) continues. Launch crews are provided by the 10th Aerospace Defense Squadron under the control of Aerospace Defense Command. Improvements to the communications system in 1965 included the installation of a submarine telephone cable from Johnston Atoll to Oahu with additional cables connecting Johnston Island to Sand, Akau and Hikina Islands (Bauer, 1973).

(8) During the years of the Vietnam conflict, Johnston Atoll continued to support the flow of air traffic enroute to and returning from Southeast Asia. Formations of tactical aircraft made use of Johnston Atoll's refueling facilities since they were dependent upon enroute stops and/or the use of inflight refueling tankers. Due to increasing demands for additional jet commercial routes to the various Pacific Islands, particularly to the Trust Territories, the Defense Department allowed the Civil Aeronautics Board to authorize commercial aircraft to make refueling stops at Johnston Atoll. This resulted in Air Micronesia service to Johnston Atoll on 17 May 1968 (Bauer, 1973).

(9) In late 1969, national decisions were made to reduce the level of support to the readiness program and to revise the NNTRP. These decisions included the inactivation of JTF-8 and the transfer of operational and funding responsibility for Johnston Atoll to the USAF (AEC-DoD, n.d). Effective 1 July 1970, operational control of Johnston Atoll was transferred to USAF, with continuing readiness planning responsibilities assumed by Director, DNA (Sec Def, 1969). The JTF-8 designator and records were retained by Director, DNA for utilizations as required. Operations and maintenance of Johnston Atoll was assumed by the 6486th Air Base Wing (PACAF), which was renamed the 15th Air Base Wing on 1 November 1971 with no change in mission. The population of Johnston Atoll, which had been approximately 1200, was reduced to approximately 600 by the end of 1970, with about one-half military and one-half civilian contract personnel. The responsibilities of Director, DNA concerning readiness facilities and the siting thereof at Johnston Atoll are defined in Dep Sec Def Memorandum for Director, DNA (Program/Budget, 1969). The relationships and responsibilities for the 15th Air Base Wing (PACAF) and the DNA (JTF-8) at Johnston Atoll concerning readiness matters were delineated in a support agreement (Sec Def b, 1970). Concurrently, the emphasis within the technical and experimental readiness related programs of the AEC and DoD laboratories was shifted to address high altitude phenomenology and effects. A high altitude development test, planned and funded prior to the decision to phase down, was carried forward to execution. In September 1970, the AEC/DNA development test was conducted at Johnston Atoll utilizing a THOR booster mated with an AEC developed non-nuclear high altitude test vehicle (HATV). The successful THOR/HATV launch was conducted by a JTF-8 organization developed for this particular test.

(10) The decision was made during 1970 to remove U,S. chemical munitions from Okinawa; however, their retention as part of the national stockpile was necessary. Political pressure which ultimately resulted in forbidding relocation of these munitions, designated RED HAT, to any point on CONUS or Alaska caused the selection of Johnston Atoll as the storage site. Movement of the RED HAT toxic chemicals (MUSTARD, GB and VX) by ships, from Okinawa to Johnston Atoll, started in early 1971 and was completed in mid-May 1971. On Johnston Atoll they were placed under the custody and control of the U.S. Army 267th Chemical Company. The construction of storage facilities for RED HAT in the southwest quadrant of Johnston Island occupies a 41-acre area. Just prior to movement of the chemical munitions to Johnston Atoll, the Surgeon General, Public Health Service, reviewed the shipment and the Johnston Atoll Storage plans and caused the Secretary of Defense in December 1970 (DNA-PACAF, 1971) to issue instructions restricting missile firings and all aircraft flights to the island except essential military flights to support the island's mission. As a result, Air Micronesia service was immediately discontinued and rocket missile firings suspended (Bauer, 1973). Again, early in 1972, another politically unpopular problem arose with the phasing down of the Vietnam conflict which necessitated the movement of herbicide Orange (a USAF defoliant spraying mixture)from Vietnam. As a result of Congressional and citizen interest in disposal problems, the Department of Defense (DoD) decided to move one and one-half million gallons (26,300 55-gallon drums) to Johnston Atoll for storage to await a means of future disposal. By April 1972, herbicide Orange was in storage at Johnston Atoll (Sec Def a, 1970) on the southwest peninsula. As a result of a DNA Joint Hazards Evaluation Group study (DNA, 1972) conducted in July 1972, concerning the hazards to both transient and island personnel from commercial aircraft use imposed by the storage of RED HAT, the commercial flight restrictions to Johnston Atoll were conditionally lifted. Air Micronesia was allowed to resume air service to Johnston Atoll on 29 April 1973.

(11) During mid-August 1972, a tropical storm, Celeste, located southeast of the Hawaiian Island, had blossomed into a full scale hurricane. Observation of Celeste's track for several days, it became apparent that Johnston AToll woul be in the path of the hurricane. The decision was made to evacuate the island and by 18 August all personnel had been flown to Hickam AFB, HI. This was the first known time the island had been completely evacuated of personnel since the Navy commenced its construction program in 1939. On 19 August, Celeste struck Johnston Atoll at approximately 1400 hours local time. The atoll was subjected to sustained winds of 100 knots with gusts up to 130 knots. The heavy surf primarily affected the north, northeast, and south sides of the island. On 22 August a seaborne cadre, consisting of an Army RED HAT checkout team and an Air Force/H&N team, were put ashore at Johnston Atoll from the Navy destroyer USS Lloyd Thomas to initiate restoration of life support activities (Bauer, 1973).

(12) In June 1973, the Deputy Secretary of Defense approved a USAF plan for the transfer of host manager responsibility of Johnston Atoll to DNA which was formulated into a joint USAF/DNA agreement (Joint Hazards, 1972) with an effective date of transfer of 1 July 1973 (DAF-DNA, 1973).

(13) Remaining still in effect, down through the years, is the executive order which origianlly designated Johnston Atoll a bird sanctuary. The bird scene today, principally at Sand Island, shows little if any effect by the numerous activities which the atoll has been committed to during its years of development.

(14) A summary of ownership and control of Johnston Atoll is shown in Table H-1.

(15) Through the past decade Johnston Atoll (environment, flora, fauna) has been the subject of numerous studies and surveys. Periodically, the Smithsonian Institution has investigated the bird life of Sand Island (bird sanctuary), its most recent effort being in 1969 when a research biologist spent several months there. Earlier studies commenced in 1963 (Bauer, 1973) by the Hawaii Marine Laboratory of the University of Hawaii, to investigate the effects on marine growth from the extensive dredging and buildup of the atoll, have continued to this day. A land management plan (Support Agreement, 1973), prepared at the request of CJTF-8 in 1964, was used as a guide for developing plant life on the atoll and for control of erosion from wind and water. Surveys conducted in 1965 for the Naval Oceanographic Office (DNA-AEC, 1973) obtained detailed information about the water flow regime around the island. Another environmental program, continuous since 1966 by the Laboratory of Radiation Ecology, College of Fisheries, University of Washington, has been to obtain information for predicting and evaluating the biological consequences of a possible nuclear test series at Johnston Atoll. Reports on this program are submitted to the AEC annually.

(16) As a result of Executive Order numbers 4467 and 6935 and their effect on the possible disposal of herbicide Orange on Johnston Island, the opinion of the General Counsel, Department of the Air Force, was requested.

b. Location and Size (Land Surface)

(1) Located at latitude 16 degrees 45 minutes north and longitude 169 degrees 30 minutes west, Johnston Atoll is one of the most isolated atolls in the Pacific. The closest reef is French Frigate Shoals, approximately 450 miles to the north. Honolulu, Hawaii is approximately 717 miles to the northeast, while the nearest land to the southeast is Palmyra Island, about 750 miles away. The Marshall Island Group is the closest land mass to the west at a distance of about 1,300 miles, see Figures H-1 and H-2 (POBSP, 1964) (Thorp, 1960)(Navy Hydro a, 1959 and Navy Hydro b, 1959).

(2) Johnston Atoll consists of a pair of low sand and coral islands, Johnston and Sand Islands, plus two entirely man-made islets, Akau (North) and Hikina (East) Islands within a shallow lagoon partially enclosed by a semicircular reef to the north and west. The southern and eastern portions of the fringing reef, however, are made up of numerous discrete fragments spread over a large area to the south and east of the main lagoon. If one uses the 4-fathom line as indicating the outer boundaries of the atoll, Johnston Atoll has a circumference of somewhat more than 21 miles. This particular depth was used since it apparently correlates almost exactly with the outer limits of the exposed reefs, with the line lying only a few yards to the seaward of the most southerly of the reefs. The atoll is roughly lens-shaped, with the long axis running on

TABLE H-1

OWNERSHIP AND CONTROL OF JOHNSTON ATOLL

| Period | "Owner" | Operational Control | Purpose of Document | Authority | Event/Use |
|---|---|---|---|---|---|
| 1923 | Dept of Agriculture | Agriculture | Plant and sealife surveys, | *Executive Order 4467 | Bird refuge (Executive Order June 29, 1926) |
| 1934 | Dept of the Navy | USN | Pacific defense | *Executive Order 6935 | |
| 1941 | " " " " | USN | Established Naval Defense Sea Area for military sea and air operations | *Executive Order 8682 | Became Johnston Island Naval Air Station |
| 1944 | " " " " | USN | --- | --- | Defense of area; Air Transport Command operations; Oceanic Air Traffic Control |
| 1947 | " " " " | USN | --- | Secretary of the Navy | Became a Naval Air Facility |
| 1948 Jul 1 | " " " " | USAF | Transfer of operational control to USAF | Agreement | Pacific Air Command (MATS, ARS, AAC, AWS Dets) (SecNav ordered transfer to USAF) |
| 1949 Jun 1 | " " " " | USAF | --- | --- | Pacific Air Command inactivated; Pacific Division MATS took over. |

*Executive Orders are still in effect; have not been amended or rescinded so as to affect "ownership."

TABLE. H-1 (Cont'd)

| Period | "Owner" | Operational Control | Purpose of Document | Authority | Event/Use |
|---|---|---|---|---|---|
| 1951-52 | Dept of the Navy | USAF | --- | --- | Korean airlift support |
| 1957 Jan 25 | " " " " | USAF | --- | --- | USAF granted Treasury Department five year use for USCG Loran Station |
| 1957 Sep 13 | " " " " | USAF | --- | --- | USAF granted Department of Commerce five year use for U. S. Weather Bureau |
| 1958 Apr 22 | " " " " | CJTF-7 | --- | Agreement | Atomic tests in Pacific area until August 19, 1958; then roll-up. |
| 1959 Jul 24 | " " " " | USAF | --- | --- | Formal meeting in Hawaii to propose transfer of operational control to Army for the Nike-Zeus test program. |
| 1959 Sep 23 | " " " " | USAF | To transfer operational control to Army | --- | Proposed agreement sent to higher headquarters |
| 1959 Jun 30 | " " " " | USAF | --- | --- | Secretary of the Treasury asked Secretary of Defense for Sand Island as Loran Station, to be under operational control of Commander in Chief, Pacific. |

TABLE H-1 (Cont'd)

| Period | "Owner | Operational Control | Purpose of Document | Authority | Event/Use |
|---|---|---|---|---|---|
| 1962 Jan 17 | Dept of the Navy | CTJF-8/AEC | --- | Agreement | USAF signed Operations Agreement for 1962 nuclear tests. |
| 1962 Jan 18 | " " " " | CJTF-8/AEC | --- | Agreement | Commander in Chief, Pacific signed agreement with Commander Joint Task Force EIGHT. |
| 1963 Jun 11 | " " " " | CJTF-8/AEC | --- | --- | Joint Chiefs of Staff reaffirmed operation control of Joint Task Force EIGHT. |
| 1970 Jul 1 | " " " " | USAF | Transfer of operational control to USAF | --- | JTF-8 inactivated. Deputy Secretary of Defense Memorandum to Secretary of Air Force for transfer of JA to USAF |
| 1973 Jul 1 | " " " " | DNA (FCDNA) | Transfer of operational control to DNA | Agreement | Department of the Air Force signed agreement with Defense Nuclear Agency |

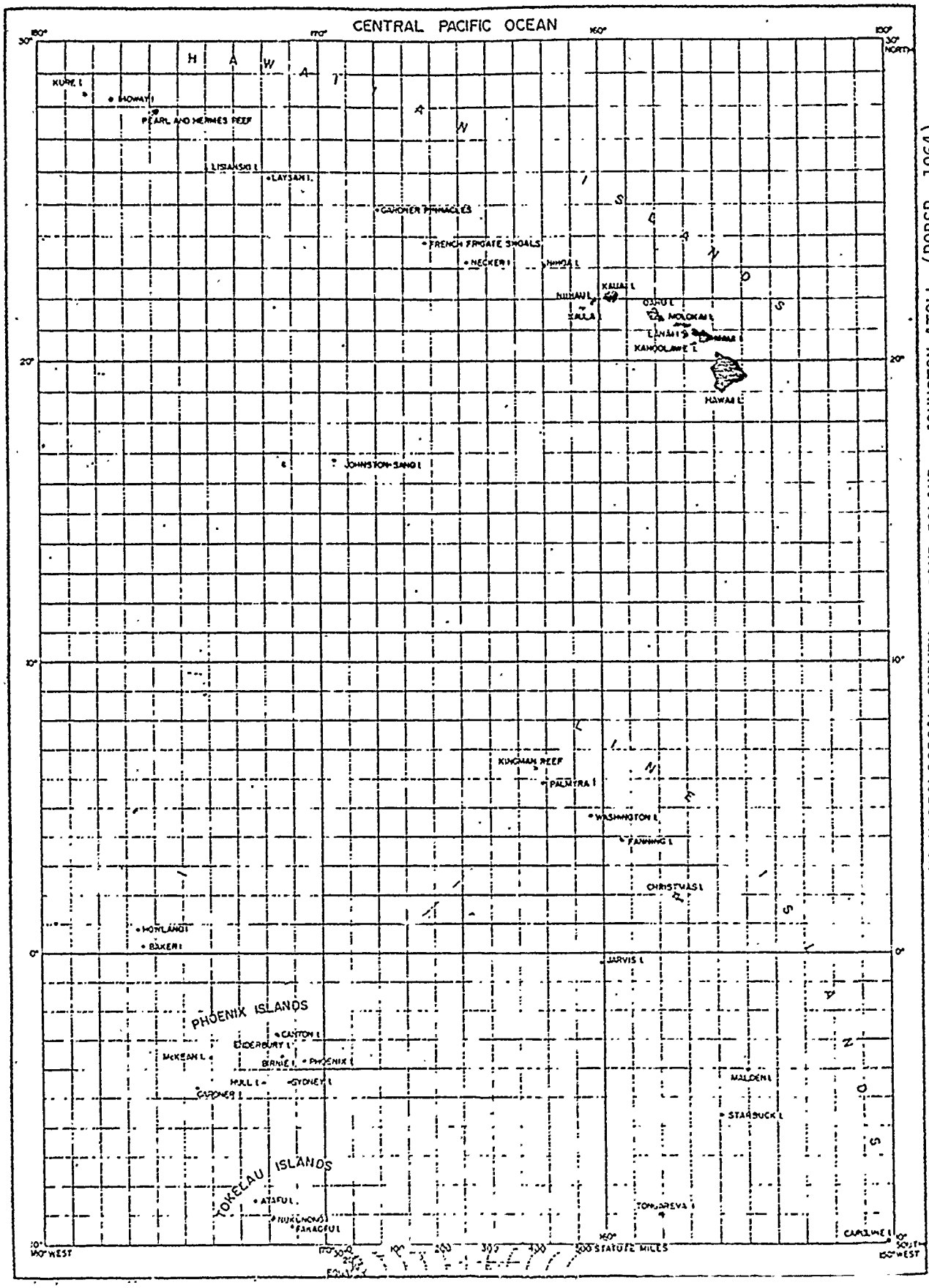



FIGURE H-1 TAKEN FROM THE PRELIMINARY BIOLOGICAL SURVEY OF SAND ISLAND - JOHNSTON ATOLL (POBSP, 1964)

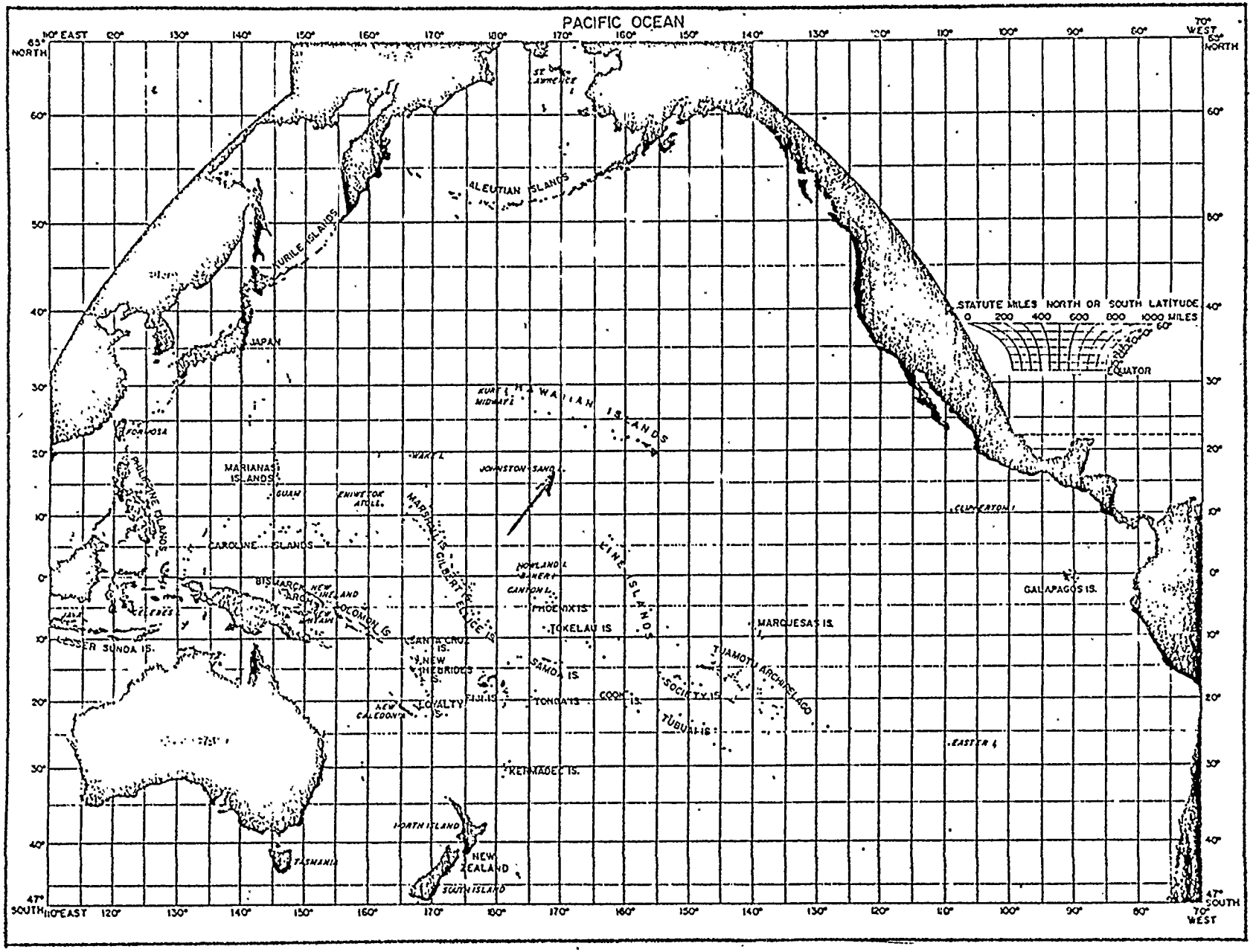



FIGURE H-2 MAP OF PACIFIC OCEAN

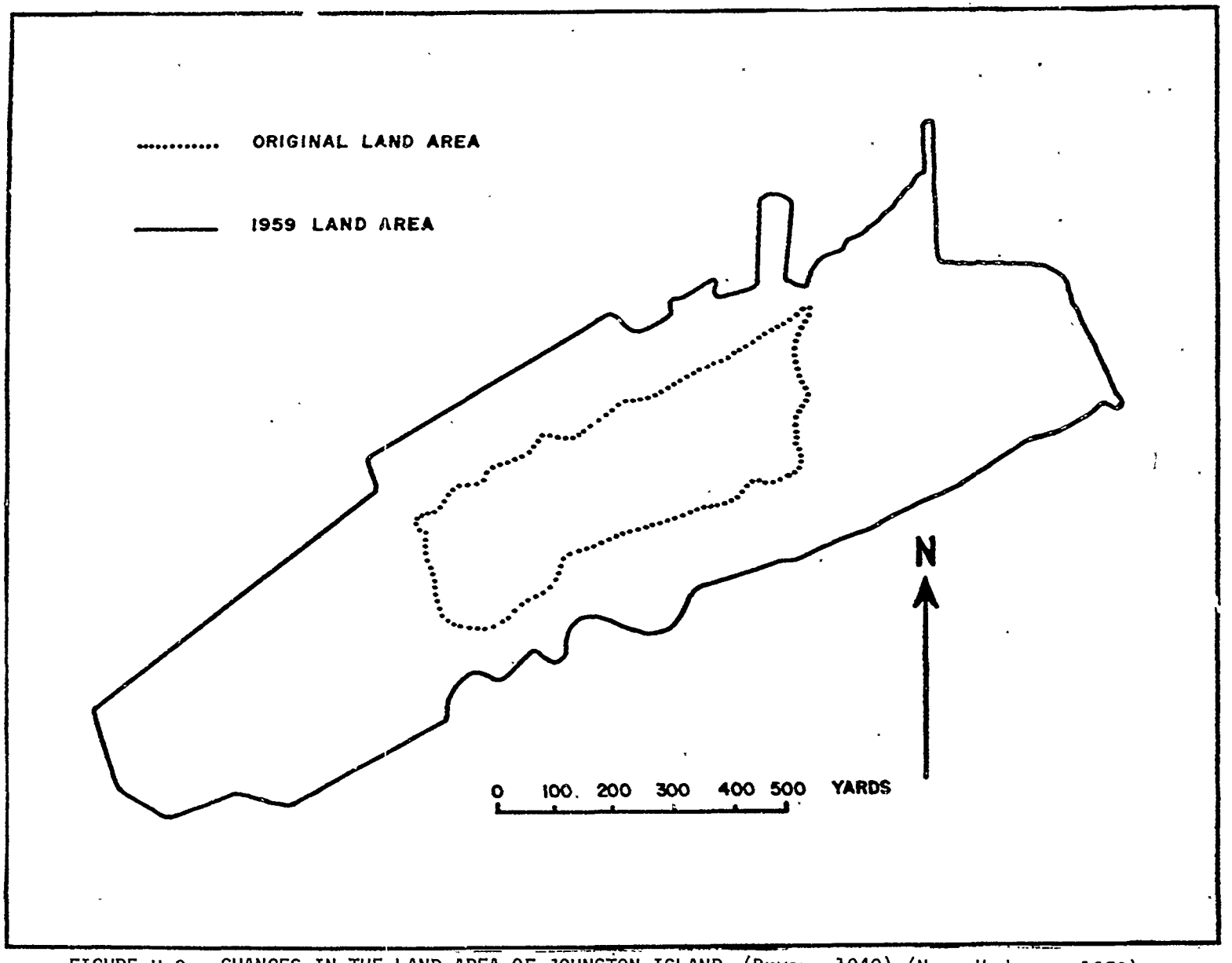



FIGURE H-3 CHANGES IN THE LAND AREA OF JOHNSTON ISLAND (Bryan, 1942) (Navy Hydro a, 1959)

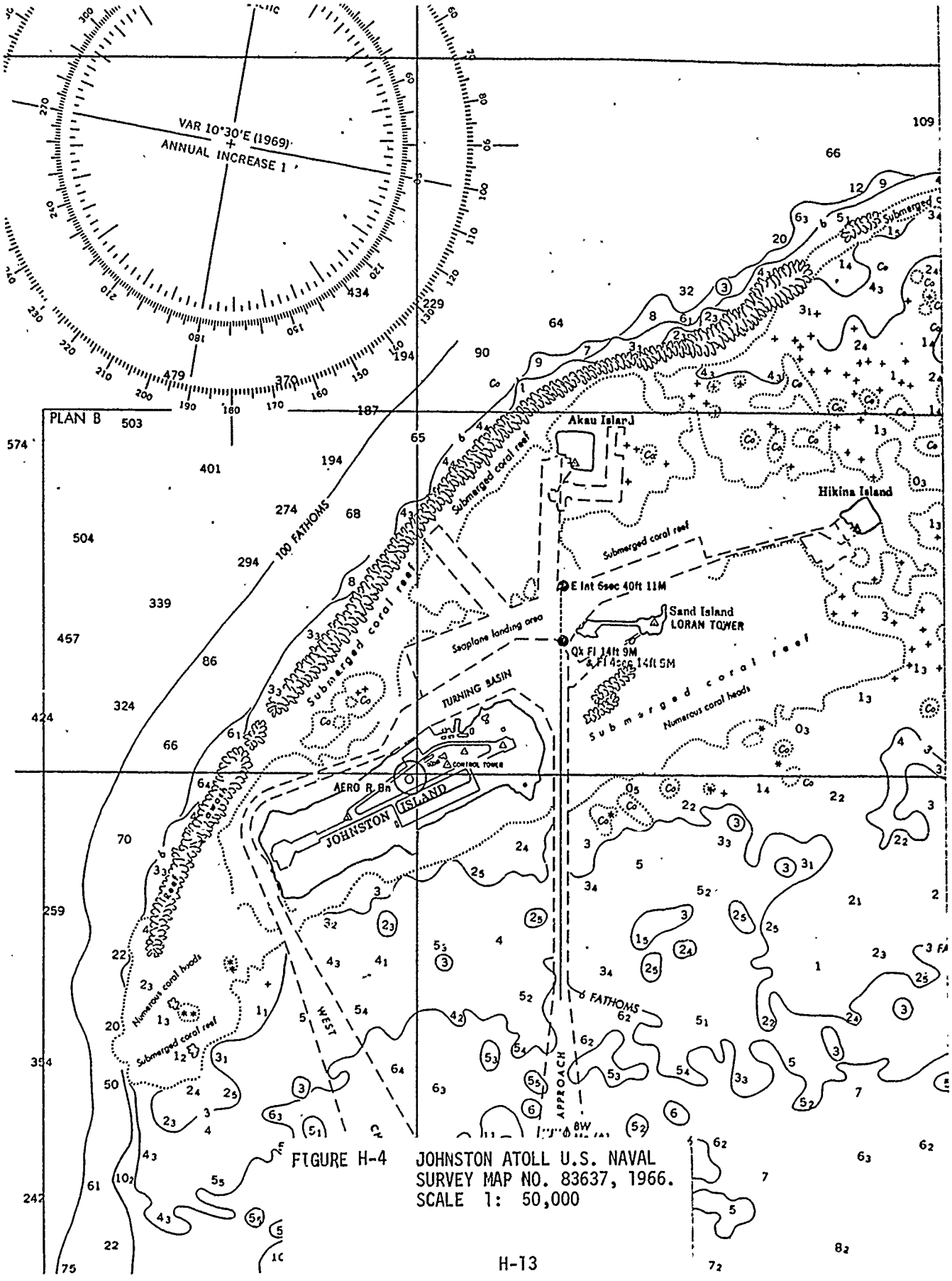



FIGURE H-4 JOHNSTON ATOLL U.S. NAVAL SURVEY MAP NO. 83637, 1966. SCALE 1: 50,000

a line almost exactly northeast to southwest (POBSP, 1964). Johnston Island, the larger of the two island, has had its area considerably modified by human activity. Figure H-3 reveals the original area of Johnston Island with the area in 1959. Originally the island was 2,850 feet long at its greatest extent. The width of the island varied from 500 to 800 feet. The original area of the island was about 40 acres or 0.06 square mile (Emery, 1956). Since 1949, however, Johnston Island has been more than tripled in size, as the lagoon was dredged with new land fills being developed at the periphery. At present (1959) the long axis of the island stretches 6,150 feet, with a greatest width of about 1,500 feet at the center of the island near the airstrip control tower. The total area of Johnston Island in August 1959, was about 0.33 square mile. None of the original shore line remains, and the addition of fill all around the original island has tended to produce an artifically smooth shore line except in the northeastern quarter where the quays and piers of the harbor area jut into the lagoon. The original rectangular orientation of Johnston has been retained, however, except for this northeastern portion of the island, see Table H-2 (Thorp, 1960)(Navy Hydro a, 1959)(Navy Hydro b, 1959). The following table depicts the major changes in the Johnston Atoll acreage as a result of the dredge and fill programs:

TABLE H-2 JOHNSTON ISLAND ACREAGE

| | Acreage | |
|---|---|---|
| | 1963 | 1973 |
| Johnston and Sand | 198 | 648 |
| North (Akau) | 0 | 25 |
| East (Hikina) | 0 | 18 |
| TOTAL | 198 | 691 |

(3) Sand Island (originally known as Agnes Island) is a small coral islet located 1,900 yards to the northeast of Johnston Island. It is roughly triangular in shape, and has not been greatly modified by man in its outline. The dimensions of Sand Island are about 600 feet by 1,500 feet, with an area of about 10 acres or about 0.016 square mile. A causeway has been built which runs about 500 yards west from Sand Island to a fill area of several acres which is adjacent to the seaplane landing area in the lagoon. The causeway, the fill area, and the original islet are locally thought of as being one unit, and "Sand Island" is used as a designation for the entire complex. Johnston Island is located a bit southwest of the center of the atoll. It is more than a mile south of the northern barrier reef, while almost abutting the first of the southern reefs. Sand Island is nearly at the center of the long axis of the atoll, but it is more than 2-1/2 miles south of the main barrier reef, while at the same time about 1-1/4 miles to the north of the first southern reefs, see Figure H-4 (Thorp, 1960).

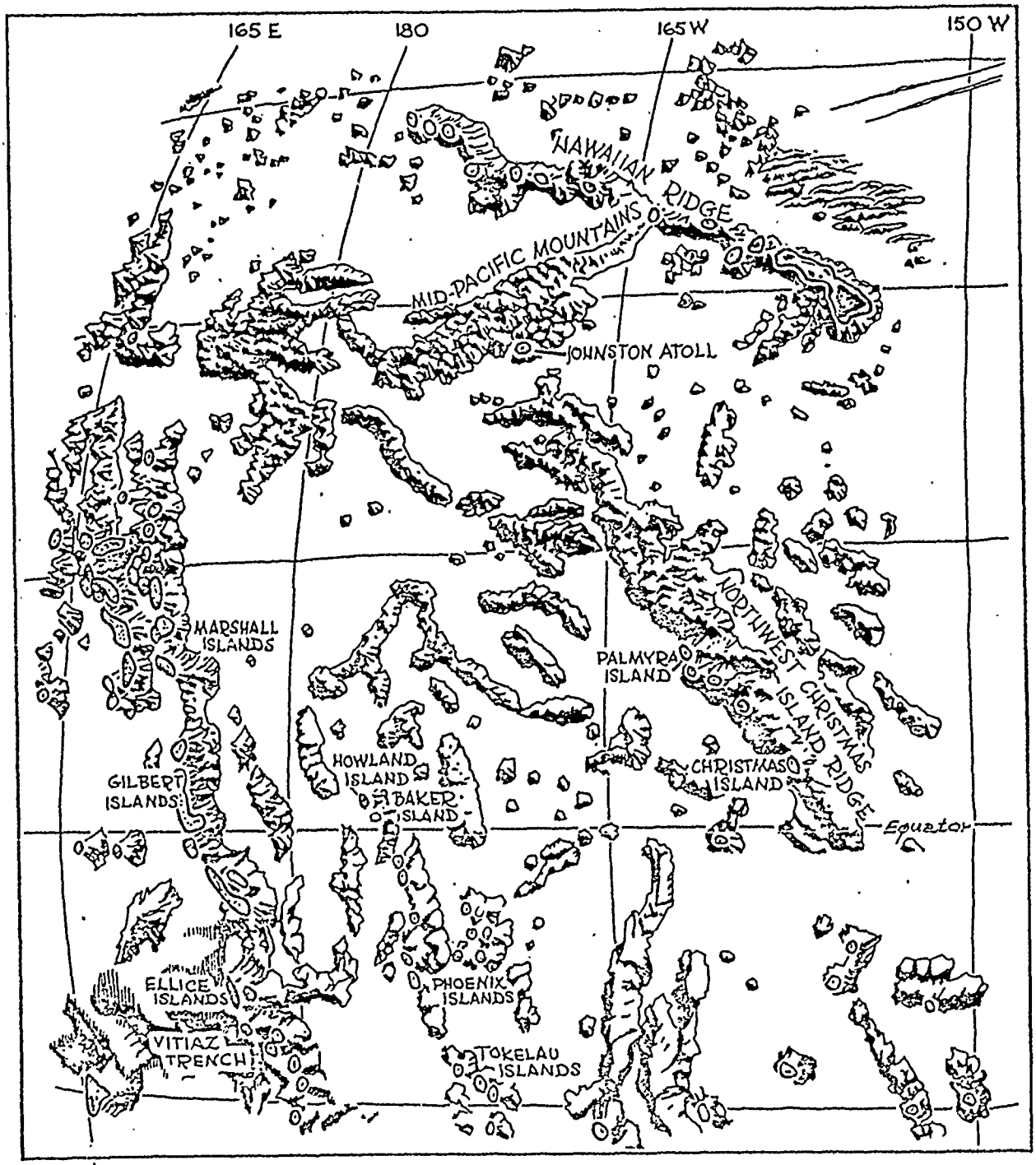



FIGURE H-5. CENTRAL PACIFIC SUBMERGED MOUNTAIN RANGES (POBSP, 1964)

c. Geology

(1) The original surface of Johnston Island was a mixture of sand, coral, and coral-derived rocks. The island rose from the southern beaches northward to a continuous sandy ridge (of an average height from 8 to 10 feet) extending along the northside of the island from end to end. This range connected Summit Peak, at the eastern end of Johnston Island, with an unnamed height of 13 feet at the western end of the island. Summit Peak, with an elevation of 44 feet, was the highest point in the atoll. At present the average height of the island is under eight feet, since both ridges and the two hills were leveled during the heavy construction which started in 1940 and changed the outline and surface of the island. Sand Island had no original height greater than eight feet, but it too has been leveled, since even a small relative relief such as that encountered on these two islands may produce a fairly rough and hummocky topography when the base material is sand under constant agitation by the prevailing winds (POBSP, 1964) (Thorp, 1960).

(2) The Central Pacific Ocean is dotted with a number of island groups, most of which are products of coral construction on worn-off volcanic upheavals. The Hawaiian Ridge stretches for a distance of some 1500 nautical miles from $20^{o}$ N at $155^{o}$W to $30^{o}$N. The Mid-Pacific mountains intercept this chain from the west but support only one small coral atoll, namely Johnston Atoll. South of the Hawaiian Ridge and Johnston Atoll are located the Line Islands, also known as the Northwest Christmas Island Ridge and the Phoenix Islands, see Figure H-5. There is indirect evidence that Johnston Atoll is intermediate in age between the Line and Hawaiian Islands, rather than between the older Mid-Pacific Mountains and the Line Islands, between which Johnston Atoll lies physically (Thorp, 1960). If this is the case, then Johnston Atoll probably has existed for slightly more than the 24-million years which is thought to be the minimum age of the Hawaiian Islands, or somewhat less than the 60 to 70-million years since the Mesozoic-Cenozoic boundary when the Line Islands were thought to have formed. If, however, Johnston is more closely allied geologically with the Mid-Pacific Mountains, it could be older, perhaps dating from the middle Cretaceous Age or approximately 100-million years ago (Amerson, 1973). Ashmore (1973) considers Johnston Atoll as a northernmost extension of the Christmas Ridge and suggests that "the terraces at Johnston Atoll probably were formed with falling sea levels at the end of the Sangamon Interglacial, or with rising levels at the end of the Wisconsin Glaciation..." If the terraces formed at the end of the Sangamon Interglacial Age they have been exposed to approximately 65,000 years of subaerial weathering and erosion. The terraces.... appear to be much too well preserved to have withstood erosion and solution for that length of time. A more recent formation would seem indicated. If the possibility of Wisconsin interstadials is neglected the time of formation would be within the last 10 to 12 thousand years, Holocene period. Ashmore (1973) believes that the tilting hypothesis explains the northwestern reef and the submerged rim, but fails to explain many of the other atoll features. He favors a sea-level-change, which assumes that lowered sea levels during some glacial period allowed portions of the original atoll to be removed. He presents evidence that this hypothesis accounts for the -60 foot terrace and -30 foot level with its sinkholes. He does acknowledge the possibility of a combination of the tilting and sea-level-change hypothesis to explain the present day configuration of the atoll.

(3) The surface of Johnston Island is mainly coral sand, with an admixture of fine coral fragments. The original shoreline of the island had several outcrops of massive beach rock. The beach rock occurred especially on the northwestern tip of the island and on the south central shore. These outcrops have been covered over by the fill which was used to expand the area of the island. However, beach rock of the same type may still be seen in some places around the shore of the island. The beach rock is composed of coral sand and coral gravel loosely cemented together by calcium carbonate. Originally it was exposed in the form of smooth platforms, but with age, its surface has been eroded biochemically to form a series of irregular solution basins and smooth water-level terraces (Thorp, 1960). Records from the Corps of Engineers have been kept of 56 borings, with a maximum depth of 36 feet, that were made for the heavy construction foundations of 12 buildings on the central and northeastern parts of Johnston Island. In addition, drill logs were kept of six deep wells which ranged from 86 to 191 feet below mean sea level. In general, a fairly thin layer (or layers) of beach rock was found a few feet below the surface under a pure sand layer. Below this sandstone (or beach rock layer) was another area of pure sand alternating with sand mixed with coral fragments. These layers ranged from 10 to 50 feet in thickness and were usually followed by the solid coral bedrock of the island which extends below drilling depths. In view of the results obtained from deep drilling on other low islands in the Pacific, it seems probable to assume that the noncalcareous bedrock may be encountered as deep as 700 to 1,000 feet (Thorp, 1960). Under parts of the island there is apparently a narrow second layer of beach rock, according to the recordings in the drill logs. In 18 of the holes, the driller hit beach rock which was between 1 and 2½ feet above mean low water, and which extended to an average of 0.7 foot below mean low water. This strata apparently correlated with the beach rock still exposed on Sand Island. It is thought that the upper layer may be correlated with the widespread occurrence of beach rock in the wave-washed zone between high and low tides on most of the low coral islands of the Pacific. The origin of the deeper layer is more complex, but samples of beach rock were collected eight feet below sea level along the bases of the fragmented reef which extends from Johnston Island to Sand Island. Emery (1956) hypothesized that the unusual straightness of the patch reefs is the result of the various types of coralline algae atop the outcropping edges of this recently submerged beach rock. The deeper parts of the wells show alternating sand, loose coral, and sand and coral with no possibility of correlation from well to well. There were several small inclusions of mud in the wells from unknown origns.

(4) There is no noncalcareous rock found on Johnston Island other than that brought by man, with the exception of pumice stone found on the beaches and one erratic piece of fine-grained rhyolite about 10 inches in diameter which was found *in situ* in the beach rock on Sand Island. The pumice which floated onto the beaches, especially in 1953, was thought to have come from the volcanic eruptions at San Benedicto Island near Mexico. Emery (1955) stated that this was probably the result of driftwood transport, since large individual pieces such as this one could be more readily carried by floating trees than by other plants or animals, while transport by icebergs or kelp is ruled out by the tropical location. The coral bedrock weathers down to a fairly coarse-grained white sand. There is no solid soil cover on Johnston Island, nor was any reported prior to the alterations of the environment by man. Since, as noted above, bedrock does not crop out on the surface of the two islets, it is necessary to build foundations to extra depths for any buildings which have a heavy bearing load.

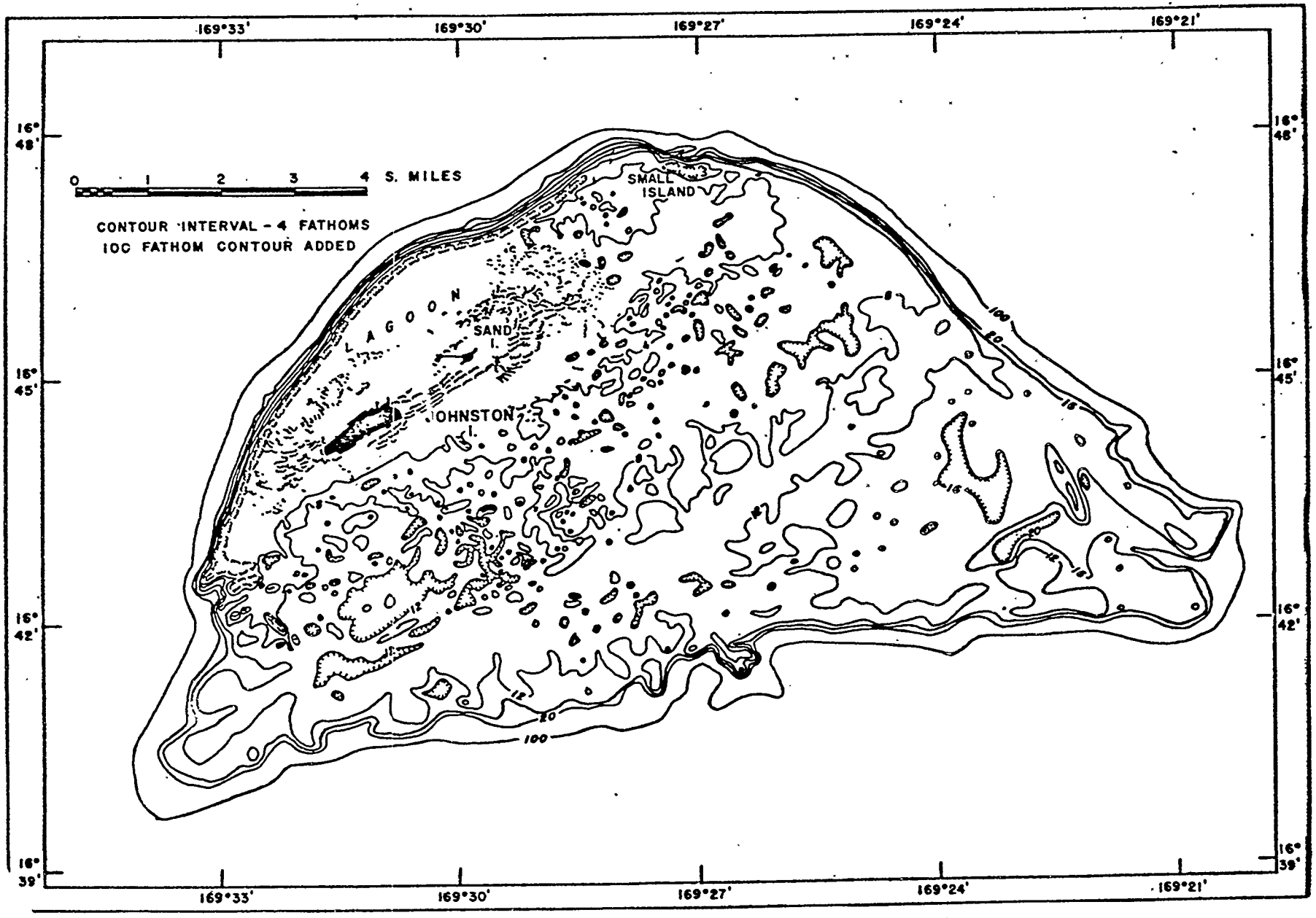
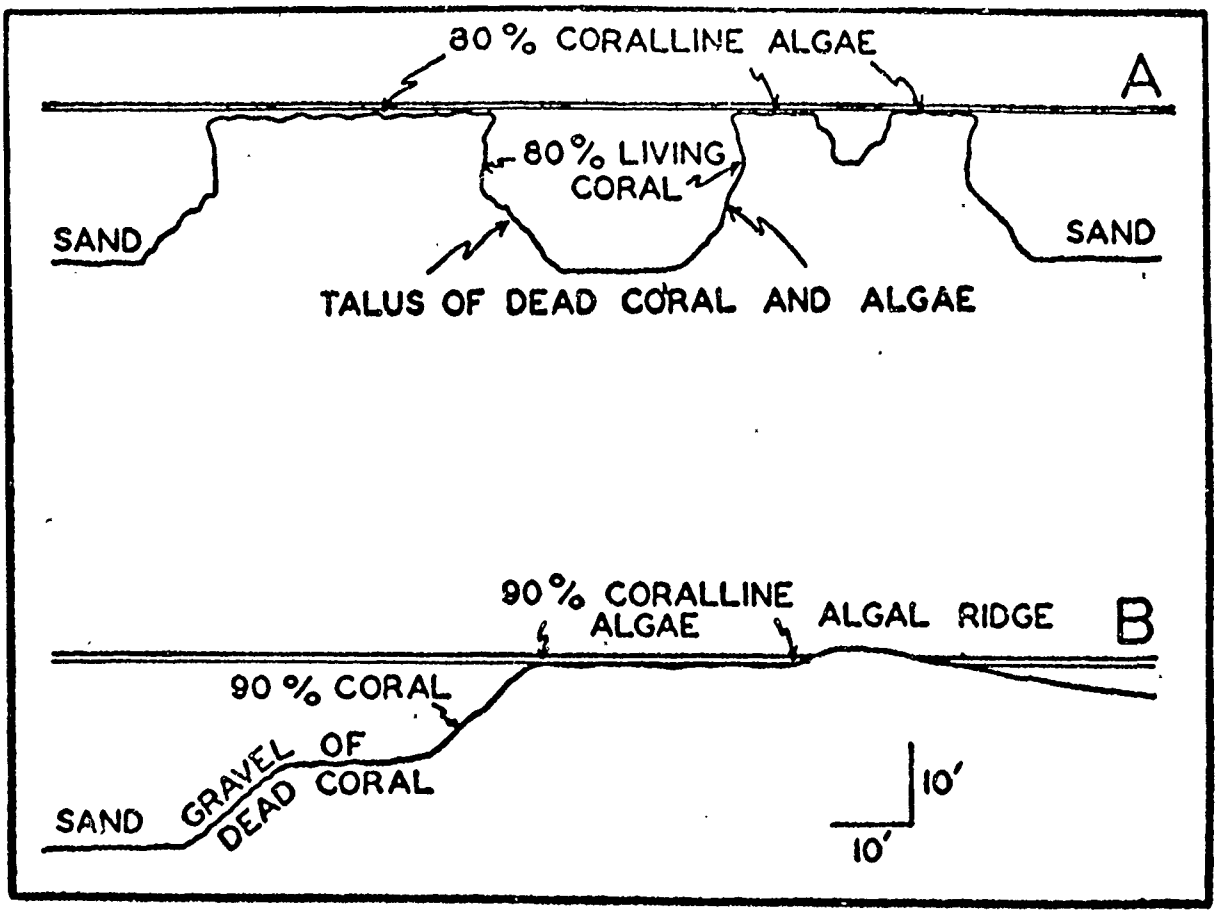



FIGURE H-6. JOHNSTON ATOLL SHOWING REEFS AND DEPTHS (AFTER EMERY, 1955)

The 56 borings for foundation piers (mentioned previously) averaged 10 feet in depth, of which the extreme depth was 36 feet. Another difficulty encountered in heavy construction work results from the porosity and toughness of the coral, which makes it hard to remove in large quantities either by blasting or bulldozing.

(5) The original shore lines of Johnston and Sand Islands were about evenly divided between sandy beaches and exposed coral formations which were usually the "beach rock." The beaches were between 50 feet and 100 feet wide generally, and they had a sand or beach rock cover. But they have all been modified, except for parts of Sand Island, with the result that the present shore lines tend to end abruptly in the water with little or no beach remaining (Thorp,1960). It is estimated that the total area of these reefs which are exposed at low tide is about two square miles, but because of the numerous small patch reefs no exact measurements have ever been made. If it were necessary to compute their area, an air photo taken at low tide could provide a fairly accurate base from which to compute the total expanse of reef exposed. Probably more than one-half of the total area of reef which lies above sea level at slack water is in the main northwestern reef, which forms an arc almost 11 miles long if one includes the break of about one mile near the northeastern end of the reef and its northeastern outlier which continues for another half mile. This latter section of reef is known locally as Small Island, although this name does not appear on the official charts.

(6) The depth in the shallow "lagoon" area to the south of the main reef ranges from 3 to 40 feet. It is in this area that the elongated and sub-circular patch reefs attain their greatest concentration. To the south of Johnston Island these patch reefs serve to define the southeastern boundaries of the lagoon area (Thorp, 1960). Profiles of the two reef types are shown in Figure H-7. The main outer reef has a gentle slope to the seaward (at least for the first few hundred feet) cut by narrow surge channels. An algal ridge forms the outer edge of the reef about one to three feet above mean sea level. However, this area is periodically inundated by waves or high tides especially during storms. On the lagoon side, there is a reef flat from 100 to 500 feet wide composed chiefly of coralline algae and small corals of various species. This reef flat has numerous potholes and narrow channels left behind as the reef migrated seaward. The lagoon edge of the reef is a fairly steep slope consisting of mainly living coral to a depth of about 15 feet. Below this, dead coral and fragments of dead coral ("coral gravel") form a more gentle slope to the fairly flat sand bottom which reaches its greatest development at from 20 to 25 feet below the surface. This flat expanse of bottom is broken repeatedly by coral heads, a few yards in diameter, which rise just as abruptly but may be several hundred feet long. Characteristically, these patch reefs are topped by an irregular, overhanging surface of coralline algae just below the low-tide level. On the sides and locally are irregular masses of branching coral, mostly composed of different species of Acropora. The lower slopes are mainly a talus of loose pieces of dark dead coral and coralline algae which extends to the sandy bottom at about a 45 angle. There were no natural bays or harbors at Johnston Atoll, since none of the entrances into the lagoon area originally had a safe depth of more than three or four feet. There were no features on the interior of either Johnston Island or Sand Island.




A.—Isolated patch reef about 1 mile northwest of Johnston Island.
B.—Outer reef at Small Island.

FIGURE H-7. PROFILES OF TWO REEF TYPES (EMERY, 1955)

(7) Topography appears to be no particular problem for the installation of any type of equipment which does not require a large area. At the present time most of the surface of Johnston Island is completely utilized by existing facilities. It is necessary to spend considerable time in the construction of foundations because of the shift from sand to bedrock, and any underground installations required special water-proofing treatment because of the high water table and the permeability of the porous coral bedrock.

d. Hydrography

(1) There are no natural permanent freshwater bodies on Johnston Atoll. This lack of surface water is primarily due to the coarse texture and extreme permeability of the coral sand and rubble which make up the first few feet of the regolith, as well as to the porous nature of the coral bedrock. Other factors contributing to the absence of any fresh water on Johnston Island are the small size of the land area, the geographic location and the narrowness of the two islets as compared to the total length (Thorp, 1960).

(2) The lagoon inside the main atoll is about 14,000 yards long at its axis, which runs southwest from Small Island through the centre of both Sand and Johnston Islands. At its widest point, just east of Sand Island, the lagoon extends about 3,500 yards from northwest to southeast. West of Johnston Island the lagoon narrows to a few hundred yards in width before coming almost to a point at the extreme southwestern corner of the atoll. East of Sand Island, as mentioned above, the boundaries of the lagoon are indistinct, as the main reef breaks down into an intricate series of linear reefs and numerous isolated patch reefs, which are usually awash at high water. The total area of the lagoon within the reef is approximately 13 square statute miles. An exact measurement is impossible unless one uses a depth curve for the boundary of the lagoon because of the difficulty of measuring the exact line of demarcation between the lagoon proper and the extensive coral flats which form the southeastern part of the atoll (Thorp, 1960) (Navy Hydro a, 1959) (Navy Hydro b, 1959). The natural depths within the lagoon (except for the dredged portions) vary from a few inches to about 40 feet, because of the presence of coral heads and patch reefs. The greatest area lies between 15 and 25 feet underwater at mean sea level. At the extreme northeastern corner of the lagoon, south of the opening between the main reef and Small Island, there is an area of deeper water in which average depths of more than 40 feet have been reported, but the bottom still has many irregularities and numerous coral heads which almost broach the surface. Artificial dredging in the lagoon has left the seaplane landing area with a depth of eight feet cleared of obstructions, while the harbor and the entrance channel were originally dredged to 23 feet and have been swept to 14-1/2 feet (Thorp, 1960).

e. Tides and Currents

(1) The tidal range at Johnston Island, in common with other mid-Pacific islands, is relatively small, and the effects of the tides upon the atoll are correspondingly minor. The absolute tidal range during the year (the difference between the lowest and highest tides of the year) is only 3.4 feet. The lowest low is minus 0.5 foot in June, while the highest high is plus 2.9 feet, also in June. The mean spring high tides are plus 2.2 feet while the mean spring low tides are minus 0.2 foot. The mean neap tides are plus 1.6 feet, while the mean neap low tides are plus 0.4 foot (Thorp, 1960) (Navy Hydro, 1959) (Wennekens, 1969). The time of the tidal crests and troughs is only slightly later than those of Honolulu, the nearest point for which a full tide table is available. High tides are 29 minutes later at Johnston Island than at Honolulu, while the low tides are 23 minutes later. The high-water interval from full tide to the change of tide is three hours and 15 minutes. Inside the lagoon, the tides have a range only slightly less than in the open waters outside the lagoon, since the structure of the reefs permit water to flow through them as well as over them. The permeability of the coral bedrock is shown by the fact that the water level in all six of the deep wells on Johnston Island rises and falls with the tides (Thorp, 1960) (Wennekens, 1969).

(2) Ocean currents in the vicinity of Johnston Island run from the east to the west at a speed of about 1/2 knot or from 10 to 15 miles per day. Johnston Island is approximately in the center of the North Equatorial Current which extends in breadth several hundred miles both to the north and to the south of the island and has a fairly constant velocity. The tidal currents at Johnston Island, within the lagoon, show a variation. The normal current flows with average velocities of 1/2 knot to the northwest. However, usually for a short time at high tide the current flows at one knot to the southeast. According to Emery (1955) the current pattern influences the distribution of sand to the south of the lagoon: "These patch reefs block the current, causing the sand to be deposited against the currentward side and leaving a depression where the water speeds through the gaps between the patch reefs. Examination of several such areas showed depths in the gaps to be about half a fathom deeper and floored with coarser sediment than that of the adjoining areas."

(3) The underwater platform on which Johnston Island is located is similar to those connected with many Pacific atolls. Like most other low islands in the Pacific the main outer reef has a typical cross section, which includes surge channels, an algal ridge, and a reef flat, with coral heads rising abruptly in the deeper waters to the south and east of the main reefs. Between 16 and 100 fathoms the outer slope is quite steep, usually less than one-half mile in linear distance, with an average slope of 19°. The platform on which Johnston Atoll rests stops fairly abruptly at about the 16 fathom line at most points around the circumference of the atoll as the bottom begins to slope steeply down (Thorp, 1960) (Navy Hydro b, 1959) (Wennekens, 1969).

(4) The shallow lagoon area and its bordering reefs together form roughly the northwester quarter of the triangular-shaped platform on which the atoll rests. At the deeper eastern end of the platform the submerged contours suggest the outline of earlier peripheral reefs. It has been suggested by Emery (1955) that some early reefs may have been submerged as a result of the tilting of the whole base structure of the atoll to the southeast. Since the reef-forming corals grow slowly, and since they will not grow at all in water

below approximately 25 fathoms, a fairly rapid tilting might "drown" the coral ridges faster than they could build up. The main difference between Johnston Atoll and other Pacific islands is the lack of continuous reef around the atoll. The main outer reef extends around less than one-fourth of the circumference of the platform. In addition, there is an extensive zone of shallows to the south of the main reef which is also an unusual feature. As noted previously, it is this zone of shallows which contains most of the patch reefs, Johnston and Sand Islands and the two islets which make up the land area of Johnston Atoll. This suggested tilting of the whole atoll would account for this area of shallows to the northwest, since this area of the atoll would be raised as the opposite side, and most of the main reef sank. This theory has been moderately received, with the result that Johnston is considered one of the "raised" atolls, even though it does not have the typical outward features of one (cliffed beaches, dry center depression, comparatively good water supply, etc.) (Thorp, 1960) (Ashmore, 1973). An alternate theory, which would account for the unusual reef formation at Johnston Atoll is the early removal of the windward reef by wave erosion, is not generally accepted. According to this theory the original outer ridge to the east was the most exposed to waves and hence eroded away, probably at some time when a climatic change or a lowering in sea level had temporarily halted the growth of the reef. The main objection to this theory is the fact that, today, the most vigorous growth of a reef is to be found on the side of an atoll because the agitation of the water provides a greater supply of nutrients for the coral-buildings organisms. It would seem that a temporary interruption in reef building would be compensated for, once conditions reverted to normal (Ashmore, 1973). It has been hypothesized that Johnston Atoll may be structurally related to the Line Islands (Christmas Island, Palmyra Island, Jarvis Island, etc.). Although they are mainly raised islands also, this theory has yet to receive any confirmation (Emery, 1956).

(5) The waters around Johnston Island have not been completely surveyed, but the deepest point on H.O. Chart 5356 (Navy Hydro a, 1959) is 1,051 fathoms, which is located about 14 nautical miles southeast of the center of Johnston Island and about five miles south of the 100-fathom line. This indicates a descent of one foot in every 4-1/2 feet horizontally.

(6) The Japanese word "tsunami" is the term used to describe long gravity waves in the central and western Pacific Ocean areas. These waves are more commonly known as tidal or seismic waves and are caused by submarine earthquakes, landslides and plutonic activity and spread annularly from an epicenter. They are "shallow water waves," i.e., a wave in which the length of the wave is long when compared to the water depth. The velocity of the Pacific Tsunami ranges between 375 and 490 nautical miles per hour. The Tsunami Research Center of ESSA and the Institute of Geophysics of the University of Hawaii maintain historical records of tsunami events in the Pacific. The largest amplitude wave recorded appears to have been about 3.4 feet as a result of the Chilean earthquake generated tsunami on May 23-24, 1960. The second highest, slightly over three feet, followed the Alaskan earthquake of March 28-29, 1964. Past records reveal that the crest of a tsunami at Johnston Atoll resembles a progressive rise in sea level with the maximum depth being reached in about 25 to 30 minutes. The period of tsunami waves at Johnston Atoll is between 45 and 60 minutes. "Historical records indicate that, so far, no large breaking waves or bases have been experienced at the island from a tsunami."

The steep off-shore slope does not enhance incoming tsunami waves and the island is partially protected by an awash fringing reef along the western and northern periphery and by numerous coral patches scattered along the southern and eastern sectors of the island platform. "Historical records and the analysis of certain unusual environmental factors indicate that the effects of a tsunami at Johnston Island should be minimal, consisting of transient rise in water levels, occasional breakers to higher than normal levels, and local flooding of low areas. Backup of water in storm sewers and drainage ditches can be expected, and some erosion of the fill material can take place when the water drains out..." (Wennekens, 1969). Past history indicates that no large breaking wave is likely to occur on the island.

f. Climatology

(1) Climate

(a) The climate of Johnston Atoll is marine and tropical in nature. Weather records are available from about 1931; however, standardized data are available only since 1952. These latter records show a climate with little variation in temperature and wind speed, but great variability in rainfall. Weather data are from Joint Task Force Seven (1959), U.S. Dept of Commerce (1972), and Shelton (ms. in prep), USAF Environmental Technical Applications Center Report 7057. Because Johnston Atoll has a maximum elevation of less than 10 feet, a land area of about one square mile, and is surrounded by shallow waters in all directions, there is little difference in climate conditions from one part of the atoll to another (Amerson, 1973).

(b) Johnston Island is under the influence of tradewind weather 98% of the time. The normal weather during this period is scattered to broken Cumulus bases normally 2000 ft, tops 7000 to 9000 ft. Scattered showers in the area will occasionally drift over the island causing light precipitation to fall. This can be expected any time during the day or night as there is no apparent diurnal variation in the showers. Occasionally cloud tops will build to 11,000 feet, seldom exceeding 15,000 feet due to easterly perturbations in the area. Scattered Altostratus are in the area during this time and an increased amount of shower activity occurs until this perturbation passes. Due to the size of the island, which is about two miles long and approximately one-half mile wide, convective type clouds due to heating do not build. Even if they were influenced by the warm land they would be far off shore before they reached shower producing proportions.

(c) Severe storms in the area are limited to thunderstorms, tropical storms and hurricanes. Thunderstorms occur infrequently in the area. The mean number of days during which thunderstorms occurred over a 26 year interval (1945-1970) are listed in Table H-3 . The + indicates less than one-half day.

(2) Temperature: The mean annual temperature is 79.3°F. Temperatures are slightly higher from June through November (80°-80°F) than from December through May (77°-79°F) (Fig H-8). Daily ranges are normally only 7° or 8°F, and the daily maximum and minimum temperatures vary only a few

TABLE H-3

MEAN NUMBER OF DAYS OF THUNDERSTORMS
JOHNSTON ISLAND

| MONTH | JOHNSTON ISLAND | MONTH | JOHNSTON ISLAND |
|---|---|---|---|
| JAN | + | JUL | + |
| FEB. | + | AUG | + |
| MAR | + | SEP | + |
| APR | + | OCT | + |
| MAY | + | NOV | + |
| JUN | + | DEC | 1 |
| | | YEAR | 1 |

Note: Plus indicates less than one-half day.
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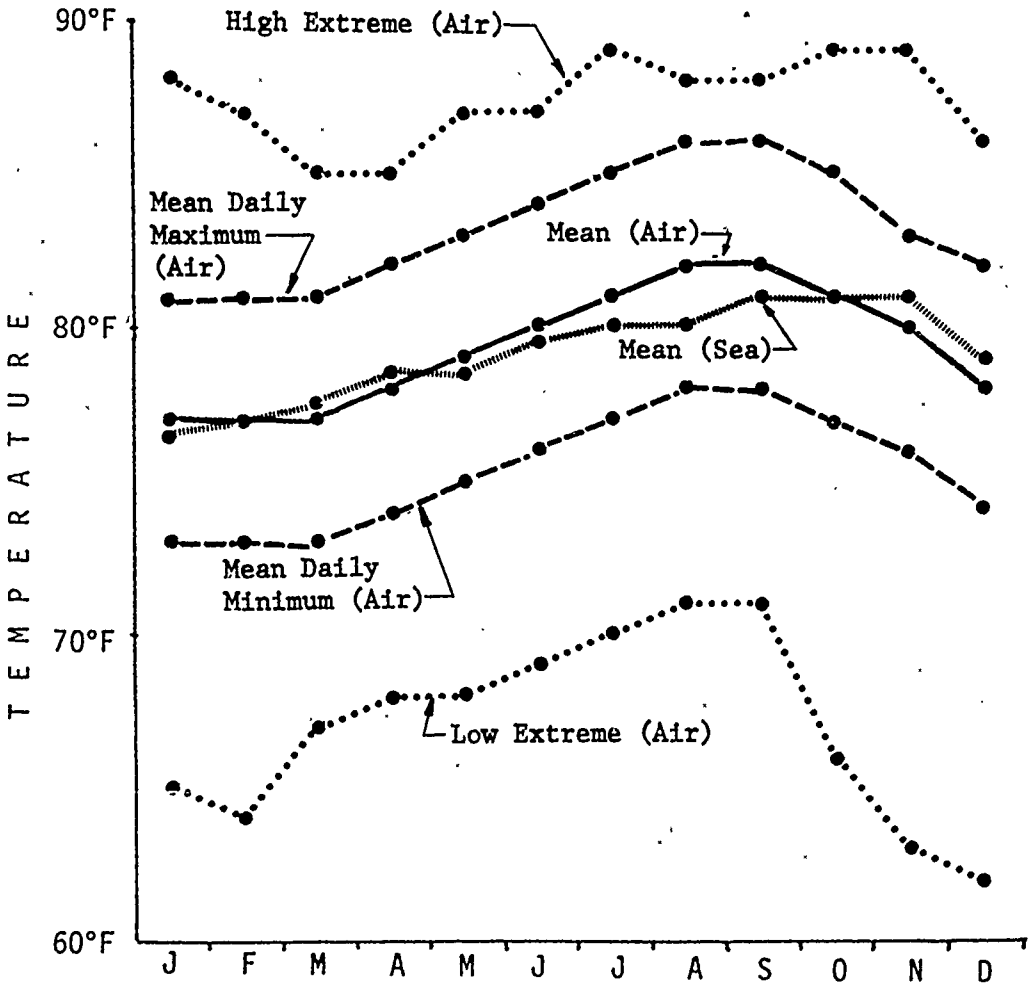



FIGURE H-8. MEAN MONTHLY AIR AND SEA TEMPERATURES, JOHNSTON ATOLL, ADAPTED FROM SECKEL (1962) and U.S. DEPARTMENT OF COMMERCE (1972).

degrees throughout the year. The extremes range from a low of 62°F (December 1964) to a high of 89°F (October 1968, July and November 1969). This is lower than the daily range frequently encountered in continental areas. This constancy of temperature results from the fact that air masses passing over the atoll having been modified by close contact with the ocean for thousands of miles. Thus the air temperature is near that of the water temperature. Sea surface temperatures vary little from day to day and change only slowly with the seasons (Amerson, 1973).

(3) Precipitation: Precipitation of 0.01 inch or more occurs 162 mean number of days each year. The mean annual rainfall is 26.11 inches, but year-to-year variation is great. For example, the total for 1968 was 42.27 - the wettest year on record - while 1969 was only 17.11, next to the lowest yearly total recorded (12.86 inches in 1953). There is little monthly mean rainfall variation (Fig H-9); rainfall averages 2.75 inches monthly from December through March and 1.87 inches monthly from April through November. Year-to-year monthly variation is, however, great (Amerson, 1973).

(4) Relative Humidity: The annual mean relative humidity is 75 percent, being highest at 0100 hours (78 percent) and lowest at 1300 hours (69 percent). Monthly mean relative humidity values vary little throughout the year, but January and February values are definitely lower (Amerson, 1973).

(5) Surface Winds: The mean annual wind speed is 15.1 miles per hour with very little variation throughout the year (Fig H-10) (monthly means = 13.6 to 16.0 mph). Monthly extremes (excluding 1972) range from 35 mph in July to a high of 49 mph in March and November (mean monthly extremes = 43 mph). On 19 August 1972, however, the wind speed hit an all time high of 104 mph when hurricane Celeste, which spawned off the southern coast of Mexico some 3,000 nautical miles to the east nearly two weeks earlier, passed only about 25 miles to the northeast of Johnston Atoll. Damage to the island was minor. Observations from weather satellites indicate that tropical storms in the Johnston Atoll area, although infrequent, may not be as unusual as was once supposed. Surface trade winds are dominant at all times of the year (Fig H-11). Winds from between NE and E are experienced 62 percent or more of the time in every month, with the annual average being 85 percent, see Fig H-10 and H-11, (Amerson, 1973) (Bauer, 1973). Basically, two seasons can be distinguished. The first extends from December through March when the wind is from trade directions (NE through E) only 20 percent, or less, of the time. During this period, light, variable winds and westerlies occur, occasionally, as organized disturbances. These disturbances bring in cooler, less humid, less stable air, which results in more cumulus buildup and heavier, more frequent precipitation. From April through November, winds are from trade directions 80 percent, or more of the time (Amerson, 1973).

(6) Trophospheric Circulation: The trophospheric winds are readily divided into two distinct currents -- the Trade Winds and the Upper Westerlies -- by the lower zero isopleth of zonal components. The Trades are largely zonal and quite persistent all months of the year and are at a maximum in depth, speed, and steadiness during the summer. The Upper Westerlies occupy the remainder of the trophosphere and are separated from the stratospheric easterlies by the second zero isopleth at approximately 55-60,000 feet. They are also quite persistent during all months of the year, but reach a

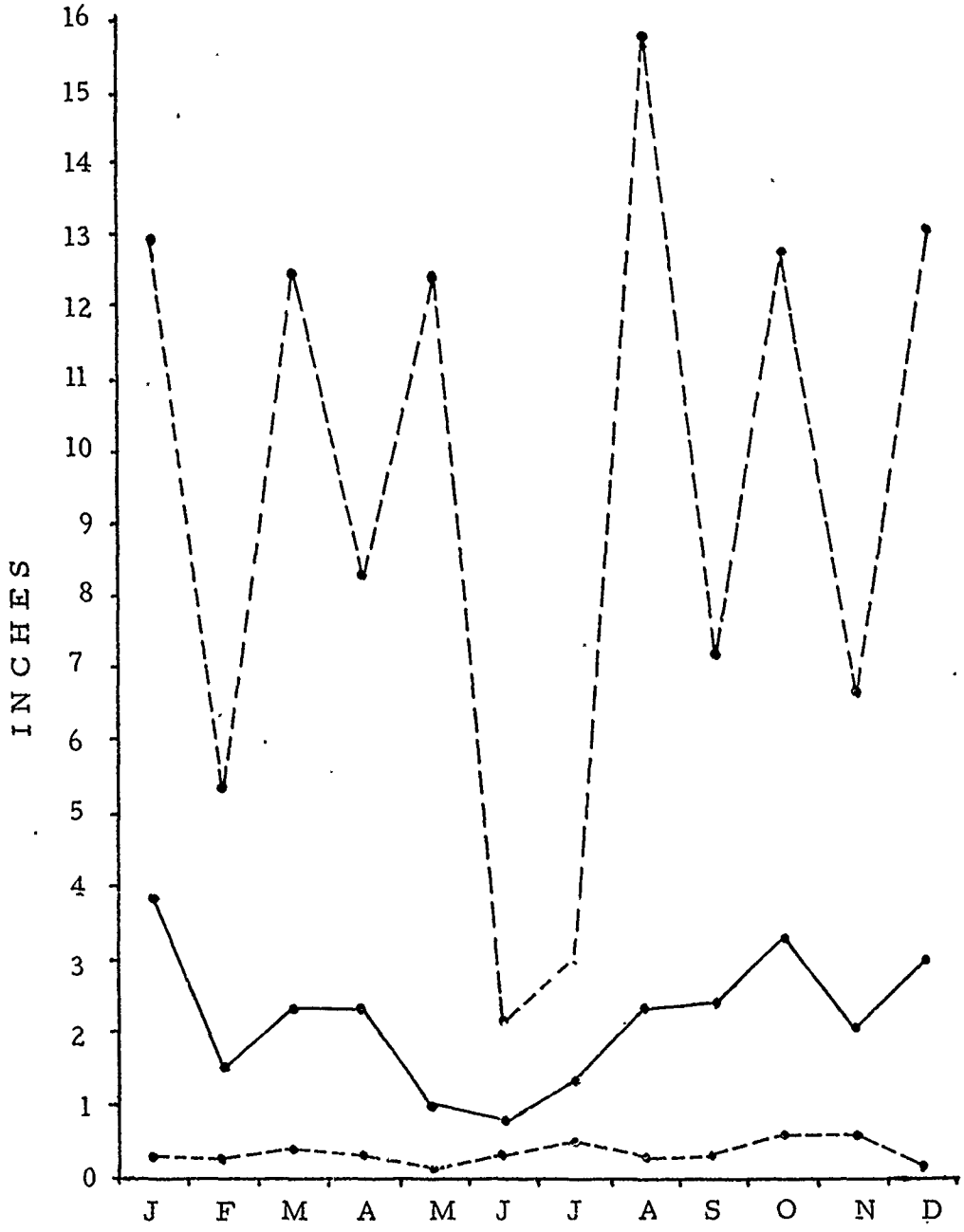



Figure H-9 Mean monthly precipitation, Johnston Atoll, 1931 - 1972; means (solid line), extremes (dashes). Adapted from U. S. Department of Commerce (1972).

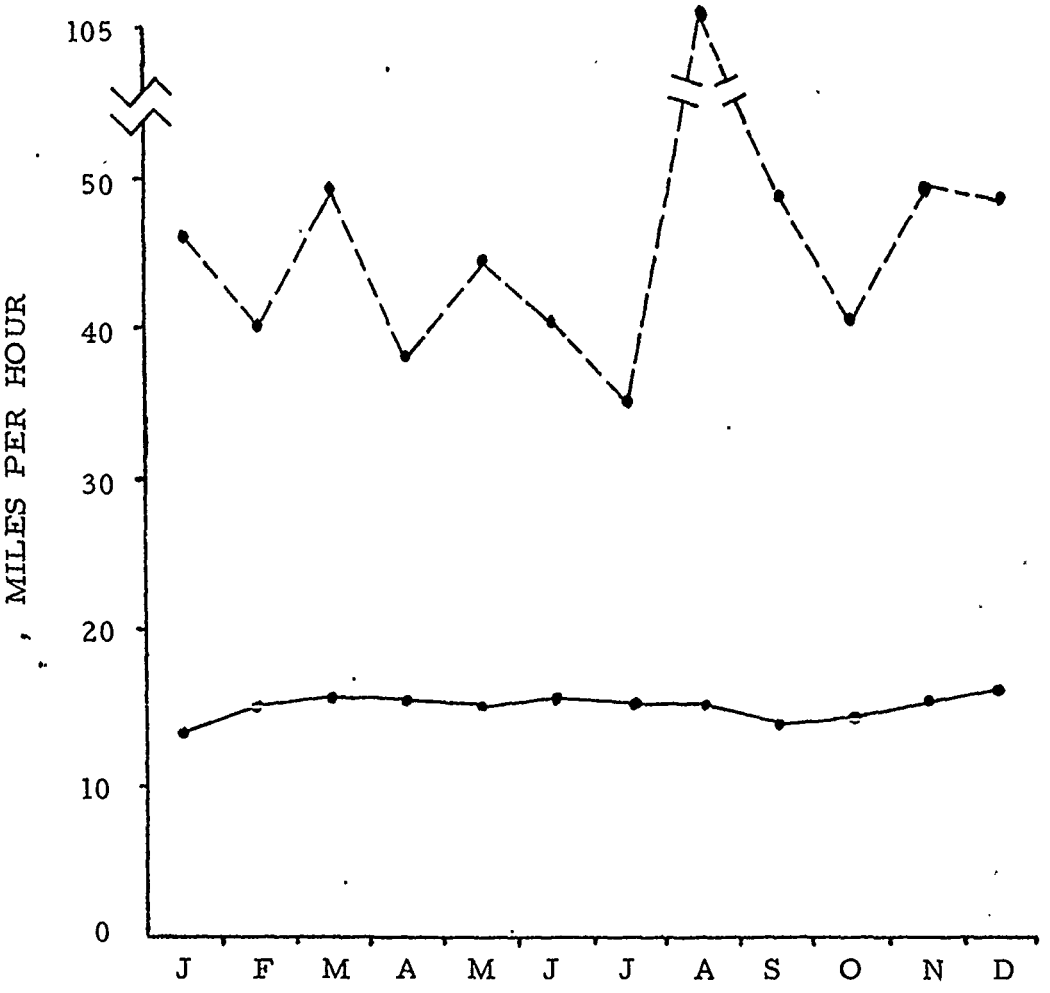



Figure H-10 Mean monthly wind speed, Johnston Atoll, 1931 - 1972; means (solid line) upper extremes (dashes). Adapted from U. S. Department of Commerce (1972).

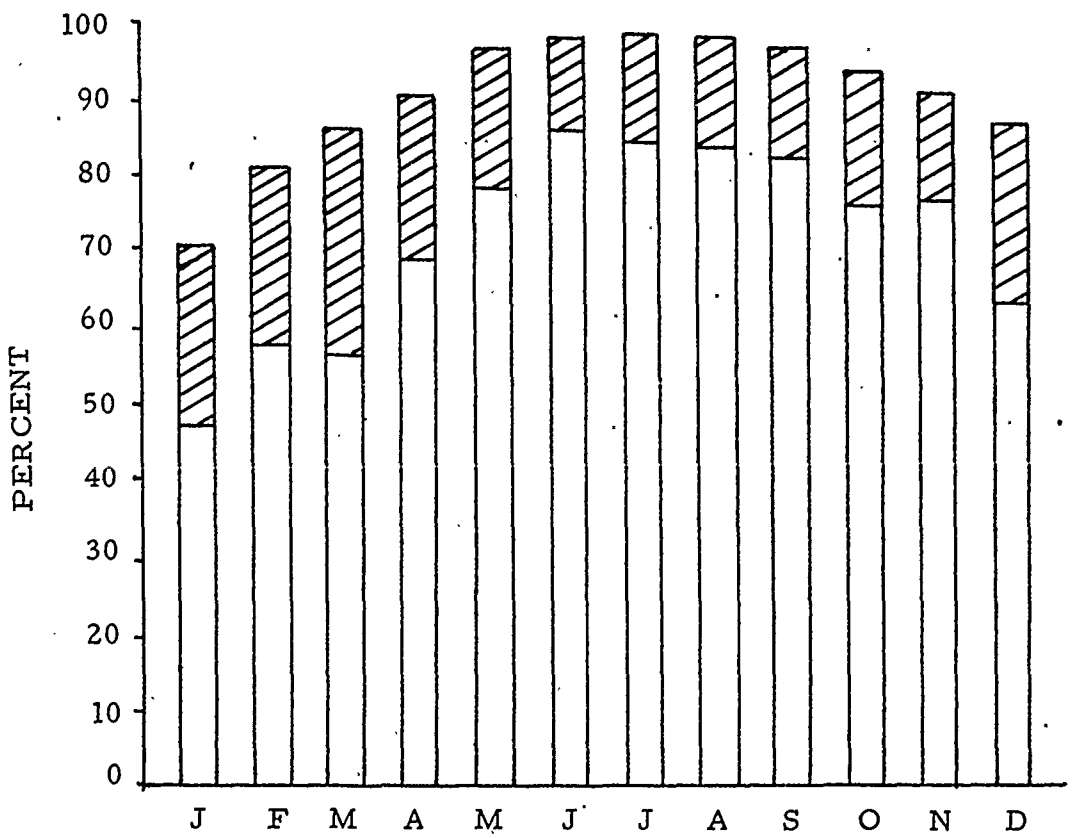



Figure H-11 Percent frequency of wind from E and ENE (open bar) and ESE and NE (striped bar), Johnston Atoll. (AMERSON, 1973)

definite maximum in speed, steadiness, and depth during March and April. The November winds are much lighter in general and westerlies and the easterlies tend to cancel each other out leaving only a small south component in the mean, while in the winter there is a fairly strong northerly component reaching a maximum in February (Amerson, 1973).

(7) Stratospheric Circulation: The mean stratospheric circulation over Johnston Atoll is dominated by the Krakatoa Easterlies, but surprisingly shows greater seasonal variability than the trophospheric circulation. The winter is characterized by relatively light winds generally with east predominating in the lower stratosphere, west in the mid-regions, and east again at levels above 110,000 feet. A fairly rapid transition occurs in spring to strong steady easterlies reaching a maximum in July and August. There is a sharp transition in the fall back to light and variable winds (Amerson, 1973).

(8) Sky Cover: Mean monthly sky cover, sunrise to sunset only, averages 6.0 on a scale of 0 to 10. There is little variation throughout the year. During an average year (again, sunrise to sunset) there are 75 mean clear days, 172 mean partly cloudy days, and 118 mean days (Amerson, 1973).

(9) Historical Data: Table H-4 shows a climatic brief for the period 1945-1970; Table H-5 shows the frequency of occurrence of different stability classes from 1949 to 1958, 86,190 observations; Table H-6 shows the frequency of stability vs wind direction for the period of Table H-5

g. Surrounding Land and Water Use and Ownership:

NOTE: THE FOLLOWING INFORMATION WAS PROVIDED LARGELY BY THE LOGISTICS PLANNING GROUP, HOLMES AND NARVER, INC., LAS VEGAS, NEVADA 89114.

(1) There are no cities or incorporated communities on Johnston Atoll. There are approximately 600 personnel currently living on the atoll. These consist for the most part of employees of Holmes and Narver, Inc., Pacific Test Division, P.O. Box 9186, Honolulu, Hawaii, 96820. This firm, operating under contract AT(29-2)-20 with the AEC, provides for general construction, maintenance and general operations on and around the atoll. The atoll is under the control of the Field Command, DNA and is currently under the command control of the USAF. There are a limited number of Holmes and Narver, Inc., subcontractor personnel. The United States AEC; U.S. Weather Bureau; 10th Aerospace Defense Squadron, Det 1; 18th Surveillance Squadron, Det 2; 2675th Chemical Company, USA; 2194th Communications Squadron; and USAF Logistics Command (SMAMA) maintain small detachments. At times a very limited number of personnel from other organizations such as the Smithsonian Institution, Sandia Corporation, USAF Space and Missile Organization, The University of Hawaii, etc., may be present on the atoll.

(2) A bird sanctuary still exists on Sand Island under the provisions of Executive Order No. 4467, dated July 29, 1926. (For detailed information regarding the present day bird population see Appendix A)

TABLE H-4

CLIMATIC BRIEF-JOHNSTON ISLAND

| Month | Temperature (°F) | | | | Precip (IN) | | Wind (KT) | | | Mean | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Extreme Maximum | Mean Daily Maximum | Mean Daily Minimum | Extreme Minimum | Mean Total | Maximum in 24 hours | Prevailing Direction | Mean Speed | Extreme (Peak Gust) Speed | Relative Humidity (%) 0400 | Relative Humidity (%) 1300 | Dew Point (°F) | Vapor Pressure (in Hg) | Clouds (Tenths) |
| JAN | 88 | 81 | 73 | 63 | 3.9 | 9.8 | ENE | 14 | 55 | 79 | 71 | 68 | .69 | 5 |
| FEB | 87 | 81 | 73 | 64 | 1.5 | 4.2 | ENE | 14 | 46 | 79 | 70 | 68 | .69 | 5 |
| MAR | 86 | 81 | 73 | 67 | 2.3 | 3.8 | ENE | 15 | 54 | 79 | 71 | 68 | .69 | 5 |
| APR | 87 | 82 | 74 | 67 | 2.3 | 3.9 | ENE | 15 | 46 | 81 | 72 | 70 | .74 | 6 |
| MAY | 87 | 83 | 75 | 68 | 1.0 | 4.6 | ENE | 14 | 47 | 81 | 72 | 71 | .76 | 6 |
| JUN | 88 | 84 | 76 | 69 | 0.8 | 1.1 | ENE | 15 | 46 | 80 | 70 | 71 | .76 | 5 |
| JUL | 89 | 85 | 77 | 70 | 1.3 | 2.0 | ENE | 14 | 43 | 80 | 70 | 72 | .79 | 5 |
| AUG | 88 | 86 | 78 | 70 | 2.3 | 8.0 | ENE | 14 | 46 | 80 | 70 | 73 | .82 | 6 |
| SEP | 88 | 86 | 78 | 71 | 2.4 | 4.0 | ENE | 14 | 48 | 79 | 70 | 73 | .82 | 6 |
| OCT | 89 | 85 | 77 | 66 | 3.3 | 9.5 | ENE | 14 | 43 | 80 | 71 | 73 | .82 | 6 |
| NOV | 89 | 83 | 76 | 63 | 2.1 | 2.8 | ENE | 15 | 48 | 80 | 72 | 71 | .76 | 5 |
| DEC | 88 | 82 | 74 | 62 | 3.0 | 9.2 | ENE | 15 | 58 | 79 | 72 | 70 | .74 | 5 |
| ANN | 89 | 83 | 75 | 62 | 26.2 | 9.8 | ENE | 14 | 58 | 80 | 71 | 71 | .76 | 5 |

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TABLE H-5

FREQUENCY OF OCCURRENCE - ATMOSPHERIC STABILITY CLASSES-
JOHNSTON ISLAND

| Stability | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| JAN | .0033 | .0254 | .0748 | .7272 | .1142 | .0551 |
| FEB | .0029 | .0253 | .0775 | .7656 | .0907 | .0380 |
| MAR | .0026 | .0257 | .1121 | .7703 | .0692 | .0200 |
| APR | .0023 | .0195 | .1097 | .8009 | .0527 | .0150 |
| MAY | .0019 | .0137 | .1258 | .8095 | .0399 | .0093 |
| JUN | .0014 | .0157 | .1470 | .7596 | .0611 | .0150 |
| JUL | .0033 | .0174 | .1423 | .7653 | .0624 | .0093 |
| AUG | .0017 | .0109 | .1481 | .7719 | .0611 | .0064 |
| SEP | .0024 | .0205 | .1352 | .7306 | .0944 | .0168 |
| OCT | .0044 | .0195 | .1017 | .7688 | .0857 | .0199 |
| NOV | .0000 | .0038 | .0370 | .8962 | .0455 | .0175 |
| DEC | .0021 | .0113 | .0477 | .8377 | .0842 | .0170 |
| ANN | .0024 | .0175 | .1062 | .7821 | .0718 | .0199 |
| ANNCALM | .0012 | .0009 | .0004 | .0002 | .0000 | .0048 |

A - Extremely Unstable
B - Moderately Unstable
C - Slightly Unstable
D - Neutral
E - Slightly Stable
F - Moderately Stable

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TABLE H-6

FREQUENCY OF OCCURRENCE
WIND DIRECTION
JOHNSTON ISLAND

| | | | |
|---|---|---|---|
| N | .0097 | S | .0038 |
| NNE | .0247 | SSW | .0030 |
| NE | .1244 | SW | .0030 |
| ENE | .3665 | WSW | .0024 |
| E | .3625 | W | .0031 |
| ESE | .0661 | WNW | .0019 |
| SE | .0159 | NW | .0032 |
| SSE | .0066 | NNW | .0033 |

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(3) There is no commercial fishing in the immediate area of Johnston Atoll. Recreational fishing is extensive and is, in fact, one of the principal forms of recreation. A wide variety of species are present within the lagoon but extreme caution is advisable since some are hazardous on physical contact (sharks, barracuda, moray eel, turkey fish, stone fish, etc.) and others are very poisonous if ingested. Other forms of recreation include scuba diving, swimming, boating, basketball, bowling, golf, tennis, softball, pool, movies, library, hobby shops, clubs and gymnasium.

h. Facilities

(1) Transportation

(a) Sea Transport: Johnston Atoll is under the administrative control of the DoD, DNA and is a Naval Defense Sea Area and Airspace Reservation. All private vessels must apply for entrance prior to their arrival except in emergencies. Unauthorized landing or the violation of other regulations governing admission to the island are grounds for Federal prosecution. Johnston Atoll is accessible from all directions, although it is distant from all supply ports except Honolulu, Hawaii. This presents a problem since any supplies not brought in from Hawaii must be scheduled sufficiently in advance to allow for extra travel time for mainland supply ports. Otherwise a smooth flow of supplies is not maintained, and this often results in the use of expensive "airlifts" of bulk supplies which could be handled more economically by ship. There is no commercial shipping which makes Johnston Atoll a port of call. All supplies brought by ship are handled by the Military Sea Transport Service. Johnston Harbor (Fig H-12 ) is an artificially dredged turning basin and harbor area inside the lagoon and located to the north of Johnston and Sand Islands. The navigable width of the channel is from 170 feet to 190 feet, and it has a minimum charted depth of 35 feet and is 400 feet wide. The harbor and turning basin vary in width from 1200 to 2000 feet, 35 feet deep and about 1.2 miles long. A 300 foot wide, 17 foot deep channel around the west end of the island continues to deep water. Separate channels 120 feet wide and 8 feet deep connect Akau and Hikina Islands to the harbor area. At one point H.O. Chart 5356 (Navy Hydro a, 1959) shows a least depth of 13 feet. Vessels which are too large for the entrance channel may anchor in the channel approach area south of the channel entrance between the southernmost channel buoy, which is moored in 62 feet of water about 2,750 yards bearing 148° from the Johnston Island Aviation Light, and the 100-fathom line, about four miles to the south of the Island (Bauer, 1973) (Navy Hydro a, 1959) (Navy Hydro b, 1959). All channels are outlined with boundary lights, and pile dolphins are located within the harbor for ship moorage. LCM boats are available to assist with docking. Two ship-to-shore radio communications channels are provided. These are Harbor Common on 2716 $KH_Z$ and Local Boat Control on 32.8 $KH_Z$. A bulkhead wharf, a 360-foot long wooden pier, and a small boat pier with an adjoining wharf (approximately 450 feet long) are located on the north side of Johnston Island. These facilities are served with freshwater lines,a saltwater fire protection System, fuel lines, power, and lighting. The bulkhead wharf provides over 180,000 square feet of dock area. There is also a bulkhead wharf at the west end of the island with 14,000 square feet of dock area, but its usefulness is impared by silting in the channel. Small boat piers and wharves are located on the smaller islands. All the wharves and piers are equipped with

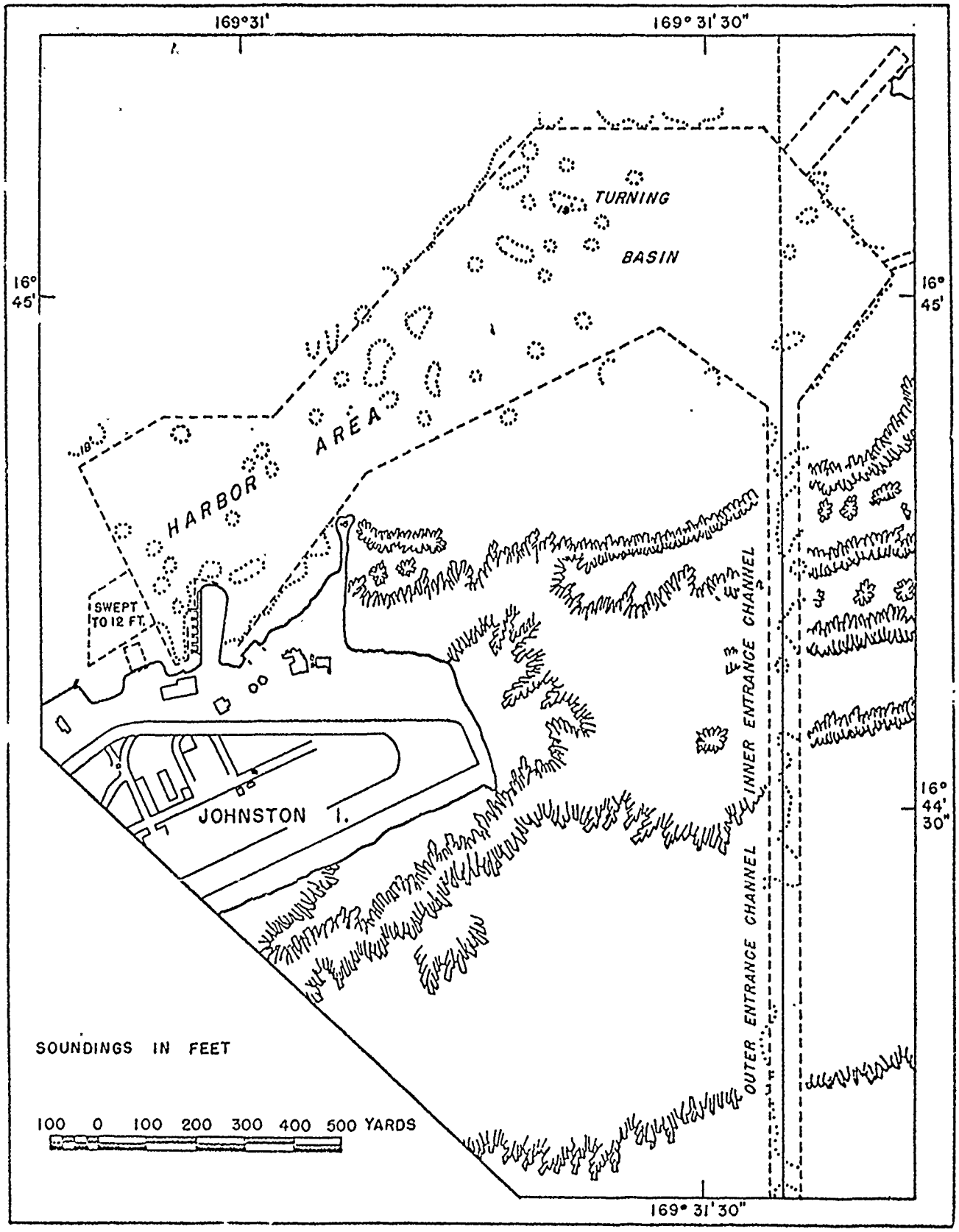



FIGURE H-12. PORT FACILITIES AT JOHNSTON ISLAND (Navy Hydro a, 1959)

protective fenders (Bauer, 1973) (Navy Hydro b, 1959). Other facilities associated with the harbor are a repair shop (Bldg 126), transformer building (Bldg 128), harbor control (Bldg 110), and marine shop (Bldg 127).

(b) Air Transport: A major activity on Johnston Island is in connection with the airstrip which is operated by the United States Air Force. There is one commercial airline providing services to Johnston Atoll. A runway on Johnston Island is oriented in a northeast-southwest direction (true bearing of 65° 13' 30") along the southern side of the island. It is approximately 9,000 feet long and 150 feet wide and has shoulders 150 feet wide on each side. The first 500 feet of the west end is concrete, and the remainder is paved with asphaltic concrete. The runway weight bearing capacity for aircraft with twin wheel type landing gear is 200,000 pounds, and for aircraft with twin tandem wheel type landing gear is 350,000 pounds. Turn-around areas, blast pads and overruns adjoin each end of the runway. The north taxiway and parking area are closed; however, there are small parking areas north and south of the west end of the runway and a large parking area (140,000 square yards) south of the middle of the runway. The runway is equipped with standard frangible type lights and with visual guide indicators for approaches from the west. Traffic signals on the island's perimeter road control the movement of vehicles across flight paths. Runway lighting control equipment is housed in Building 501 which has a 75-KW standby generator for emergency power. AGE, personal equipment, and parking areas are also lighted. Air/ground communications facilities include a control tower (Bldg 505) located north of the runway near its midpoint, air/ground tactical communications (Bldg 507), antenna tower (Bldg 506), and a generator shed (Bldg 508). Airfield navigational aids are a base beacon tower (Bldg 635), a low frequency base beacon (Bldg 901), several aircraft obstruction lights, and a Tactical Air Navigation (TACAN) unit. The tower and UHF/DF are normally operational 30 minutes prior to and after all departures, and 30 minutes prior to an ETA until landing and parking of all arrivals. A newly constructed air passenger and freight terminal (Bldg 285) is located east of the aircraft parking area on the south side of the island. It is 14,000 square feet in Area, and contains a freight handling area, waiting area, baggage and ticket offices, lounges, restrooms, and a security briefing area. The island is currently serviced by both commercial and Military Airlift Command flights on a regularly scheduled basis. Since 1966, Johnston Atoll has adhered to USAF safety regulations, and approved waivers thereto, pertaining to airfields and their surrounding air-space. Current and future planning of new facilities will conform to the dimensions, clearances, and transitional slopes stipulated in these regulations. The seaplane base at Johnston Island has landing aprons and ramps on the north side of the island; a dredged landing area in the lagoon north of the boat turning basin and harbor area. The longest runway in the lagoon is 11,000 feet, running from the northeast to the southwest. There are also two shorter runways running north and south and northwest and southeast, with lengths of 6,000 and 4,000 feet respectively. The entire seaplane landing area has been swept to a minimum depth of eight feet. The first facility on Johnston Atoll was originally based on Sand Island; the causeway and fill to the west of Sand Island were constructed for this original seaplane base in the late 30's. The seaplane base is little used today, since, with the coming of the long-range land plane to the Pacific, the flying boat lost much of its utility and is at present being used mainly for air-sea rescue operations (Bauer, 1973). In the interest of

completeness and to provide information not contained in the Holmes and Narver report, Change 12, U.S. Naval Oceanographic Office Publication, H.O. Pub. 80 (formerly No. 166) "Sailing Directions for the Pacific Islands" Vol. III, pages 354a - 375, 6th Ed., 1952 is included in Appendix C.

(c) Ground Transport: There are several miles of roads on Johnston Island including a perimeter road which varies from 20 to 26 feet in width. Some sections are paved with asphaltic concrete and others are compacted coral. The road network is excellent and allows easy access to all major facilities (Bauer, 1973).

(2) Communications: In addition to those discussed previously under Sea and Air Transport, there are numerous other communications facilities. A 1080 automatic dial telephone exchange provides on-atoll administrative telephone service, and off-island dialing to Oahu through a submarine cable. The Defense Communications Agency furnishes worldwide tele-communications services on a 24-hour, seven-day week, again through the submarine cable, and there is a backup communication link provided by a long haul radio trunk to Hickam AFB,HI. On-island there is a non-tactical VHF/FM mobile radio system with enough stations activated to meet local requirements. There are also from one to three civilian amateur radio stations, an Armed Forces Radio Station, a television station, a MARS station, a public address system, a disaster control system, and a fire alarm system (Bauer, 1973).

(3) Utilities

(a) Water Supply System: Johnston Atoll's Water system uses both fresh and salt water. Raw sea water is pumped from the lagoon through a traveling screen to the Salt Water Pump House (Bldg. 3). From there it is pumped to the Distillation Plant (Bldg. 45), and also into the salt water distribution system where it is used for sanitary purposes, fire protection, air conditioning condenser units, power plant waste heat dissipation, distillation Plant (Bldg. 45) which houses twelve distillation units and related equipment; the Freshwater Treatment Plant (Bldg. 44) with a pump station, soda-ash treatment area, and a chlorination room; the Freshwater Pump House (Bldg. 650); an Auxiliary Freshwater Pump House (Bldg. 649); and, storage facilities for approximately 740,000 gallons. The fresh water system is designed to support a population of approximately 4,500. Its total rated capacity is 318,000 gpd, but, allowing for maintenance and miscellaneous downtime, about 240,000 gpd can be expected. Fresh water for Akau, Hikina and Sand Islands is barged there in tank trucks (Bauer, 1973).

(b) Electrical Power System: The Power Plant (Bldg. 48) contains seven diesel-driven generators, each rated at 1400 kw with an 80 percent power factor. Outgoing power of 4160 volts is distributed through thirteen feeders. Two feeders serve the power plant's auxiliary equipment and utility load, two serve the smaller islands, one serves the LOX plant, and the remainder serve Johnston Island through approximately eighty substations. The distribution system consists of a network of underground duct banks in a modified loop radial configuration, and submarine cables which carry power to Akau, Hikina and Sand Islands. Although a loop tie-in arrangement provides 100 percent power back-up for the small islands, each also has one or more standby generators.

(c) Sanitary Sewerage System: Johnston Island has insufficient relief to permit use of a gravity sewage collection system; therefore, a forced system employing pumps and lift stations is used. The force main is a series of 3" to 16" cast iron and asbestos cement pipes in parallel runs along the north and south shores with connecting laterals. Raw effluent is discharged on the ocean bottom at a depth of 25.6 feet through a 10" pressure outfall pipeline which extends approximately 520 feet out from the southwest peninsula of the island. Sewage on the three smaller islands is collected in septic tanks, and the effluent from the septic tanks drains by gravity into the sea (Bauer, 1973).

(d) Storm Drainage System: The drainage system consists of inlets, french drains, and ditches which discharge into the lagoon. It is separate from the sewage system and does not use piping of any kind except for culverts under roads, runway, and taxiways and where ditches drain through outfalls into the ocean. Drainage is adequate for normal conditions, but problems may arise after heavy prolonged rainfall or severe storms (Bauer, 1973).

(4) Housekeeping

(a) Housing: Johnston Atoll housing can be classified as enlisted men's, officer/professional, and VIP. Dependents are not authorized; therefore, there is no dependent housing. Enlisted men's quarters are provided by six 4-story reinforced concrete barracks and two 3-story concrete block barracks. The former contain dormitory type accommodations (two-man cubicles) with a centrally located latrine on each floor. Each has a recreation lounge on the first floor and storage, janitorial,and equipment space. Each floor of the latter has twenty-four two-man rooms, a centrally located latrine, or recreational lounge, and laundry facilities. Each barrack also has storage, janitorial and equipment space. Total design capacity for the eight EM barracks is 1808. Two 4-story reinforced concrete professional barracks and twelve 2-story concrete block apartment buildings provide accommodations for officers and professional type personnel. The barracks have two-man bedrooms with each room accessible from an outside balcony. Each two bedrooms are connected by a latrine and closet area. Space is provided for storage, janitorial supplies, and equipment, and a recreational lounge is located on the first floor. Each apartment building contains six apartments with three bedrooms, a kitchen, combination living/dining area, and a bathroom. Total design capacity for officer/professional personnel is 824. There are four small cottages on Johnston Atoll which are reserved for use by the Commander and other VIPs. These contain kitchens, bathrooms, living and dining areas, and three bedrooms. Total capacity of the VIP quarters is 12 (Bauer, 1973).

(b) Messing: There are two mess halls on Johnston Atoll, Building 519 (Mess Hall No. 1) and Building 4 (Mess Hall No. 2). Mess Hall No. 1 is of concrete block construction with a built-up roof and a concrete floor. It can seat 1000 men for either family or cafeteria style meals and can be turned three times during each dining period for a serving capacity of 3000. Mess Hall No. 2 is constructed of concrete blocks with a precast roof. It was designed to seat 500 men, but it is not operational at the present time. One dining wing is now serving as a chapel and the other as the Officer's Club (Bauer, 1973).

(c) Recreation: Because of the remoteness of Johnston Atoll, its physical characteristics, and its use, emphasis has been given to providing excellent and varied recreation facilities. Indoor facilities include a bowling alley, gymnasium, hobby shops, library, pool and NCO, Officers and civilian clubs. Outdoor sports available are basketball, boating, fishing, golf, scuba diving, softball, swimming, tennis and volleyball. There is also an outdoor theater which seats approximately 1,000 men (Bauer, 1973).

(d) Dispensary: Medical facilities similar to those of a clinic or small hospital are located in Building 405, an underground structure of reinforced concrete with approximately 6,600 square feet of useable floor space. Included are rooms for minor and/or emergency surgery, examination and treatment, x-ray and associated darkroom equipment, isolation, 20-bed ward, offices, laboratory,storage, waiting room, library, latrine, and a dental operating room and laboratory. Two medical doctors and one dentist are normally on the island; however, treatment is generally confined to minor or emergency type ailments while patients with major problems are air-evacuated to Hawaii (Bauer, 1973). Facilities associated with the dispensary but located in separate structures are a decontamination station (Bldg 404), air conditioning equipment (Bldg 407), oxygen storage (Bldg 409), and emergency power (Bldg 416).

(e) Miscellaneous: In addition to the above, there is a post office, base exchange, barber shop, tailor shop, laundry, and fire station. All of these are adequate to support an island population of 4,500 personnel, if necessary.

(5) Storage

(a) Warehouses: Twelve steel frame buildings on the north side of Johnston Island, two similar structures near the south aircraft parking area, and Building 400, a wood frame structure with metal siding, provide a total of over 74,000 square feet of warehouse space. However, the latter (Bldg 400) was severely damaged during a recent hurricane and replacement facilities are being planned. There are also numerous storage facilities throughout the island designed and used for the storage of various types of munitions, and there are facilities reserved for special useage which are now used for storage.

(b) Open Storage: Open storage areas are located east of the north aircraft parking area, north of Bldg 390, and along the northwest shore of Johnston Island. Because of corrosion caused by the high humidity and blowing coral, the type of supplies which can be placed in outdoor storage is limited unless such supplies are enclosed in weather resistant packaging or coatings.

(c) POL/LOX: Petroleum, oil and lubricants (POL) stored in bulk include aviation gasoline (AVGAS), jet fuel (JP-4), motor gasoline (MOGAS), and diesel fuel. There are also storage facilities associated with the liquid oxygen (LOX) plant. MOGAS and diesel fuel facilities are located in the northeast portion of the island. Tanker-delivered fuels are conveyed to a 13,500 gallon diesel fuel tank near the power plant, and to six 25,000 gallon tanks (two for diesel and four for MOGAS) near the distillation plant. Associated facilities are a tank truck loading area and a vehicle fuel pumping station. The aircraft POL installation is located in an isolated area in the southeastern

part of the island. It includes a 13,500-barrel storage tank and a 1,500-barrel ready tank for AVGAS, and the same for JP-4. This complex also has a tank truck loading assembly area, an electrical equipment shop, a pump complex, and a propellant and lube storage area (Bauer, 1973). The LOX plant, located on the northwest corner of the island, has two 28,000-gallon tanks for liquid oxygen storage, and a 28,000-gallon tank and 13,500-gallon tank for liquid nitrogen storage.

(6) Construction: Construction of new facilities and modification of existing facilities is normally accomplished by the support contractor under a Cost-Plus-Fixed Fee contract with the Atomic Energy Commission. However, special projects are sometimes awarded by competitive bidding. An assortment of construction equipment including trucks, tractors, cranes, etc., is available on the island, but all construction materials, with the exception of coral aggregate and salt water, must be imported.

i. Terrestrial and Marine Flora and Fauna

NOTE: The following sections were extracted from a document entitled "Preliminary Biological Survey of Sand Island - Johnston Atoll" (POBSP, 1964). The work was accomplished under DoD Contract No. DA-18-064-AMC-56-A. For a more detailed discussion of Johnston Atoll, its history, terrestrial and aquatic flora and fauna, see Appendix A.

(1) Vegetation: The low-lying coral islands of the central Pacific are characterized by flora that contain few species. Plants are dominantly wide-ranging tropical species along with a few endemics (Fosberg, 1949). Only three plant species occurred on the original Johnston and Sand Islands. One hundred and twenty-four terrestrial plants have been introduced by man. In general, the indigenous flora of the atolls increases in number of species as one proceeds westward in the Pacific. This would be expected from the closer proximity of western islands to larger islands and land masses with their complex floras. Rainfall plays a particularly decisive role in the plant life of the coral atolls. Those with little rainfall, such as Sand - Johnston Atoll, have a very low, sparse vegetation consisting of a few grasses, herbs, and dwarf shrubs. This contrasts strikingly with the luxuriant growth and many trees to be found on atolls with high rainfall.

(2) General Animal Life: The animals of the Pacific show an increase in number of species from east to west as is true of plants. Central Pacific Atolls, like Johnston-Sand, with their small size, sparse and relatively uniform vegetation, and dry climates cannot support a large variety of species. With increasing size, diversity of habitat, and increased rainfall the number of species increases. Proximity to large land areas is a factor that is of great importance in causing an increase in the number of species. Many species, however, that reach the islands cannot find habitat suited to their survival.

(a) Mammals: The first men to visit the north central Pacific islands probably found only one mammal present, the Hawaiian Monk Seal. The various tribes, however, probably brought along semi-domestic dogs and unintentionally the Polynesian rat (Rattus exulans). With the arrival of whalers, guano diggers, and traders, almost every island received by accident or intention

one or more mammals. Most of these either brought about their own destruction, rabbits (Oryctolagus) on Laysan Island ate all available food (Bailey, 1956), or were destroyed by other introduced species, e.g., rats usually were exterminated by cats. Domestic animals, such as dogs, horses, sheep, goats, pigs, etc., generally cannot survive without human care. In some areas, cats and Polynesian rats occur on many uninhabited islands, and rabbits (Oryctolagus) occur on Phoenix Island, while Rattus rattus, Rattus norvegicus, and Mus musculus occur only on islands inhabited by man. These last three always occur in fairly close proximity to human activities and are probably dependent upon man for their large populations if not their existence. Several dogs are kept as pets on various islands and a monkey has existed for several years in a wild state on Kure Island.

(b) Birds: The bird population with few exceptions is composed entirely of oceanic birds or transient shorebirds. The total number of breeding sea birds in the central Pacific is twenty-four with the maximum number occurring at the present time on any one island is seventeen. The number of species which breed on any one island is dependent primarily on mammals present and secondarily on suitable nesting sites. A few individuals will usually nest on an island even if good nesting sites are absent, but the presence of cats will prevent nesting by some three to seven species. Fifty-six bird species have been recorded on the atoll. Twelve seabird species nest on the islands and six migratory shorebirds have been regularly observed in recent years. Endemic land birds (excluding the main Hawaiian forms) are represented only by the Laysan Finch of Laysan Island, a finch on Nihoa, and a parakeete and warbler in the Line Islands. An endemic duck is present on Laysan Island and a considerable variety of migrant ducks and small land birds have been recorded on the various islands. Finally wild populations of canaries and domestic pigeons occur on Midway.

(c) Reptiles: The reptile fauna usually consists of one skink, one gecko, and the Green turtle. Wetter islands support several species of geckos and skinks.

(d) Amphibians: None are present in the Johnston Atoll area and no suitable habitat is present to permit their survival.

(e) Fish: This group is still very poorly known and most authorities feel that the fish fauna of the various atolls will be very similar once complete collections have been made. Occasionally, sea turtles and porpoises are present in the lagoon. There are at least 94 species of inshore fish known and additional species probably exist.

(f) Insects and Other Arthropods: This is another group that has been incompletely studied. In general, the terrestrial invertebrate fauna consists of 68 species, many of them introduced. This is to be expected in view of small land areas, little variety of habitat, and long distances from land masses. Man has been instrumental in introducing many new species to inhabited atolls, however, where this has happened insect faunas can be expected to be more varied.

(g) Land Crustaceans and Mollusks: Several types of crabs are found on most Pacific coral atoll islands; land crabs, coconut crabs, and hermit crabs. Their occurrence in the central Pacific varies. Hermit crabs are not presently found north of the Line Islands. Terrestrial mollusks are not common on central Pacific atolls. Some, however, are found in close association with the sea. These are called "shore-zone" mollusks (Wiens, 1962).

# APPENDIX I

# TRANSPORTATION REQUIREMENT

1. INTRODUCTION: Transportation of the Orange herbicide presently stocked at the NCBC, Gulfport, Mississippi to Johnston Island, Central Pacific Ocean will be dependent on whether the proposed action, incineration at sea, or the principal alternative, incineration on Johnston Island, is selected. For incineration at sea, approximately 860,000 gallons would be removed from the drums and transferred by rail to the incinerator ship. For incineration on Johnston Island the drums of Orange will be transported to Johnston Island by ship from Gulfport. Shipment overland to a West Coast Port and then by vessel to Johnston Island or shipment via air flight only were also considered. Both of these alternatives are considered impractical because of higher cost, increased risk of product loss traversing the country overland, and the huge consumption of fuel connected with an air delivery of this magnitude.

2. CLASSIFICATION: Under the "Hazardous Materials Regulations" of the Department of Transportation (DOT), Code of Federal Regulations 49, Parts 100-199, Orange herbicide is not hazardous. Extensive experience over a number of years in the mid-1960's substantiates the adequacy of the shipping procedures which were then employed.

a. Flammable Classification: The DOT Transportation Regulation Section 173.115 defines a flammable liquid as one which gives off flammable vapors (as determined by flash point from Tagliabue's open-cup tester as used for test of burning oils, ASTM Test D1310) at or below a temperature of 80°F. Orange herbicide has a flash point of 295°F and vapor pressure less than 1 mm of mercury at 35°C. Therefore, it is not a flammable liquid.

b. Poisons-B-Classification: Code of Federal Regulations Title 49 - Transportation, Chapter 1 - Hazardous Materials Regulations Board, 173.343. Less dangerous poisons, Class B, liquid or solid, poison label are described below:

(1) For the purposes of Parts 170-189 of this chapter and except as otherwise provided in this part, Class B poisons are those substances, liquid or solid (including pastes and semisolids), other than Class A or Class C poisons, which are known to be so toxic to man as to afford a hazard to health during transportation; or which in the absence of adequate data on human toxicity, are presumed to be toxic to man because they fall within any one of the following categories when tested on laboratory animals.

(a) Oral Toxicity: Those which produce death within 48 hours in half or more than half of a group of ten or more white laboratory rats weighing 200 to 300 grams at a single dose of 50 milligrams or less per kilogram of body weight, when administered orally.

(b) Toxicity on Inhalation: Those which produce death within 48 hours in half or more than half of a group of ten or more white laboratory rats weighing 200 to 300 grams, when inhaled continuously for a period of one hour or less at a concentration of two milligrams or less per liter of vapor, mist, or dust, provided such concentration is likely to be encountered by man when the chemical product is used in any reasonable foreseeable manner.

(c) Toxicity by Skin Absorption: Those which produce death within 48 hours in half or more than half of a group of ten or more rabbits tested at a dosage of 200 milligrams or less per kilogram body weight, when administered by continuous contact with the bare skin for 24 hours or less.

(2) The foregoing categories shall not apply if the physical characteristics or the probable hazards to humans as shown by experience indicate that the substances will not cause serious sickness or death. Neither the display of danger or warning labels pertaining to use nor the toxicity tests set forth above shall prejudice or prohibit the exemption of any substances from the provisions of Parts 170-189 of this chapter.

c. For Truck Shipment: National Motor Freight Classification (NMFC) 50320 compounds, tree or weed killing (herbicides), not otherwise indexed (NOI) or 2,4-D (dichlorophenoxyacetic acid) or 2,4-D formulations.

d. For Rail Shipment: Uniform Freight Classification (UFC) 96465 weed killing compounds, not otherwise indexed by name (NOIBN).

3. PROPOSED METHODS OF SHIPMENT:

a. General: Overland shipment from NCBC, Gulfport, Mississippi to the Port of Gulfport will move by rail, a distance of 2 1/2 to 3 miles. While not classified as hazardous under Hazardous Materials Regulations, the uncontrolled release of Orange herbicide can have a harmful effect on crops and aquatic life. For these reasons the precautions listed below will be enforced. These precautions are deemed reasonable and adequate for the situation. Some of these actions are routinely accomplished regardless of the product being shipped. In addition to the basic precautions discussed in the following paragraphs, an Operations Plan will be written to describe the transportation aspects with an emphasis on personnel and environmental safety. All parties who come into possession of the product will be instructed in writing of actions to be taken in the event of an accident.

b. Bulk Shipment: For incineration at sea as the disposal method, the Orange stored at NCBC, Gulfport, Mississippi would be transferred from drums to tank cars for rail shipment to the Port of Gulfport. The Orange would then be loaded aboard the incinerator ship for transport to the incineration location. Necessary precautions will be taken during all phases of this operation.

c. Shipment in Drums: For incineration on Johnston Island as the disposal method it would be transported to Johnston Island in drums. The product will be packaged in drums of 16 gauge steel or 18 gauge steel. This action satisfies Department of Transportation (DOT) requirements for Class B poison container, as defined in Code of Federal Regulations, Title 49 - Transportation, Chapter 1 - Hazardous Materials Regulation Board, 173.346(a)(2). Drums will be inspected prior to shipment to determine that no leakage exists. Any leaks detected during inspection will be positively corrected by tightening of closures, replacement of gaskets, or by drum replacement. Product in drums of questionable condition for safe and leak free transit will be redrummed. Shipment will be made in gondola cars with steel floors. These are open top cars

with sides of 5 1/2 to 6 feet high. Use of this type car will permit overhead loading and unloading of drums with cranes, thus reducing time and cost in the loading and unloading operation. Lading will be blocked and braced in accordance with rules of the Association of American Railroads (AAR rules). Prior to loading rail cars, the floor of the cars will be covered with plastic sheeting of sufficient width and length to allow sheeting to be folded up 10 to 12 inches along sides and ends of each car. This lining would serve to contain any product leakage while cars are loaded. Lifting of product from port will be scheduled aboard one vessel. Consideration will be given to lining the floor of the cargo holds with plastic sheeting prior to herbicide loading. Also to be considered will be the shipment of absorbent material in sufficient quantity to absorb minor product leakage. This absorbent material would be discharged with the product at Johnston Island either for use or disposal.

# APPENDIX J

# ANALYTICAL METHODS

# I THE DETERMINATION OF 2,4-D AND 2,4,5-T HERBICIDES IN WATER

## A. REAGENTS

1. Benzene distilled in glass, pesticide analysis grade

2. Ether distilled in glass, pesticide analysis grade

3. Concentrated $H_2SO_4$

4. Concentrated $H_3PO_4$

5. Acid washed anhydrous $Na_2SO_4$ or (5% solution of anhydrous $Na_2SO_4$ pH <5) anhydrous $Na_2SO_4$

6. Anhydrous $Na_2SO_4$

7. Florisil activated at 650°C and kept at 130°C

8. N-methyl-N'-nitro-N-nitrosoquanidine

9. Potassium Hydroxide

10. Sodium Bicarbonate

## B. MATERIALS

1. Pyrex glass tubing, 1/8 inch O.D.

2. Glass wool

3. Gas-chrom[1] Q 60/80 mesh

4. 9" Disposable pipet

## C. EQUIPMENT AND GLASSWARE

1. Varian Aerograph HY-FI III Model 1200 with a proportional temperature programmer, or similar instrument with electron capture detector.

2. Varian Aerograph Model 30 Recorder, 0-1 MV, half inch per minute or equivalent.

3. Dohrmann Microcoulometric Halide Titrating System/G.C.

4. A small oven, maximum temperature 150°C.

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[1] Applied Science Laboratories, Inc., State College, Pa.

5. Prepurified nitrogen with pressure regulator

6. Fluidized sand bath

7. Kuderna-Danish evaporator, 125 ml with various size concentrator tubes

8. One-liter separatory flask

9. Two-liter separatory flask

10. 125 ml and 250 ml Erlenmeyer flask

11. Various size volumetric flasks

12. Quart mason jars with teflon lined covers

13. Ultra pure oxygen with pressure regulator

D. COLUMN PREPARATION

1. DC-200 silicone grease is coated 2.5 percent by weight on 60/80 mesh Gas-chrom Q. The material is also coated with 0.25 percent carbowax 20M, and packed into 1.5 mm - ID, 3 mm - OD heat resistant glass column 6 feet long.

2. OV-17 1.5 percent by weight, QF1 - fluorinated silicone 1.95 percent by weight, carbowax 20M 0.25 percent by weight are coated on 60/80 mesh Gas-chrom Q and packed into 1.5 mm - ID, 3 mm - OD heat resistant glass column, 6 feet long.

3. EGSS-X is coated 3 percent by weight on 100/120 mesh Gas-chrome Q and packed into a 2 mm - ID, 4 mm - OD, glass column, 6 feet long.

E. PREPARATION OF STANDARDS

Herbicide standards are prepared from their methyl esters to contain from $2 \times 10^{-9}$ g to $5 \times 10^{-12}$g per µl (microliter) in hexane or benzene in a volumetric flask.

F. PROCEDURE

1. Sample Collection of Herbicides: The water sample is collected, using a precleaned quart mason jar with a teflon lined cover. The jar is submerged directly into water source to collect sample. One-inch air space is left on top in the container.

2. Cleaning of glassware

a. All glassware, except volumetric glassware, is heated to 300°C for eight hours to eliminate organic contamination after detergent washing and rinsing in acid water pH <2 and rinsing clean of the acid with organic free water.

b. Volumetric glassware is cleaned with sodium dichromate in concentrated sulfuric acid cleaning solution, rinsed clean of sodium dichromate with organic free water and final rinse with acetone nanograde distilled in glass and dried in oven.

3. Operating Parameters of the Gas Chromatograph

a. Oven temperature: 170°C

b. Electron-capture detector, concentric tube design, D.C. mode, 90 volts temperature: 210°C.

c. Injection port temperature: 210°C.

d. Nitrogen (prepurified) carrier gas: 40 ml per minute.

e. Injection volume: 5 µl (microliter).

4. Herbicide in Water

a. Total phenoxy acid herbicides and its esters.

(1) Acidify (pH 2.0) the one-liter water sample with concentrated sulfuric acid.

(2) Pour the sample into a two-liter separatory funnel. Add 50 ml diethyl ether to the sample bottle, rinsing the sides, and pour the solvent into the separatory funnel. Shake the mixture vigorously for one minute. Repeat three times. Since ether is highly soluble in water, the sample must be saturated with ether before extraction. Dissolve 5 grams of $Na_2SO_4$ to water before extraction.

(3) Pour ether extract into a ⅄ joint 250 ml Erlenmeyer flask containing 2 ml of 37 percent aqueous potassium hydroxide. Add 15 ml $H_2O$ and insert a one-ball Snyder column. Evaporate the ether on a steam bath; reflux for approximately 90 minutes.

(4) Transfer the concentrate to a 60 ml separatory funnel. Extract the basic solution three times with 20 ml ether and discard the ether layer. Acidify the aqueous layer with 2 ml of cold 4:1 aqueous sulfuric acid to pH 2 and extract the herbicides with 20 ml ether three times. Transfer the ether layer to a 125 ml Erlenmeyer flask containing about 0.5 gram acid washed anhydrous $Na_2SO_4$ in an explosion proof refrigerator for two hours or overnight.

(5) Transfer the ether solution into a Kuderna-Danish evaporator-concentrator apparatus with a 5 ml volumetric flask and add 0.5 ml benzene. Concentrate the extract to about 0.5 ml, using a fluidized sand bath at 70°C or lower. During the ether transfer, it is necessary to crush the caked $Na_2SO_4$ to obtain a quantitative transfer.

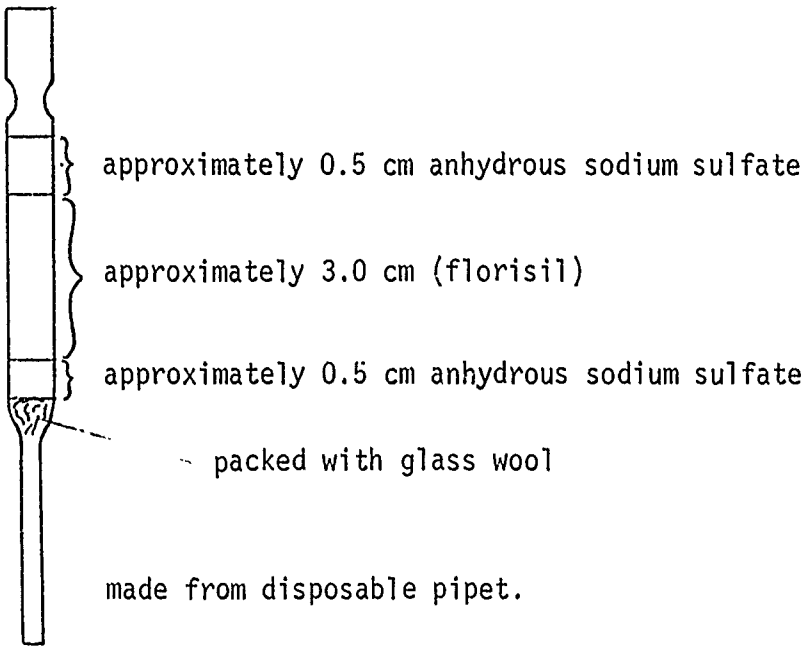
(6) When the concentrated extract is cool, add 0.5 ml of 14 percent $BF_3$-methanol reagent. Heat the contents at 50°C for 30 minutes in a sand bath or water bath.

(7) Cool and add 4.5 ml of 5 percent aqueous $Na_2SO_4$ solution to the reaction mixture, shake for one minute, allow to stand for approximately three minutes for phase separation.

(8) The benzene layer is pipetted from the receiver and passed through a micro cleanup column of florisil with more benzene to a volume of 5 ml. Then concentrate down to 0.5 ml for analysis.

(9) Gas chromatograph the methyl ester of chlorinated phenoxy acid through the same chromatographic columns as chlorinated pesticides.

(10) Compare with known quantities of prepared herbicide standards.




b. Butyl and Isooctyl Esters of 2,4-D and 2,4,5-T

(1) To a 1-liter water sample, add 1 N.NaOH to bring the pH to 8 or higher. (Caution: immediately start extraction; hydrolysis of the ester will take place if left standing).

(2) Pour the water sample into a two-liter separatory funnel. Add approximately 50 ml diethyl ether to the sample bottle, rinsing the sides, and pour the solvent into the separatory funnel. Shake the mixture vigorously for one minute. Repeat three times. Since ether is quite soluble in water, the sample must be saturated with ether before extraction. Total extracted ether volume is 150 mls. Dissolve 5 grams of $Na_2SO_4$ in water before extraction. Save the water sample for extraction of the chlorinated phenoxy-acids and chlorinated phenols.

(3) Pour the ether extract into a ⅀ joint 250 ml Erlenmeyer flask containing sufficient anhydrous acidified $Na_2SO_4$ to remove the water and store in an explosion proof refrigerator for two hours or overnight.

(4) Transfer the ether solution into a Kuderna-Danish evaporator-concentrator apparatus with a 1 ml volumetric flask and add 0.5 ml benzene. Concentrate the extract to 0.5 ml, using a fluidized sand bath at 70° C or lower. During the ether transfer, it is necessary to crush the caked $Na_2SO_4$ to obtain a quantitative transfer.

(5) Cool the concentrate overnight.

(6) The benzene layer is pipetted from the receiver and passed through a micro cleanup column of florisil with more benzene to a volume of 5 ml. Concentrate to 0.5 ml for analysis using the columns normally used for chlorinated herbicides.

(7) Gas chromatograph the esters of chlorinated phenoxyacid. The 3 percent EGSS-X coated column has a better ester separation for e-c detection.

(8) Compare with known quantities of prepared herbicide standards.

(9) Proceed with the extraction of the chlorinated phenoxy-acid and chlorinated phenols from step "(2)" by acidifying the water to pH 2 with concentrated sulfuric acid.

(10) Pour the sample into a two-liter separatory funnel. Saturate the sample with ether. Add 50 ml diethyl ether to the sample bottle, rinsing the sides and pour the ether into the separatory funnel. Shake the mixture vigorously for one minute. Repeat three times. Total extracted volume: 150 mls.

(11) Pour the ether extract into a ⅀ joint 250 ml Erlenmeyer flask containing anhydrous acidified $Na_2SO_4$ in an explosion proof refrigerator. Allow to stand for two hours or overnight.

(12) Transfer the ether solutions into a Kuderna-Danish evaporator-concentration apparatus with a 5 ml volumetric flask and add 0.5 ml benzene. Concentrate the extract to about 0.5 ml, using a fluidized sand bath at 70 C or lower. During the ether transfer, it is necessary to crush the caked $Na_2SO_4$ to obtain a quantitative transfer.

(13) When the concentrated extract is cool, add 0.5 ml of 14 percent $BF_3$-methanol reagent. Heat the contents at 50°C for 30 minutes in a sand bath or water bath. When chlorinated phenols are determined with the chlorinated phenoxyacids, add diazomethane dropwise until a yellow color persists.

(14) After methylation with the $BF_3$-methanol reagent sample, cool and add 4.5 ml of 5 percent aqueous $Na_2SO_4$ solution to the reaction mixture, shake for one minute, allow to stand for approximately three minutes for phase separation. After methylation with diazomethane, slowly warm the sample in a sand bath or water bath to 50°C for one-half hour; then use filtered air to evaporate the diazomethane.

(15) The benzene layer is pipetted from the receiver and passed through a micro cleanup column of florisil with more benzene to a volume of 5 ml. Then concentrate down to 0.5 ml for analysis.

(16) Gas chromatograph the methyl ether of chlorinated phenoxyacid and the methyl ethers of chlorinated phenols through the gas chromatographic columns.

(17) Compare with known quantities of prepared chlorinated herbicide and phenol standards.

(18) Confirmation of the chlorinated herbicides and the chlorinated phenols by Dohrmann Microcoulometric Titrating System.

(a) The left over sample from the electron capture detection analysis is further concentrated down to approximately 0.100 ml, and the whole sample is injected into the gas chromatograph and detected by the microcoulometric system for halogens.

c. Extraction or Partition of Chlorinated Phenoxy Acids and Chlorinated Phenols

(1) Pour the ether extract from Step b. of the total phenoxyacid herbicides and its esters into another 250 ml separatory funnel with 50 ml of 5 percent $NaHCO_3$ solution. Shake and wait for a few minutes for the two layers to separate. Repeat twice. Save both layers. The aqueous layer will contain the chlorinated phenoxy acid and chlorinated phenols. The ether layer will contain the esters.

(2) Dry the ether layer over anhydrous $Na_2SO_4$ and add 0.5 ml benzene. Transfer to a Kuderna-Danish evaporator-concentrator apparatus with 1 ml volumetric flask. Concentrate the extract to about 0.5 ml, using a fluidized sand bath at 70°C or lower. During the ether transfer, it is necessary to crush the caked $NaSO_4$ to obtain a quantitative transfer.

(3) The benzene layer is pipetted from the receiver and passed through a micro cleanup column of florisil with more benzene to a volume of 5 ml, then concentrated down to 0.5 ml for gas chromatography.

(4) Transfer the aqueous layer containing the chlorinated phenoxy acid and chlorinated phenols from Step a. to a separatory funnel and acidify with $H_2SO_4$ acid. Saturate the aqueous layer with ether and extract with 50 mls diethyl ether three times. Dry the ether layer over anhydrous acidic $Na_2SO_4$. Discard aqueous layer. Allow the extract to remain in contact with $Na_2SO_4$ in an explosion-proof refrigerator for two hours or overnight.

(5) Transfer the ether solution into a Kuderna-Danish evaporator-concentrator apparatus with a 5 ml volumetric flask and add 0.5 ml benzene. Concentrate the extract to about 0.5 ml, using a fluidized sand bath at 70°C or lower. During the ether transfer, it is necessary to crush the caked $Na_2SO_4$ to obtain a quantitative transfer.

(6) When the concentrated extract is cool, add 0.5 ml of 14 percent $BF_3$-methanol reagent for phenoxy acid. When chlorinated phenols are analyzed together with phenoxy acid, then use diazomethane (dropwise until yellow color persists). Heat the contents at 50°C for 30 minutes in a sand bath or water bath).

(7) Cool the methylated sample and add 4.5 ml of 5 percent aqueous $Na_2SO_4$ solution to the reaction mixture, shake for one minute, allow to stand for approximately three minutes for phase separation. Cool the sample which has been methylated with diazomethane and completely destroy the diazomethane.

(8) The benzene layer is pipetted from the receiver and passed through a micro cleanup column of florisil with more benzene to a volume of 5 ml. It is then concentrated down to 0.5 ml for analysis.

(9) Gas chromatograph the methyl ester of chlorinated phenoxy acid through the same gas chromatographic columns as chlorinated pesticides.

(10) Compare with known quantities of prepared herbicide standards.

G. ACCURACY AND COMMENTS

1. Minimum Measureable Concentration of Herbicide in the Water Sample

| | |
|---|---|
| 2,4-D | 200 ppt |
| 2,4,5-T | 20 ppt |

2. Discussion of the above minimum measurable concentration of herbicide:

a. Using the procedure, accurate analysis of most water samples can be routinely accomplished. Amounts less than the above detectable limits can be detected by analyzing a larger sample volume or reducing the volume of extract to less than 5 ml. Not all extracts, however, can be reduced to such a low volume without an accompanying buildup of excessive interferences.

b. Ultramicro analytical techniques must be used to determine nanogram concentrations of pesticides found in the environment. For analytical results to be meaningful, glassware should be properly washed and heat treated at 300°C. Extensive cleanup is required because interfering impurities are greater than pesticide found. Recovery of pesticides from the environment averages from 85 percent to 114 percent.

c. All glassware and reagents used should be free of interfering compounds. A blank and standard should be analyzed with the samples until the analyst becomes proficient.

"It was found that prompt handling of samples is necessary if the results of the analysis are to be representative of the condition of the water at the time of sampling. A water sample was selected from an area which had been sprayed for about 1-1/2 years with 2,4-D. Added 2,4-D almost completely disappeared after the spiked sample was allowed to stand at 72° - 74°F. in a stoppered bottle for 10 days. Apparently, in water courses and soils which are regularly exposed to 2,4-D, certain organisms may develop the capability to degrade the chemical. Shipping samples from the collection point to the laboratory may take too long and means for resolving this problem must be found. Perhaps 'icing' or chemical fixing' and air shipment may be required."[1]

[1]Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas-Chromatography, by D.F. Goelitz and W.L. Lamar, U.S.G.S. WSP-1817-C. Draft copy from authors.

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## II. GENERAL METHOD FOR CHLOROPHENOXY ACIDS FOR BIOLOGICAL MATERIAL

### A. REAGENTS

1. Benzene, Pesticide Grade Quality
2. Hexane, Pesticide Grade Quality
3. Ethyl Ether, Pesticide Grade Quality
4. Petroleum Ether, Pesticide Grade Quality
5. Concentrated Sulfuric Acid
6. Anhydrous Sodium Sulfate
7. Florisil, Calcined at 650°C and stored at 130°C
8. $BF_3$-Methanol Reagent
9. Acetonitrite, Pesticide Grade Quality
10. Methanol, Pesticide Grade Quality

### B. GLASSWARE

1. Liquid Chromatography Column, 22 mm ID
2. Separatory Funnels
3. Kuderna-Danish Evaporator
4. Erlenmeyer flasks
5. Beakers

### C. EQUIPMENT

1. Gas Chromatograph, Tracor, Model 220, Dual Column, with two $Ni^{63}$ Electron capture detectors and a digital integrator, VIDAR 6300, Autolab, with teletype attachment.

a. A 6 ft U-tube, glass column packed with 1.5% OV-17/1.95% QF-1 on 80/100 mesh Gas Chrom Q was connected to detector No. 1.

b. A 6 ft U-tube, glass column packed with 4% SE-30/6% QF-1 on 80/100 mesh Gas Chrom Q connected to detector No. 2.

c. Oven Temperature - 190°C.

d. Detector Temperature - 350°C.

e. Injector Temperature - 225°C.

f. Carrier Gas - Nitrogen (prepurified) 80 ml per min.

2. Gas Chromatograph/Mass Spectrometer, Finnigan Model 3000D interfaced with a system/150 data handling system.

a. Gas Chromatograph

(1) Column - 5 ft U-Tube, glass, packed with 3% OV-1 on 80/100 mesh Gas Chrom Q.

(2) Column Oven Temp. - 160°C.

(3) Injector Temperature - 225°C.

(4) Carrier Gas - Helium 25 ml per min.

(5) Sample injection - 5 µl.

(6) Transfer line - 180°C.

b. Mass Spectrometer

(1) Electron Energy - 70 eV

(2) Mass Range - 50-300 amu

(3) Pressure - $3 \times 10^{-5}$ Torr.

(4) Sensitivity - $10^{-7}$ amp per volt

D. PREPARATION OF STANDARDS: Herbicide standards were prepared from the methyl esters, of 2,4-D and 2,4,5-T. Concentration of the standard solution for Gas Chromatography was 10 picograms ($10 \times 10^{-12}$g) per microliter (µl) of each ester, in hexane. Concentration of standard for GC/MS was 0.1 nanograms ($0.1 \times 10^{-9}$g) per microliter (µl) of each ester, in benzene.

E. PROCEDURE

1. Extraction of Acids

a. Biological Material

(1) One third of total sample material is placed in a blender and homogenized with anhydrous $Na_2SO_4$ until a uniform mixture is obtained.

(2) Transfer mixture to a beaker, add 25 ml of 10% $H_2SO_4$ in methanol and then enough ethanol to cover entire sample by 1 inch. Stir for 20 min.

(3) Pour into Erlenmeyer flask and evaporate on steam bath with a jet of air until about 35 ml ethanol remains.

(4) Transfer to 500 ml separatory funnel with 200 ml 50% ethyl ether in petroleum ether, add 50 ml 4% $NaHCO_3$ and shake carefully.

(5) Extract by isolation of acids procedure.

b. Non-biological Material

(1) Sediment Material

(a) Weigh 2g of dry sample material into a screw cap tube about 15 cm in length.

(b) Add 10 ml of 1:3 benzene-propanol mixture and rotate on a Fisher "Roto-Rack" at 40 rpm for 2 hours.

(c) Filter suspension thru a hexane washed Whatman #2 filter paper and collect the filtrate in a clean test tube.

(d) Evaporate to about 0.5 ml.

(e) Sample ready for methylation.

(2) Coral Material

(a) 100 g of coral are broken up into small pieces and placed in a 400 ml beaker.

(b) Add sufficient slightly acidified benzene to cover the coral.

(c) Stir mixture for about 30 minutes using a magnetic stirrer. Decant benzene and save. Repeat extraction two additional times. Collect benzene in same container.

(d) Evaporate benzene to almost dryness using gentle heat with a slow air current.

(e) Sample ready for methylation.

2. Isolation of Acids (Biological Material)

a. After releasing pressure in the separatory funnel several times, shake vigorously for 1 minute. Let layers separate.

b. Drain bottom aqueous layer into another 500 ml separatory funnel. Repeat extraction twice using 15 ml ethanol and 40 ml $NaHCO_3$ solution each time.

c. Combine the aqueous phases and discard the organic phase. Extract the combined aqueous phase twice using 25 ml $CHCL_3$ each time. Drain off the $CHCL_3$ and discard.

d. Carefully acidify the aqueous solution with 25 ml 10% aq. $H_2SO_4$. Extract acidified solution three times, using 30 ml benzene each time. Drain each benzene extract through a plug of cotton into a beaker.

e. Rinse cotton plug with benzene after the third benzene extract has filtered through. Remove cotton and replace funnel in beaker.

f. Evaporate sample just to dryness on a steam bath.

g. Sample ready for methylation.

3. Methylation of Acids

a. Make sample to a volume of 0.5 ml with benzene. Add 1 ml of $BF_3$/methanol reagent and mix.

b. Place on steam bath and boil for approximately two minutes.

c. Cool and add about 4.5 ml of 5% aqueous $Na_2SO_4$ solution; shake and allow to stand for phase separation.

d. Benzene layer is ready for clean-up.

4. Clean-up of Methylated Acids

a. Acetonitrite Partitioning: Only fatty samples were partitioned with petroleum ether - acetonitrite prior to florisil clean-up. The non-fatty samples were passed through florisil column for clean-up without partition.

(1) Add petroleum ether to the sample extract so that total volume in a 125 ml separatory funnel is 15 ml.

(2) Add 30 ml of acetonitrite saturated with petroleum ether. Shake vigorously 1 min. and let layers separate.

(3) Drain acetonitrite into a 1 liter separatory funnel containing 650 ml $H_2O$, 40 ml saturated $NaCl$ solution and 100 ml petroleum ether.

(4) Extract petroleum ether solution in the 125 ml separator with three additional 30 ml portions of acetonitrite saturated with petroleum ether, shaking vigorously for 1 min each time. Combine all extracts in the 1-liter separator.

(5) Mix 1 liter separator thoroughly 30-45 seconds. Let layers separate and drain aqueous layer into second 1-liter separator.

(6) Add 100 ml petroleum ether to second separator, shake vigorously 15 seconds, and let layers separate.

(7) Discard aqueous layer, combine petroleum ether with the petroleum ether in original separator and wash with two, 100 ml portions $H_2O$.

(8) Discard washings and drain petroleum ether layer through column of anhydrous $Na_2SO_4$. Rinse column with three (about 10 ml) portions of petroleum ether.

(9) Evaporate combined extract and rinses to 5-10 ml in Kuderna-Danish concentrator for transfer to florisil column.

b. Florisil Column

(1) Prepare 22 mm ID column that contains approximately four inches of activated florisil topped with about 1/2 in. anhydrous $Na_2SO_4$.

(2) Pre-wet column with 40-50 ml petroleum ether. Place Erlenmeyer flask under column to receive eluate.

(3) Transfer sample extract to column letting it pass through at about 5 ml/min.

(4) Rinse extract container and transfer rinses to column, and rinse walls of chromatographic column with additional small portions of petroleum ether.

(5) Elute column at about 5 ml/min. with 200 ml 10% ethyl ether/petroleum ether eluant.

(6) Concentrate eluate to appropriate volume for analysis.

c. Gas Chromatography - Electron Capture Detector (EC): 5 microliters of the eluate are injected into each of the two columns. Chromatograms are analyzed for peaks which have the same retention time as that of the methyl ester standards of 2,4-D and 2,4,5-T. The practical sensitivity of the Electron Capture to standard solutions of methyl esters of 2,4-D and 2,4,5-T is 50 picograms ($50 \times 10^{-12}$ grams) of each.

d. Gas Chromatography/Mass Spectrometry (GC/MS): Samples which have peaks of the same retention times as the methyl esters of 2,4-D and 2,4,5-T are analyzed by GC/MS. 5 µl of sample are injected into the injector part of the GC/MS systems. The methyl esters of 2,4-D and 2,4,5-T can be confined by using the data handling system of the GC/MS by comparing the fragmentation patterns of the suspected compounds with those of the standards. The practical sensitivity of the GC/MS to standard solutions of the methyl esters of 2,4-D and 2,4,5-T is 0.5 nanograms ($0.5 \times 10^{-9}$ grams) of each.

III. TCDD ANALYSIS: The TCDD analyses reported in the Environmental Statement Part III were accomplished by the EPA Pesticide Laboratory at Bay St Louis MS and the Perrine Laboratory, Perrine FL; therefore, the analytical procedures are not included in this appendix.

# APPENDIX K

## DISPERSION MODEL STUDY


| | | PAGE |
|---|---|---|
| 1. | GENERAL | K-1 |
| 2. | DIFFUSION MODEL AND INPUT PARAMETERS | K-1 |
| 3. | RESULTS | K-2 |
| 4. | ENVIRONMENTAL IMPLICATIONS | K-6 |
| 5. | REFERENCES | K-14 |

1. GENERAL: The main effort, in attempting to define the effects of burning Orange herbicide on the air quality at and around Johnston Island, was directed toward the use of diffusion equations to predict the ground level concentrations.

2. DIFFUSION MODEL AND INPUT PARAMETERS:

a. The concentration, C, of gas or aerosols (particles less than about 20 microns diameter) at the coordinate points x, y, z, from a continuous source with an effective emission height, H, is given by equation (1). The notation used to depict this concentration is C (x, y, z, H). H is the height of the plume center line when it becomes essentially level, and is the sum of the physical stack height, h, and the plume rise, $\Delta H$. The following assumptions are made: the plume spread has a Gaussian distribution in both the horizontal and vertical planes, with standard deviations of plume concentration distribution in the horizontal and vertical of $\sigma y$ and $\sigma z$, respectively; the mean wind speed affecting the plume is u; the uniform emission rate of pollutants is Q; and total reflection of the plume takes place at the earth's surface, i.e., there is no deposition or reaction at the surface.

$$C(x,y,z;H) = \frac{Q}{2\pi\sigma z\, u} \exp\left[-\tfrac{1}{2}\left(\frac{y}{\sigma y}\right)^2\right] \left\{\exp\left[-\tfrac{1}{2}\left(\frac{z-H}{\sigma z}\right)^2\right] + \exp\left[-\tfrac{1}{2}\left(\frac{z+H}{\sigma z}\right)^2\right]\right\} \quad (1)$$

For concentrations calculated at ground level (z=o), the equation simplifies to:

$$C(x,y,o;H) = \frac{Q}{\pi\sigma y\, \sigma z\, u} \exp\left[-\tfrac{1}{2}\left(\frac{y}{\sigma y}\right)^2\right] \exp\left[-\tfrac{1}{2}\left(\frac{H}{\sigma y}\right)^2\right] \quad (2)$$

Where the concentration is to be calculated along the center line of the plume (y=o):

$$C(x,o,o;H) = \frac{Q}{\pi\, \sigma y \sigma z\, u} \exp\left[-\tfrac{1}{2}\left(\frac{H}{\sigma z}\right)^2\right] \quad (3)$$

At distance equal to or greater than 2 $x_L$:

$$C(x,o,o;H) = \frac{Q}{\sqrt{2\pi}\,\sigma y\, L\, u} \quad (4)$$

$X_L$ is the distance downwind where the vertical diffusion starts being affected by the inversion.

The Holland Plume Rise equations was used to determine H:

$$\Delta h = \frac{Vsd}{u} \left[ 1.5 + 2.68 \times 10^{-3} p \left( \frac{Ts - Ta}{Ts} \right) d \right] \quad (5)$$

This is modified for atmospheric stability so the result is:

$$H = h + \Delta h \, (1.4 - .1 P) \quad (6)$$

The mixing depth, L:

$$L = (6 - P)(121)(T - T_d) / 6 + \frac{(P)(0.087)(u_z + 0.5)}{12 f \ell n (z / zo)} \quad (7)$$

The mixing depth of the atmosphere (thickness of the boundary layer) can be defined as that layer where vigorous mixing takes place due to thermal and mechanical turbulence.

TABLE K - 1

INPUT PARAMETERS

| | J. I. | Ship |
|---|---|---|
| Stack height (m) | 15.24 | 12 |
| Stack diameter (m) | 1.5 | 3 |
| Stack temperature ($^{o}$F) | 1600 | 1625 |
| Stack velocity (m/sec) | 18.17 | 20 |
| Air temperature ($^{o}$F) | 76.5 | 76.5 |
| Air pressure (mbs) | 1024 | 1024 |
| Mixing depth (m) | 719 | 719 |

3. RESULTS:

a. In order to determine a conservative estimate of the ground level concentration, the following parameters and considerations were used: the highest ground level concentration will occur with high winds and an unstable atmosphere; no deposition or reaction at the surface; no rain-out of the plume; the ship standing still in the water; and using the Holland Plume Rise Eq.

b. Figure K-1 shows the center line ground level concentration for a HCl plume at Johnston Island. The emission rate is 37,000 lbs/day. The maximum (1.85 ppm) concentration occures at 0.2 km downwind and decreases to 0.007 ppm at 10 km downwind. Figure K-2

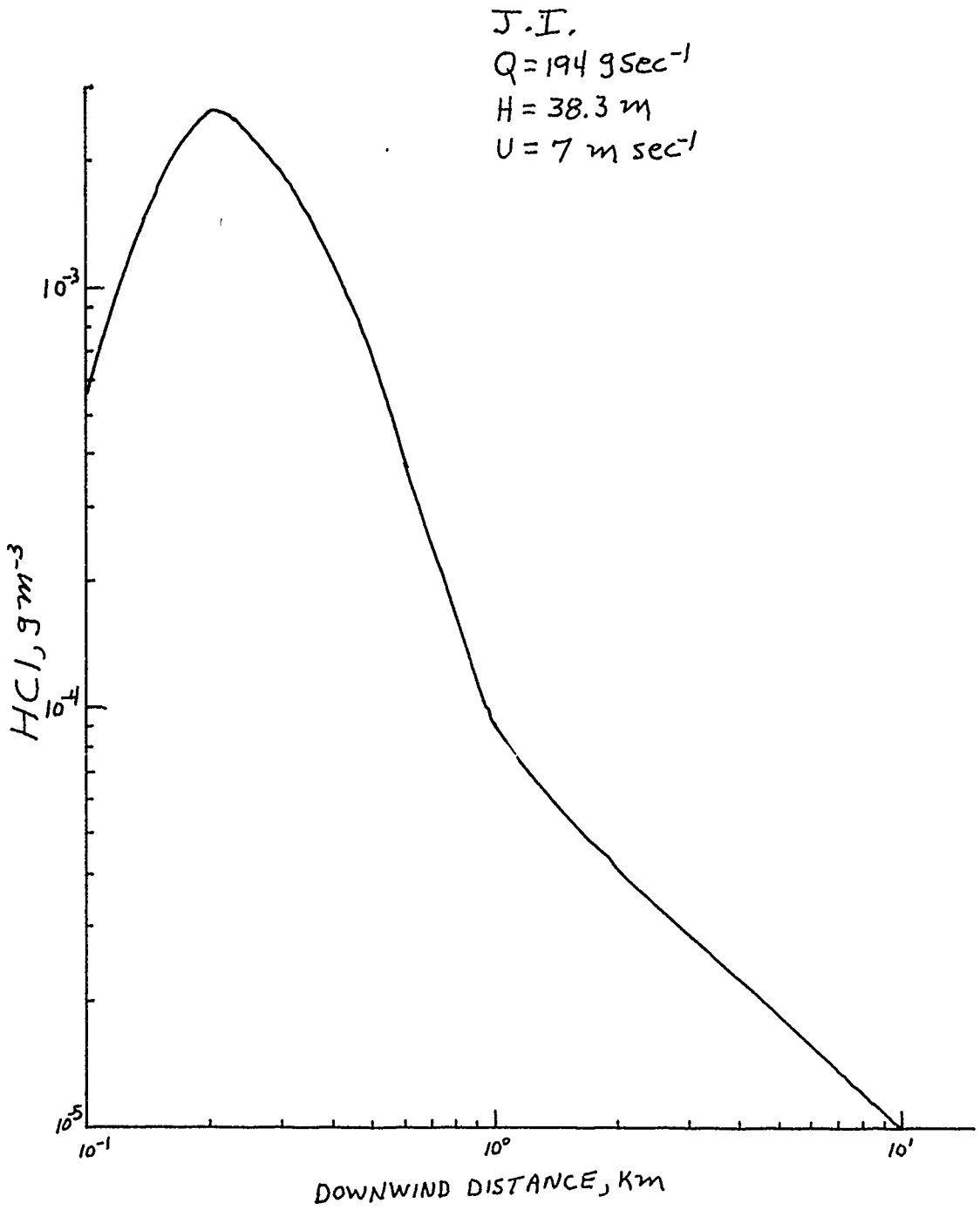



Figure K-1. Center line ground level HCl concentration, Johnston Island.

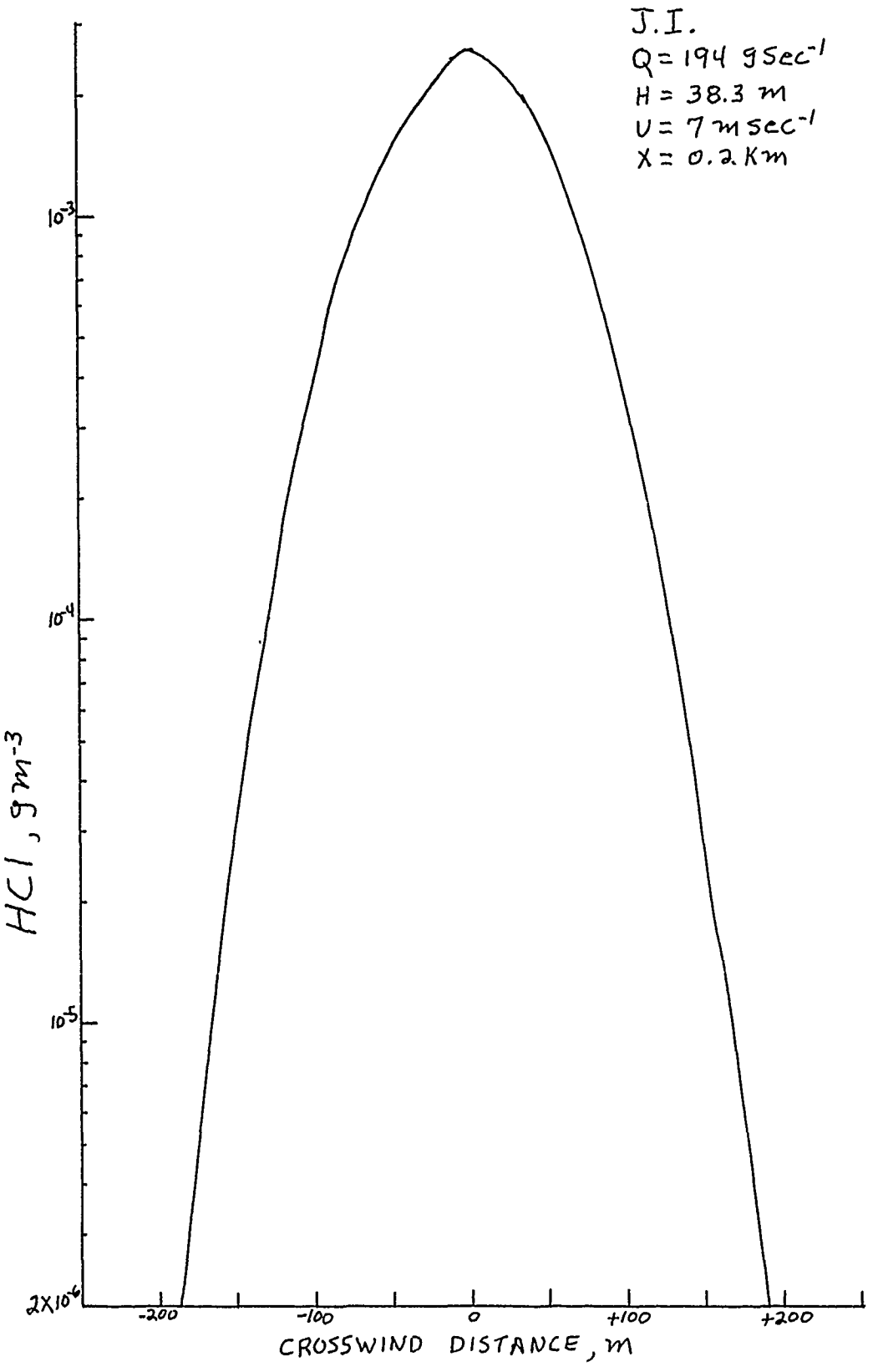



Figure K-2, Horizontal HCl concentration at 0.2 km downwind, Johnston Island.

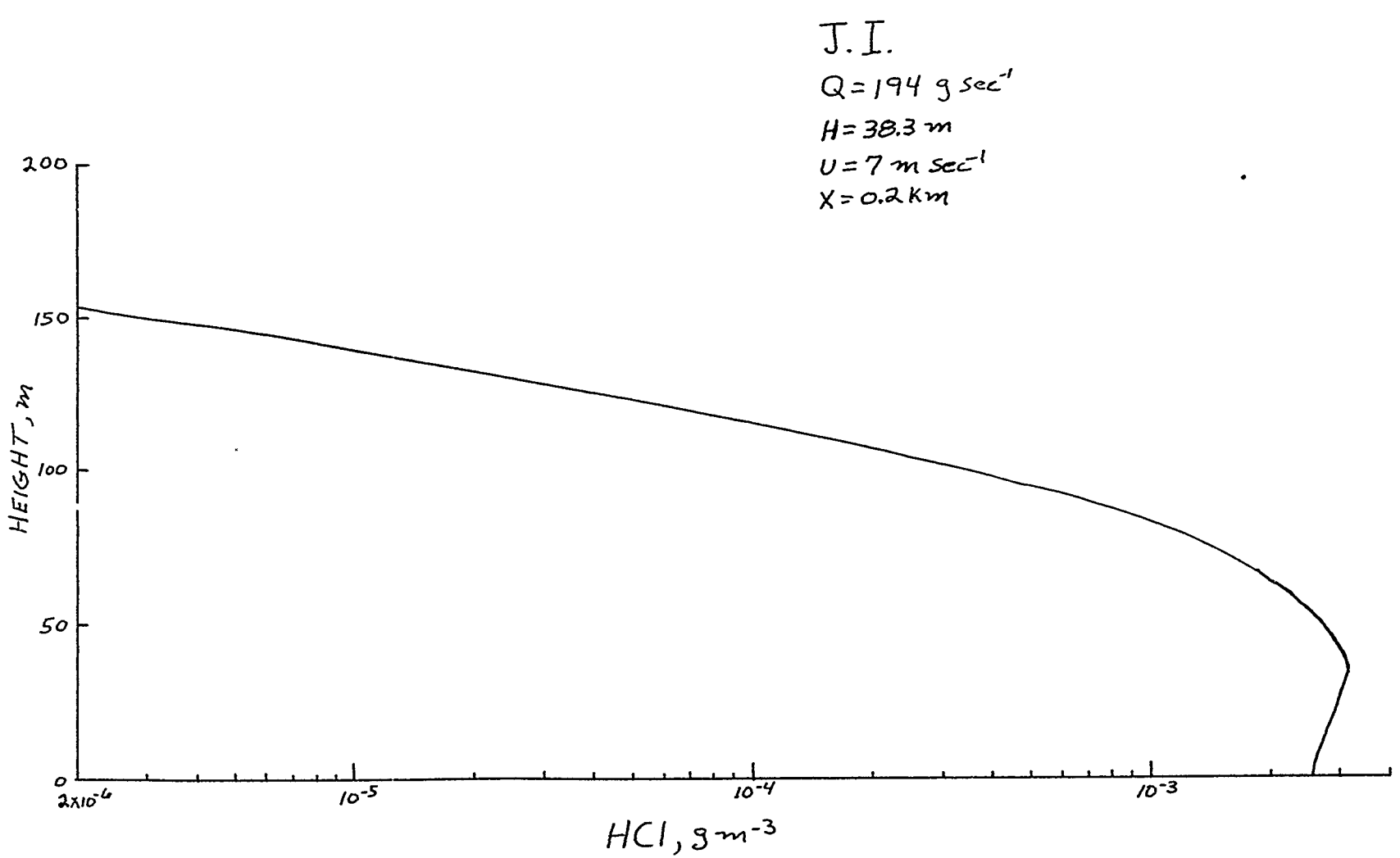



Figure K-3. Vertical HCl concentration at 0.2 km downwind, Johnston Island.

shows the horizontal extent of the concentration at 0.2 km downwind. Figure K-3 shows the vertical extent of the plume. Figure K-4 shows the ground level isopleths and area, A, enclosed by the isopleths.

Figures K-5 through K-10 are for a ship operating west of Johnston Island. Emission rates of 170 tons/day of Orange herbicide were used. Figure K-5 and K-8 show the center line ground level concentrations. The maximum 2.28 ppm (HCl) and 0.81 ppb (Orange) occur at 0.47 km downwind. At 10 km downwind the concentrations are 50.0 ppb (HCl) and 19.4 ppt (Orange). Figures K-6 and K-9 show the horizontal concentration, while figure K-7 and K-10 show the vertical.

4. ENVIRONMENTAL IMPLICATIONS:

a. It is very difficult to extrapolate these results to the actual situation at and around Johnston Island. The parameters used for the study are not necessarily those which will exist when the incineration takes place. These parameters were used in order to provide a conservative estimate (worst case) and these conditions are never expected to be reached.

b. Factors that will decrease the ground level concentration shown in this study for the ship are: the ship will be moving during incineration; the atmosphere is more towards neutral or stable, than unstable; the mixing depth will be higher; and there will be a certain amount of deposition and reaction with the surface and rain-out of the plume. For Johnston Island incineration, all of these factors, except movement of incinerator, also apply.

c. Another fact evident is that under all conditions studied, a majority of the time, the concentrations of interest will exist over the ocean, due to the prevailing wind direction at Johnston Island.

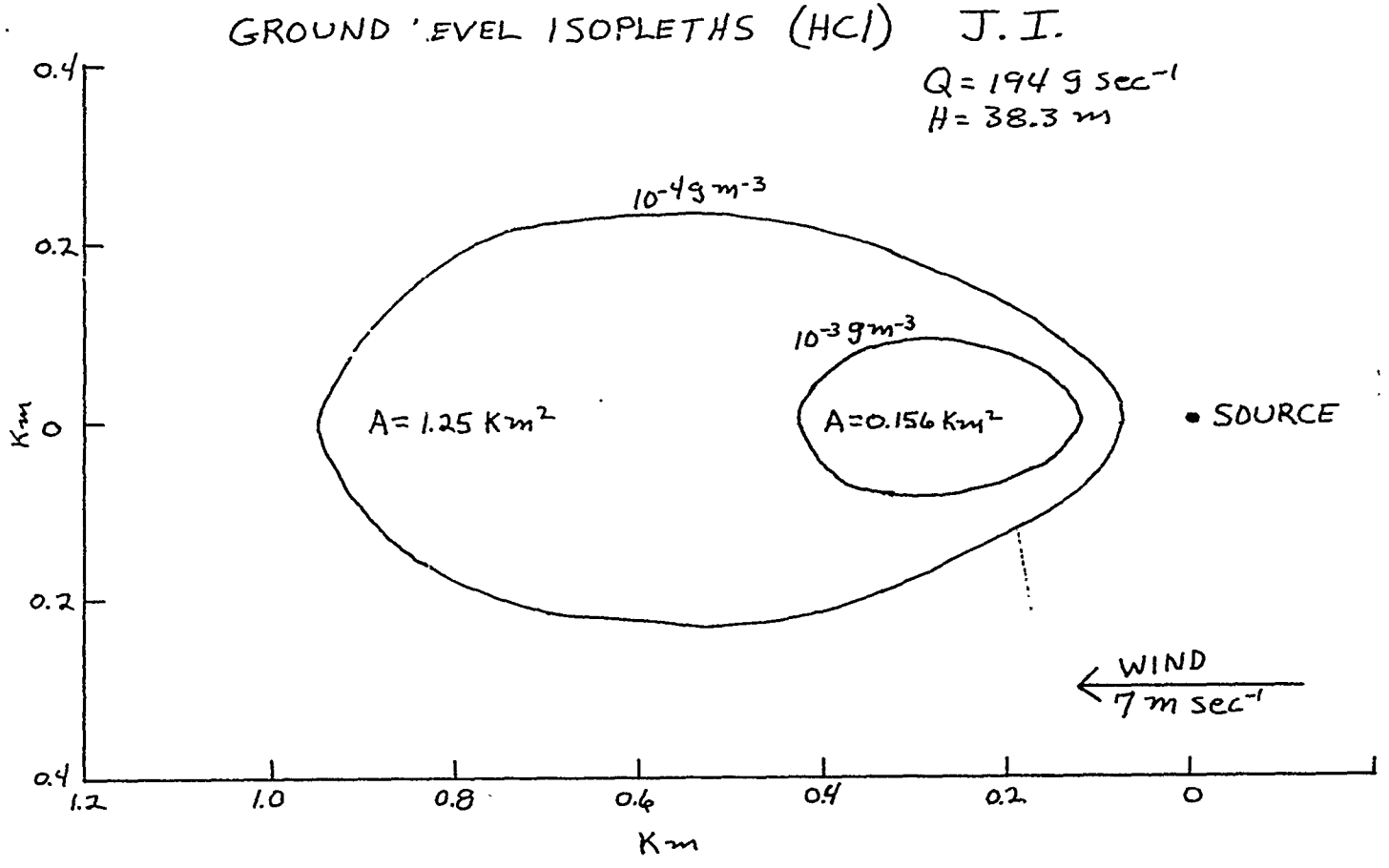



Figure K-4. Ground level isoplethes, Johnston Island.

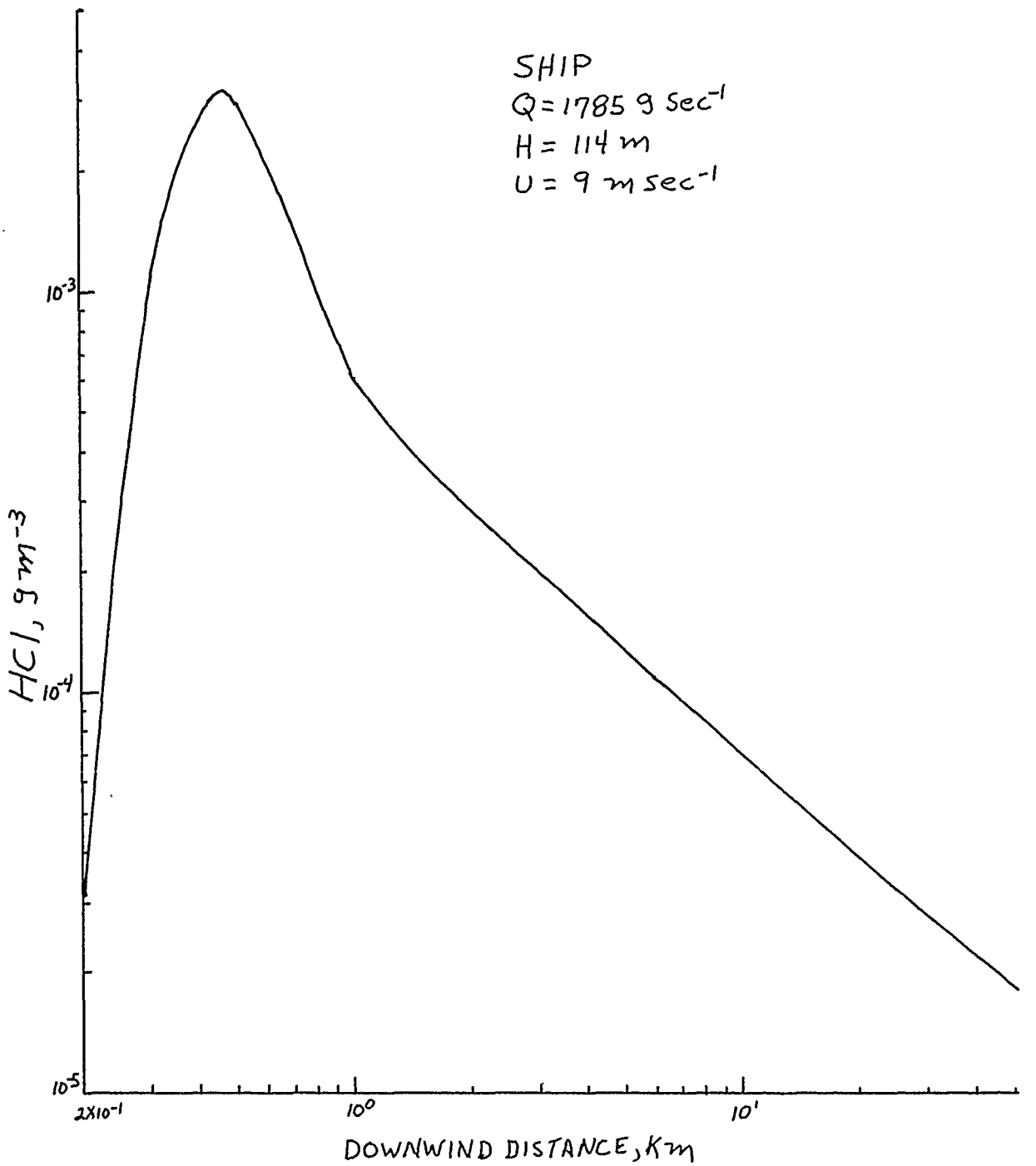



Figure K-5, Center line ground level HCl concentration, ship incinerator.

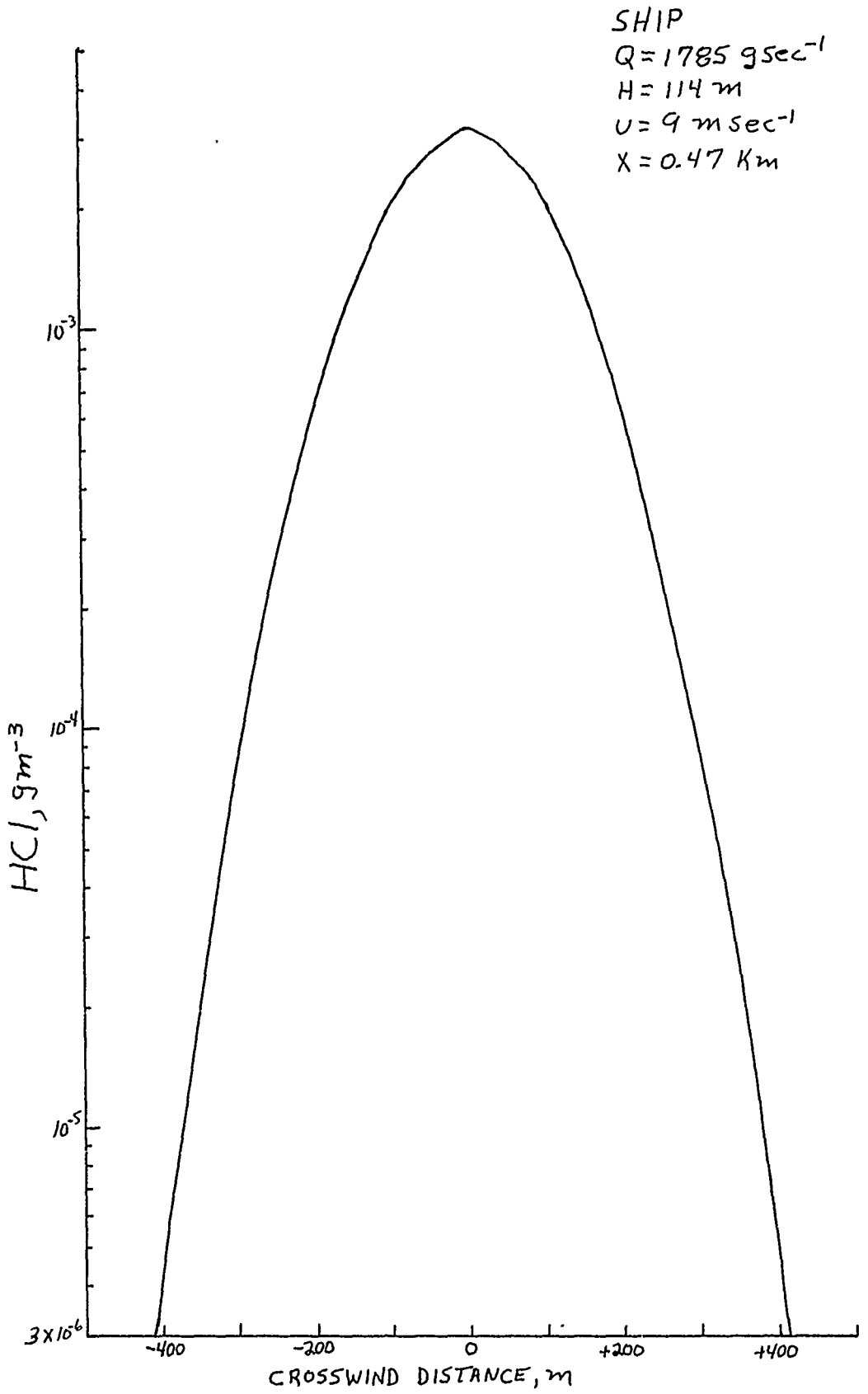



Figure K-6. Horizontal HCl concentration 0.47 km downwind, ship incinerator.

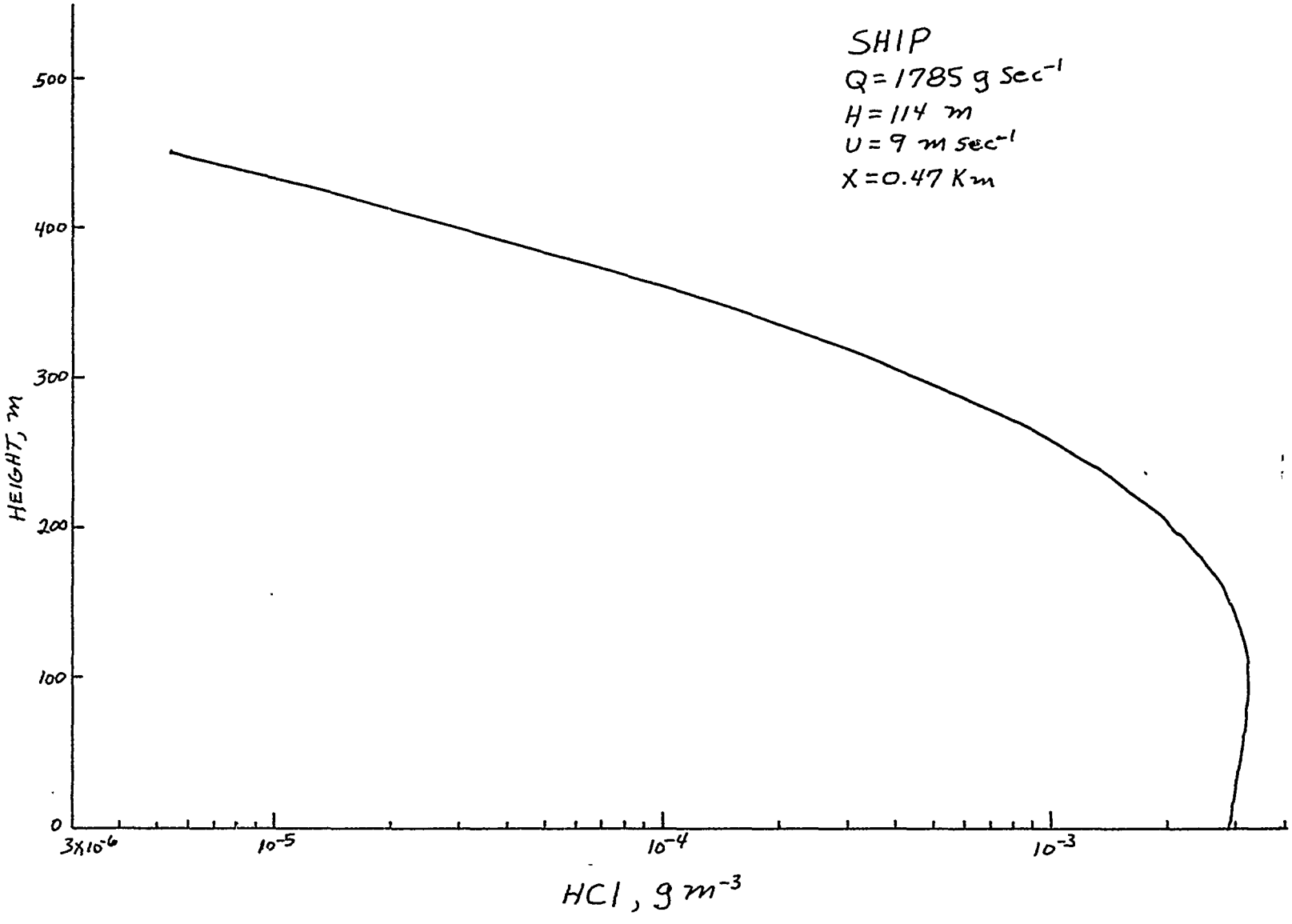



Figure K-7. Vertical HCl concentration at 0.47 km downwind, ship incinerator.

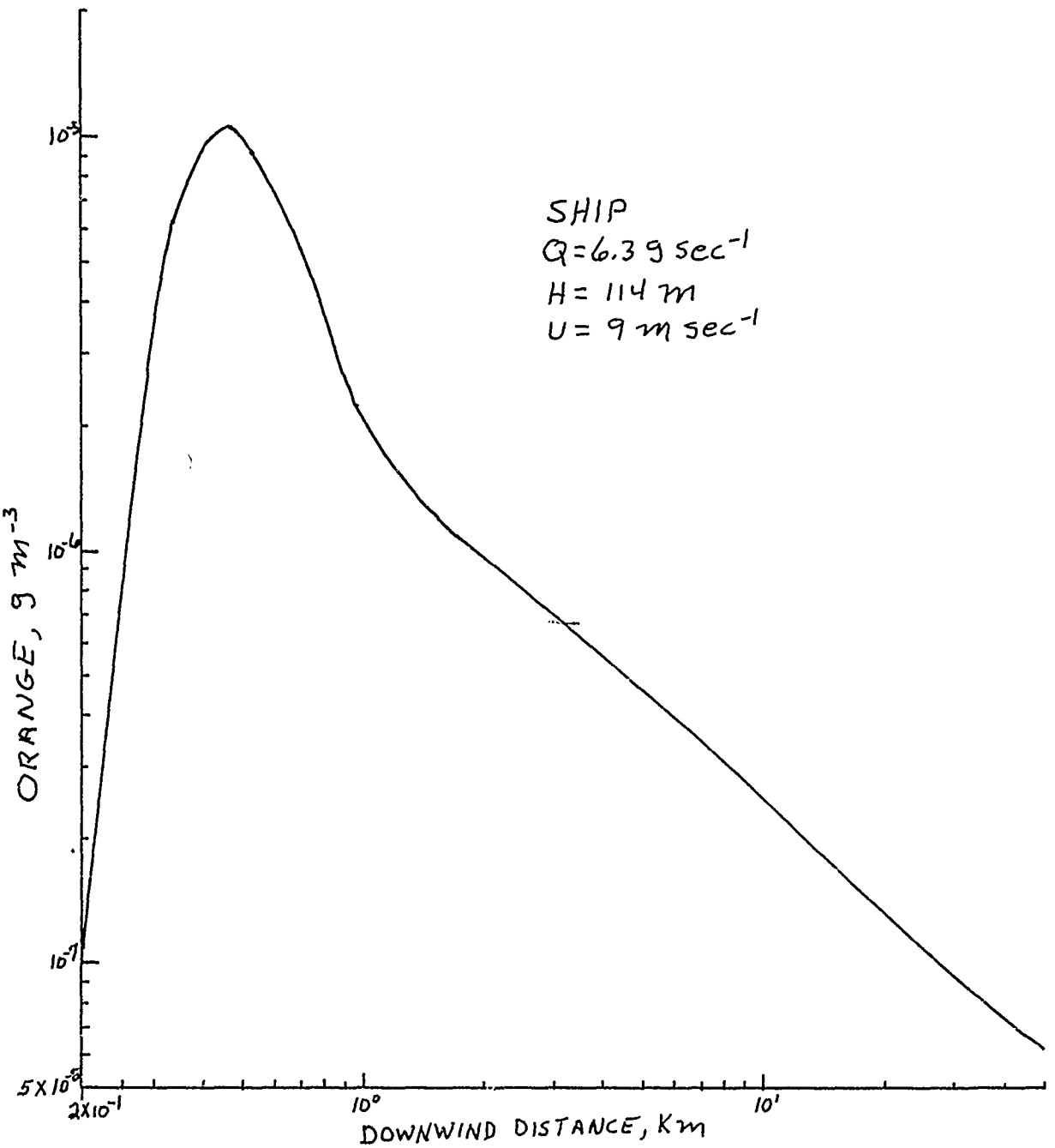



Figure K-8. Center line ground lever Orange herbicide concentration, ship incinerator.

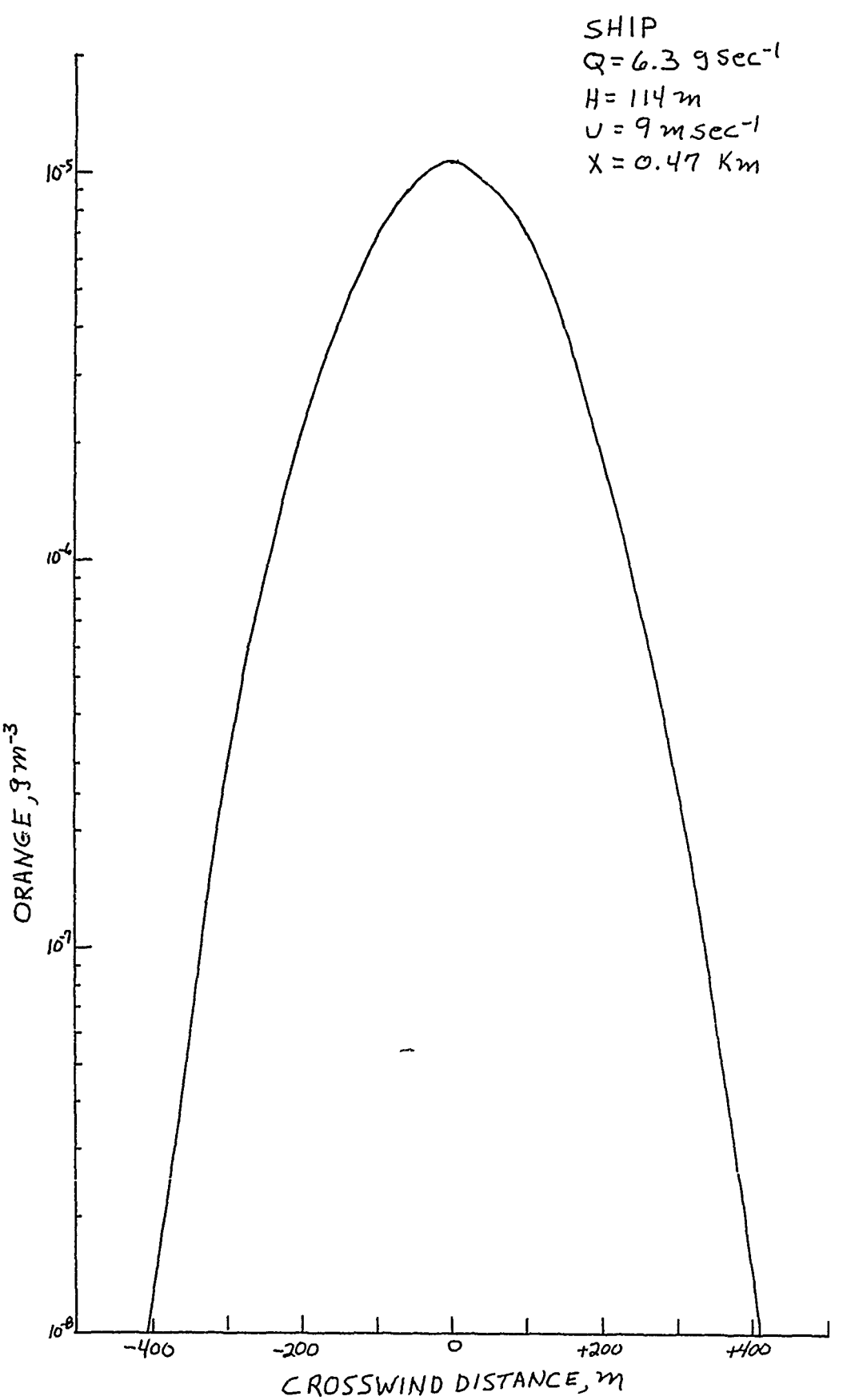



Figure K-9. Horizontal Orange herbicide concentration at 0.47 km downwind, ship incinerator.

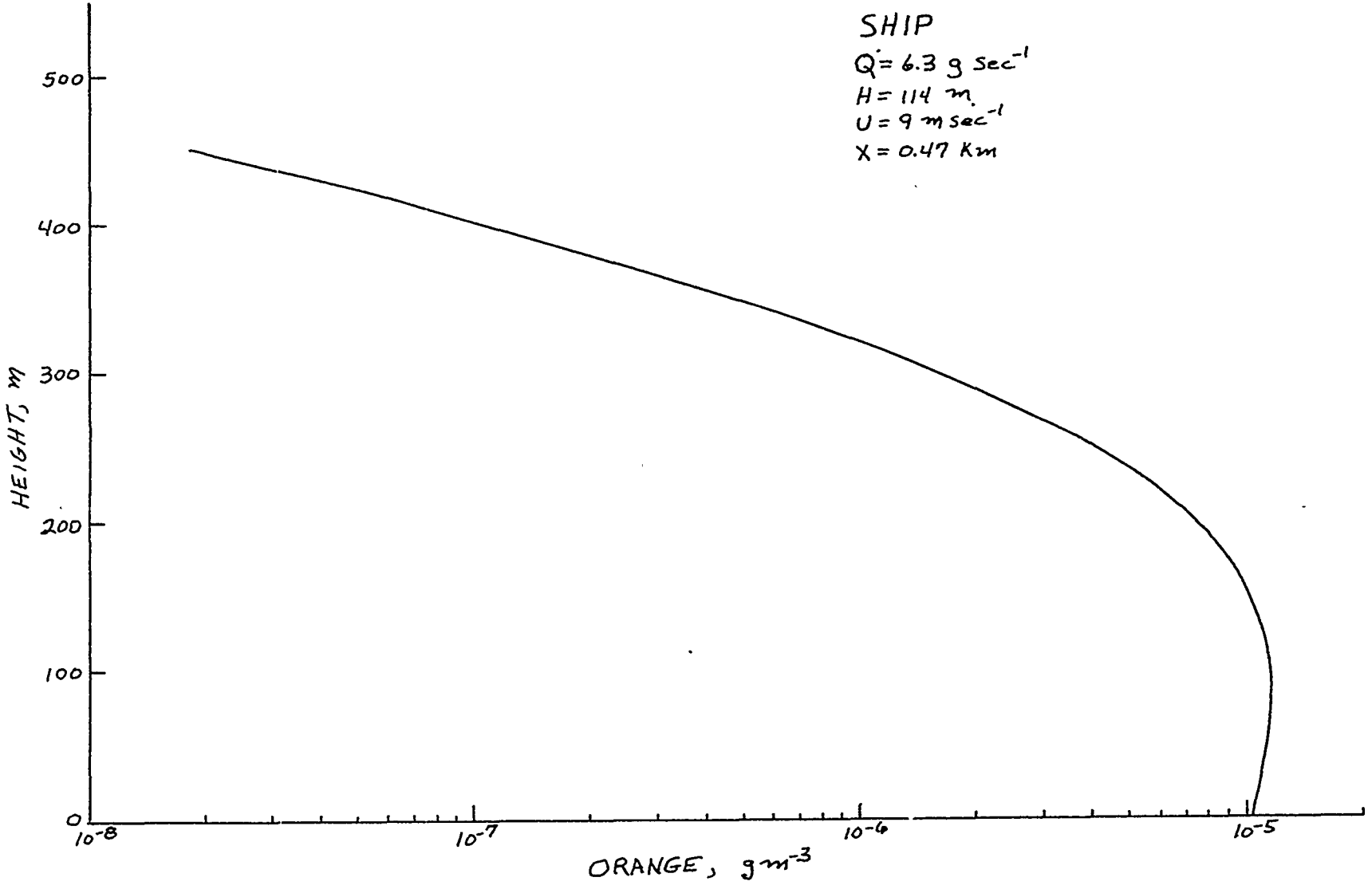



Figure K-10. Vertical Orange herbicide concentration at 0.47 km downwind, ship incinerator.

5. REFERENCES:

Beals, G.A., "Guide to Local Diffusion of Air Pollutants," Air Weather Service Technical Report 214, (1971).

Lydon, D., Plume Rise, USAF Environmental Technical Applications Center Report No 6611, (1973).

Nozaki, K.Y., Mixing Depth Model Using Hourly Surface Observations, USAF Environmental Technical Applications Center Report No 7053, (1973).

Turner, D.B. "Workbook for Atmospheric Dispersion Estimates," US Department of Health, Education and Welfare, Cincinnati, OH, Revised 1969.

"Meteorology and Atomic Energy 1968" United States Atomic Energy Commission.

APPENDIX L

COMMENTS TO:

DRAFT ENVIRONMENTAL STATEMENT -
DISPOSITION OF ORANGE HERBICIDE
BY INCINERATION

January 1972--AF-ES-72-2D

(This Appendix consists of comments received from 9 agencies resulting from their review of the above Draft Statement)

STATE OF MISSISSIPPI
EXECUTIVE CHAMBER
JACKSON

WILLIAM LOWE WALLER
GOVERNOR

February 11, 1972

Honorable Aaron J. Racusin
Acting Assistant Secretary of the Air Force
Installation and Logistics
Office of the Secretary
Department of the Air Force
Washington, D. C. 20330

Re: Draft Environmental Statement-Disposition of Orange Herbicide by Incineration - January 1972--AF-ES-72-2D

Dear Mr. Racusin:

In compliance with applicable regulations, the above captioned environmental statement has been reviewed by appropriate State agencies concerned with various aspects of the disposition. Comments from State agencies are summarized in the latter prepared by the Air and Water Pollution Control Commission, and are enclosed herewith.

It is my opinion that the attached environmental statement is satisfactory.

I recommend that full consideration be given to the comments of our agencies in the final review.

Sincerely,

BILL WALLER
GOVERNOR

# Air & Water Pollution Control Commission

STATE OF MISSISSIPPI

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ASSFIELD
TATE PLANT BOARD
I. T. GUICE, JR., VICE CHAIRMAN
IIL & GAS BOARD
. F. BORTHWICK
OARD OF HEALTH
OE D. BROWN
IARINE CONSERVATION
OMMISSION
/. J. DEMORAN
/. E. GUPTON
ACKSON
IERMIT A. JONES
'ANTON

Glen Wood, Jr.
EXECUTIVE DIRECTOR
POST OFFICE BOX 827 TELEPHONE 354-6783
SIXTH FLOOR ROBERT E. LEE BUILDING
JACKSON, MISSISSIPPI 39205

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JACK PEPPER
CHARLES W. ELSE
YAZOO CITY

ASSOCIATE MEMBERS
STATE PARK SYSTEM
SPENCER E. MEDLIN
A & I BOARD
PAUL BURT
GEOLOGICAL SURVEY
W. H. MOORE

February 8, 1972

Mr. Edward A. May, Jr.
Assistant to the Coordinator
Federal-State Programs
Office of the Governor
510 Lamar Life Building
Jackson, Mississippi

Dear Mr. May:

This letter is in reference to yours of January 26, concerning the draft environmental impact statement entitled "Disposition of Orange Herbicide by Incineration". A meeting was held in our office with concerned agencies of the State on February 3, to conduct a technical review of this statement and to coordinate the state's position in this matter. Copies of the impact statement had previously been forwarded to these agencies.

The consensus of this meeting is enumerated below:

1. Department of the Air Force should explore further possibilities for use of the material under adequate control measures, preferably by the federal government, as in national and state forests or by returning to commercial use through some acceptable channel. Apparently the alternative of giving this material away was not explored. It is felt that destruction of the material would be a needless waste and would create further expense. It is recognized that such action as suggested might require some emergency authority from Environmental Protection Agency but this should pose no great difficulty since a similar material is in everyday use.

2. In the event incineration is taken as the alternative, it is requested that the federal government assume the responsibility for all transportion of the material to the point of incineration and provide all necessary safety measures, such as, but not limited to, shipping materials in small quantities and providing the necessary absorbents at the convenient locations if shipped by rail.

3. It is requested that the material be removed from its present location at Keesler Air Force Base beginning immediately and without regard to the final disposition of the material. It is felt this is absolutely essential because of the proximity of the material to recreational and shellfish waters, as well as large densely populated areas, and further because of the history of hurricanes and tornadoes in that particular section of the country. It is our feeling there are many other areas in the continental United States which would provide a much safer depository for this material.

4. The Mississippi Air and Water Pollution Control Commission should be notified in advance of any proposed movement of the material, of the routes to be taken, and of the safety precautions.

Copies of this statement are being forwarded to all of the involved agencies, as noted on the attached sheet.

Yours very truly,

Glen Wood, Jr.
Executive Director

GWjr:js

Copies furnished:

Mr. Billy Joe Cross, Director
Mississippi Game & Fish Commission
Post Office Box 451
Jackson, Mississippi

Mr. Joe D. Brown, Director
Division of Sanitary Engineering
State Board of Health
Post Office Box 1700
Jackson, Mississippi 39205

Mr. William T. Demoran
Marine Biologist
Gulf Coast Research Lab
Post Office Box AG
Ocean Springs, Miss. 39654

Mr. Bobby R. Tramel
Bureau of Sport Fisheries
and Wildlife
Post Office Drawer FW
State College, Miss. 39762

Mr. Jack W. Pepper, Water Engineer
Mississippi Board of Water Commissioners
416 North State Street
Jackson, Mississippi 39201

Dr. R. A. McLemore, Director
Mississippi Department of Archives and History
Post Office Box 571
Jackson, Mississippi 39205

Attention: Mr. Elbert Hilliard

Colonel Wendell D. Lack, State Forester
Mississippi Forestry Commission
1106 Woolfolk State Office Building
Jackson, Mississippi 39205

Mr. O. T. Guice, Jr., Director
Division of Plant Industry
P. O. Box 5207
State College, Mississippi 39762

Mr. William H. Moore
Director and State Geologist
Mississippi Geological Survey
Post Office Box 4915
Jackson, Mississippi 39216

Mr. Spencer E. Medlin, Comptroller
Mississippi Park System
717 Robert E. Lee Building
Jackson, Mississippi

THE ASSISTANT SECRETARY OF COMMERCE
Washington, D.C. 20230

February 18, 1972

Department of the Air Force
HQ USAF/PREV
Washington, D. C. 20330

Dear Sir:

The draft environmental statement titled "Disposition of Orange Herbicide by Incineration," was received by the Department of Commerce for review and comment.

The Department of Commerce has reviewed the draft environmental statement and has the following comments to offer for consideration.

The key question is the completeness of combustion - i.e., the fraction not exidized but carried up the stack. Once this can be estimated, then there is the atmospheric transport and diffusion problem to a point at the nearest habitation or unrestricted area around the disposal plant. There is a 100 foot stack. Combustion temperature is 2500°F (1400°C) for 3 second dwell (p. 11).

Tentative data show orange decomposes at 900° C. (but how long does it take at this temperature? e.g., water boils at 100° C, but a large pot of water must remain at this temperature for sometime before it boils away). See page 15 - the Illinois plant would release 5% of the HCl as a stack effluent.

The combustion of gasoline in an auto engine is only partially complete - and hydrocarbons are emitted as wastes; i.e. unburnt gasoline. The combustion temperature of an auto is undetermined and the dwell time is about 4 millisec, so the analogy may be poor.

The safety of this operation will also depend on how continuously reliable and constant are the actual temperature/pressure/dwell

conditions inside the burner - because it will take more than a year of continuous burning to complete the job. The constancy, uniformity and reliability of the contractors' facility are therefore important questions which probably should be treated in the statement.

We hope these comments will be of assistance to you in the preparation of the final impact statement.

Sincerely yours,

Sidney R. Galler
Deputy Assistant Secretary
for Environmental Affairs

DEPARTMENT OF AGRICULTURE
OFFICE OF THE SECRETARY
WASHINGTON, D. C. 20250

FEB 22 1972

Mr. Aaron J. Racusin
Acting Assistant Secretary
of the Air Force
Washington, D.C. 20330

Dear Mr. Racusin:

We have reviewed the Draft Environmental Statement on "Disposition of Orange Herbicide by Incineration". Several questions have arisen that you may wish to consider.

The environmental statement does not contain data to show that effluent emissions would not contain biologically active dioxins. Data to show that dioxins are not emitted into the atmosphere must be provided. The statement does not provide for monitoring stack flume emissions from either of the proposed incinerators.

Information should be provided to assure that the orange herbicide remaining in the emptied containers does not have a higher concentration of dioxin than was present in the lot as a whole. Such a situation would arise if the dioxin settles to the bottom of a drum. If that happens, much of the dioxin would go into the soil instead of being combusted.

Damage to vegetation can occur from 2,4-D and 2,4,5-T in the vapor phase. Shipment of orange to the incineration site should be geared to incineration capacity so that large stocks are not kept in storage at the incineration site.

We believe the environmental impact statement must contain data on temperatures required for total combustion. The statement must also identify the effluent gases, and intermediate breakdown products. For example, incomplete combustion may occur when the incinerator is shut down. Intermediate combustion products may be potentially hazardous.



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D-59

The biological activity of the effluent gases must be documented and a scrubbing system specified that will assure safety.

The volume of water into which the sodium chloride is discharged and the rate and volume of fresh water inflow should be specified so that the increased salt content of the water can be determined.

We hope these comments are helpful to you.

Sincerely,

T. C. BYERLY
Assistant Director
Science & Education

Enclosure:
1 copy of Environmental
Statement

EXECUTIVE DEPARTMENT
DIVISION OF PLANNING COORDINATION
BOX 12428, CAPITOL STATION
AUSTIN, TEXAS 78711
PHONE 512 475-2427

ESTON SMITH
GOVERNOR

ED GRISHAM
DIRECTOR

February 25, 1972

Mr. Aaron T. Racusin
Acting Assistant Secretary
of the Air Force
Headquarters USAF/PREV
Washington, D.C. 20330

Dear Mr. Racusin:

The Office of the Governor, Division of Planning Coordination (State Planning and Development Clearinghouse), and affected Texas State agencies have reviewed the draft environmental impact statement for the disposition of Orange herbicide by incineration in Deer Park, Texas.

The Texas Air Control Board presently objects to the proposed project for several reasons which include insufficient technical information in the draft environmental statement and the possible harmful effects to the area by adding additional air pollutants to the atmosphere. The Texas Air Control Board (TACB) has statutory responsibility and authority in matters of air contamination.

The comments received from State agencies are enclosed.

Thank you for the opportunity to review this draft environmental impact statement.

Sincerely,

Ed Grisham

Ed Grisham
Director

EG:gtt

Encl. (4)

cc: Mr. Charles R. Barden, TACB
Mr. James U. Cross, TP&WD
Mr. Hugh C. Yantis, Jr., TWQB
Dr. James E. Peavy, TSDH
Mr. A. T. Traynor, USAF



TI. 5??

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EXECUTIVE DIRECTOR

JOHN H. REAGAN BUILDING
AUSTIN, TEXAS 78701

February 14, 1972

Mr. Ed Coker
Division of Planning Coordination
Executive Department
Capitol Station
Austin, Texas 78711

Dear Mr. Coker:

We have reviewed the draft environmental impact statement for the disposal of Orange Herbicide by incineration, and are in general agreement with the method of disposal and the draft statement.

We would recommend that stack gases be monitored for 2,4-D; 2,4,5-T and dioxin to prevent any escape to the atmosphere. If other precautions are taken to prevent loss or spillage of the barrels and if the empty barrels are disposed of properly, the Parks and Wildlife Department would not object to the incineration of Orange Herbicide.

We appreciate having had the opportunity to comment on this draft statement.

Sincerely,

James U. Cross

JAMES U. CROSS
Executive Director

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FEB 15 1972
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A.C. 512

314 WEST 11TH STREET 78701
P.O. BOX 13246 CAPITOL STATION 78711
AUSTIN, TEXAS

February 1, 1972

Mr. Ed Grisham, Director
Division of Planning Coordination
Office of the Governor
Capitol Station
Austin, Texas 78711

Dear Mr. Grisham:

In response to your memorandum of January 26, 1972, I would like to restate the comments of our letter of November 10, 1971, a copy of which is included in the Draft Environmental Statement for the Disposition of Orange Herbicide by Incineration by the Department of the Air Force.

In restating our previous opinion, I would like to suggest that insofar as water quality is concerned, no environmental statement or special permission is required so long as the disposal by Rollins Purle is carried out within the conditions of waste control order No. 01429 and so long as the solid waste disposal of decontaminated drums is carried out pursuant to state statute. It should be understood that if the disposal of either the Orange herbicide or the drums was proposed to be carried out contrary to state statutes, then this office would decline to authorize the disposal.

Very truly yours,

Hugh C. Yantis, Jr.
Executive Director

HCYjr:go

ccs: All Board Members - Texas Water Quality Board
Mr. Josiah Whea., Legal Counsel, TWQB

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# Texas State Department of Health

JAMES E. PEAVY, M.D., M.P.H.
COMMISSIONER OF HEALTH

J. B. COPELAND, M.D.
DEPUTY COMMISSIONER

AUSTIN, TEXAS

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ROYCE E. WISENBAKER, M. S. ENG.

February 15, 1972

Honorable Preston Smith
Governor of Texas
State Capitol
Austin, Texas 78701

ATTENTION: Mr. Ed Grisham

Dear Governor Smith:

The Draft Environmental Statement for the "Disposition of Orange Herbicide by Incineration," prepared by the Department of the Air Force has been reviewed by this Department.

In considering the proposal with regards to possible pollution of the waters of the State, we are in accord with the viewpoints expressed by Mr. Hugh C. Yantis, Jr., Executive Director of the Texas Water Quality Board, in his letter of February 1, 1972, to Mr. Ed Grisham, Director of your Division of Planning Coordination. Mr. Yantis stated that if the project is carried out in such a manner as to control the discharge so that the limitations set forth in Waste Control Order Number 01429 are not exceeded, no conditions will exist which will require special or extra permission.

However, when disposal by incineration is viewed from the standpoint of potential adverse air pollution conditions, we concur with the statements and recommendations offered by Mr. Charles R. Barden, Deputy Commissioner of the Air Control Section of this Department, who also serves as Executive Secretary of the Texas Air Control Board.

Respectfully,

J. E. Peavy, M.D.
Commissioner of Health

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# TEXAS AIR CONTROL BOARD

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AUSTIN, TEXAS – 78756

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February 14, 1972

Mr. Ed Grisham, Director
Division of Planning Coordination
Office of the Governor
Capitol Station
Austin, Texas 78711

Dear Ed:

Following are our comments on the Draft Environmental Impact Statement for Disposition of Orange Herbicide by Incineration, prepared by the Department of the Air Force in January, 1972:

"Information received since the draft environmental statement on the incineration of Orange herbicide from Kelly Air Force Base was written in October of 1971 makes it inadvisable to allow this operation to be conducted in the State of Texas at this time.

The following factors were considered in evaluating the proposal to incinerate the Orange herbicide in the Rollins Purle incinerator in Deer Park, Texas:

1. The information submitted in the impact statement does not indicate that alternate methods of disposing of the herbicide have been thoroughly explored, or that these methods will be more harmful to the environment than burning the herbicide would be.

2. Technical information submitted with the impact statement is insufficient to determine the feasibility of destroying great quantities of Orange herbicide by incineration. Although the impact statement indicates


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that Rollins Purle, Incorporated will comply with air pollution control regulations, methods of compliance and technical data are lacking; and no mention is made of laboratory facilities or the analytical capability of the Rollins Purle facility. On page twelve of the impact statement, the gravity of the problem is indicated by reference to the need for complete destruction of the Orange material in order to avoid contamination of the environment with hazardous combustion materials or unburned herbicide chemicals. The next sentence reveals that combustion stack emissions and liquid effluent monitoring systems and test methods have not yet been developed. The ultimate responsibility for technical errors and accidents is not clear.

3. The area around the proposed site of incineration, Air Quality Region VII, is a highly industrialized area which has relatively high concentration of air pollutants. The addition of combustion products from the incineration of over two million gallons of Orange herbicide into the atmosphere of this area over a prolonged period could compound an existing problem and might very well prove harmful. It might be desirable to explore the possibility of incinerating the Orange in a federally-owned facility located in a relatively unpopulated area.

In view of the factors enumerated above, we feel that the destruction of Orange herbicide in the State of Texas, as outlined in the Air Force impact statement, would be imprudent at this time."

We appreciate the opportunity to comment on this project. If I may be of further service to you, please let me know.

Sincerely yours,

Charles R. Barden, P.E.
Executive Secretary
Texas Air Control Board

cc: Mr. Jim Menke, Regional Supervisor, Baytown Regional Office

Robert Seamans
Secretary of the Air Force
Washington, D.C.

1 March 1972 MAR 4 RECD

Dear Mr Seamans: Subject: DISPOSITION OF ORANGE BY INCINERATION

A letter from John J Shaughnessy, Colonel, USAF, Chief Plans Group, Office of Legislative Liaison, to the US Congressman James W Symington on 11 February 1972, did invite comments from the citizens regarding the above subject as outlined within AF-ES-72-2D January 1972.

I take the following exceptions to the basic study:

1. The basic "SUMMARY SHEET", page 1, paragraph 3, in part; the description of the size and location of one incineration plant, located on a 200 acre site just Southeast of Houston, in a city called Deer Park, Texas, and then describes a second incineration plant located at Sauget, Illinois.

(a) This would infer that the plant described at Deer Park, Texas is just Southeast of Houston, Texas, a well known city, and it also infers the second plant is located at Sauget, Illinois and where is Sauget, Illinois?

(b) If you start searching for this city of Sauget, Illinois, you will not find it on any road map of the state of Illinois, but if you should find a blow-up map of the St Louis, Missouri and its metropolitan area, you might notice a small city located across the Mississippi River from the Corps of Engineers, whose mooring and base depot is located at the foot of Arsenal Street and only one block further, the Headquarters of one of the major USAF Agencies, The Aeronautical Chart and Information Center, located at Second and Arsenal Street, St Louis, Missouri.

(c) I invite you to read through the basic report, on pages 10, 11 and 12, you will notice the Deer Park, Texas incinerator stastics:

(1) A COMMERCIAL INCINERATION Plant, capable of burning ORANGE Herbicide.
(2) Located Near Houston, Texas, in a city called Deer Park.
(3) Presently burning liquid waste from the surrounding industrial complex consisting of oil refineries and chemical plants.
(4) The INCINERATOR is located on a 200 acre site, 15 miles from the center of Houston and 4 miles from the nearest population center of Deer Park, that lies to the Southwest of the incinerator.
(5) There is a prevailing wind from the Southeast.
(6) There are 35 people working at this incinerator.
(7) Natural gas is available for fuel, however, the natural combustion properties of the herbicide will provide the fuel required.
(8) ORANGE would normally be mixed with other waste combustib le liquids during the incineration operation.
(9) The incinerator is equipped with caustic scrubbers which convert the hydrogen chloride into sodium chloride (salt).
(10) The incineration of the 2.3 million gallons of herbicide will produce aproximately 44.6 million pounds of carbon dioxide and 12.4 million pounds of salt to be discharged into the surrounding environment.
(11) The daily rate of discharge would be for about 468 days, based on the incineration of 5000 gallons of ORANGE per every 24 hour day.

Subject: DISPOSITION OF ORANGE BY INCINERATION,
AF-ES-72-2D January 1972

(d) I invite you to read further through the basic report, on pages 13, 14 and 15 you will notice the Sauget, Illinois Monsanto Company Chemical Plant's incinerator stastics, the description of the before undescribed facility located within an unknown city!

(1) A Commercial FACTORY that has an incinerator capable of burning ORANGE and its ingredient materials.
(2) Located just across the Mississippi River from St Louis, Missouri, within the city of Sauget, Illinois.
(3) Presently is used to burn in-house and customer-returned contaminated polychorinated byphenols.
(4) The Factory is located on a 134 Acre site, 1.5 miles from the downtown center of St Louis, Missouri, the company has approximately 10 acres of stor age area available.
(5) There is a prevailing wind from the Southeast.
(6) There are 1303 employees working at this manufacturing factory.
(7) The basic report makes no mention of natural gas availability for incineration. (Ed.comment: Natural gas in excess quanities is available to the local gas company for underground storage only during the non cold months, for recycling into their system for cold month residential heating needs).
(8) ORANGE would not be mixed with other waste combustible liquids, during the incineration operation.
(9) The incinerator is not equipped with a caustic scrubber which would convert the hydrogen chloride into sodium chloride (salt), but it has only a system for processing the incinerated products stack exhaust gas through a water wash system including a venturi scrubber which diffuses the gases with water, to wash out 95% of the hydrogen chloride as a liquid effluent and discharges this into a municipal waste plant, then into the Mississippi River about 1 mile away.
(10) The incineration of the 2.3 million gallons of ORANGE will produce approximately the same 44.6 million pounds of carbon dioxide, but without caustic scrubbers and processed only through a water wash system, followed by the use of a venturi scrubber, this will release the unrecovered 5% of the hydrogen chloride along with a voluminous amount of water vapor to condense into varied concentrations of Hydrochloric Acid Mist fallout. The amounts to be considered is not referenced in the report, but is dismissed by:"This liquid effluent and stack discharge is within the existing permit limits".
(11) The daily rate of discharge would depend upon the industrial factory need to dispose of their own waste material in an incinerator whose capicity is only 2880 gallons every 24 hour period, and if this capicity is used only to incinerate ORANGE, it would take over 800 days.

(e) My excention to this basic paragraph is, why didn't the SUMMARY SHEET state this, instead of trying to leave the insinuation that Sauget, Illinois is just some small place, where no one has ever heard of, and probably would assume it is located out in the back country. If you would consider a 15 mile radius circle drawn about Sauget, Illinois, you would discover a metropolitan area with a population of much more than 1 millón people. At Deer Park you would discover thi. same 15 mile circle encloses a much smaller population due to the location of Deer Park 15 Miles from Houston, and the incinerator plant falls within the area of the "Tideland Oil Area", where a large concentration of oil wells may be found, as well as the surrounding area is semi-salt marsh flat, that is sparsely populated.

Subject: DISPOSITION OF ORANGE BY INCINERATION.
AF-ES-72-2D January 1972.

2. The basic study's request for comment from the Governmental Agencies: Why was not the State of Missouri, The County of St Louis and/or The City of St Louis requested to comment on the effect of this incineration of the ORANGE would have on their enviroment, especially since they have a pollution code more restrictive that that of the State of Illinois or the U.S.Government.

3. The question of water dilution of the 95% of the Hydrogen Chloride into the waste treatment plant in the form of Hydrochloric Acid, and then passed on into the Mississippi River? What effect would this have on the fish, the water fowl, the people downstream who depend on the water from the Mississippi River for the water they drink? What effect would this have on the National Goal of reaching the secondary sewa ge treatment system by 1975.

4. If the Sauget, Illinois Monsanto Company Plant's incinerator would be selected to dispose of this ORANGE, what security could be given that a 100% destruction of this herbicide could be accomplished? If an almost impossible 99% destruction was obtained, this would release 23,389 gallons of pure ORANGE in a vaporous state being discharged into the atsmosphere, along with the 5% of the Hydrogen Chloride reported volume that could not be recovered which would also be air discharged along with a tremendous quanity of water vapor to be dispersed over the metropolitan area of St Louis, where this 1 million plus human persons reside and are employed. One of my concerns is: What would happen if a malfuntion of equipment would result in less than total destruction of this ORANGE, how long of a time span before the reaction in operations to bring to a halt the discharge and remedy would be made available to undo the damage created by such a malfuntion?

5. The alternate methods suggested to dispose of this dangerous materisl. I would offer the following additional methods be considered:

(a) Burial in abandoned salt or sulphur mines, in the same fashion and method used to dispose of hot radioactive waste material.

(b) Burial at sea, in an obsolete ship within an submarine trench, the same method the U.S. Army used to dispose of the unwanted Nerve Gas.

(c) Atomic incineration within an underground cavern with a small atomic energy device, that would produce the necessary destructive heat for the incineration instananeously.

(d) Pumping into either an abandoned or dry oil well drilled to a minimum depth of below 10,000 feet. In a legal sense belongs to the Government since either depletion of oil reserve or dry hole status payments have been allowed for tax purposes to the drilling company.

Mr Seamens, to quote the U.S. Government's stand on envioromental pollution, that pollution is a condition that knows no boundaries, either National, State, Regional or community.

(a) A recent meeting of the NATO Country representatives at Scott AFB, Illinois within 15 Miles of the Downtown St Louis, did discuss, world envioromental pollution problems. It was indicated at that time that the metropolitan St. Louis was the third dirtest, foulest and/or polluted city within the NATO Countries, exceeded only by a city in Turkey and by a city in Northern Europe.

Subject: DISPOSITION OF ORANGE BY INCINERATION.
AF-ES-72-2D January 1972

(b) A recent enviromental study of St Louis Metropolitan area indicated that Sauget, Illinois was located within one of the two heaviest chemically polluted areas within the region under study. Have you read the recent magazine article: A tree grows in Sauget? Where it describes the last lone surving tree within the city, how the shrubs if they grow at all, enter a early dormant period with leaves turning yellow by early summer, how the grass has died completely or is a sick yellow brown depending on how far they may be located from the source of the airbourne pollution, a disaster at its very best, the Monsanto Chemical Company and its incinerator.

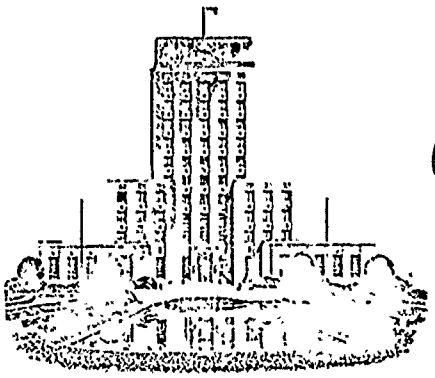
(c) For the location of the second polluted area within the St Louis Metropolitan area, I refer you to the USAF ENVIRONMENTAL HEALTH LABORATORY, McClellan AFB, California, Report No. 69M-10 (Project No. E68-69) July 1969 entitled: Air Pollution Study Aeronautical Chart and Information Center, South Annex, located at 8900 South Broadway, St Louis, Missouri.

In conclusion, I implore you to reconsider some other method of destroying this monstor other than by incineration and releasing the contaminating chemicals into the environment.

Sincerely yours,

Douglas D Thornberry

Douglas D Thornberry
10414 Melvich Drive
St Louis, Missouri
63137



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DEPARTMENT OF PUBLIC HEALTH
1115 N. MACGREGOR
HOUSTON, TEXAS 77025

March 8, 1972

Cliff M. Whitehead, Colonel, USAF
Chief, Environmental Protection Group
Directorate of Civil Engineering
Department of the Air Force
Headquarters United States Air Force
Washington, D. C.

Dear Colonel Whitehead:

The environmental impact statement "Disposition of Orange Herbicide by Incineration, January, 1972" has been carefully reviewed by members of the City of Houston Pollution Control Division. However, we do wish to point out that this facility is not within our jurisdiction. According to the information in this impact statement, the Orange herbicide can be incinerated at 1908° F resulting in the formulation of hydrogen chloride and carbon dioxide. However, this information is based on tentative combustion data awaiting detailed results of a combustion analysis program to be completed by the Department of Agriculture by July, 1972.

In addition the impact statement listed the normal stack discharges for the Rollins Purle plant as carbon dioxide and steam. According to visual observations by our agency smoke discharges from the incinerator indicated that complete combustion is not always attained.

Considering these factors, it is the opinion of this agency that the final combustion data is needed before a decision is made to incinerate the Orange herbicide. Also a complete efficiency study is needed for the Rollins Purle incinerator plant before a decision is made on whether or not it can be incinerated at this facility.

We appreciate the opportunity to comment on this project. If additional information is needed from this agency, please contact our office.

Sincerely,

Victor N. Howard

Victor N. Howard, P. E.
Director
Pollution Control Division

VNH/fh

Read and Approved:

Albert G. Randall

Albert G. Randall, M. D.
Director of Public Health

ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 8 1972

—DCS/P&R
—Asst DCS
—Executive
—Asst Exec
—Asst Exec
—Action
—Susp
—Info

Mr. Aaron J. Racusin
Acting Assistant Secretary
of the Air Force
Office of the Secretary
Headquarters USAF/PREV
Washington, D.C. 20330

Dear Mr. Racusin:

We have reviewed the U.S. Air Force draft environmental impact statement on the disposal of Orange herbicide by incineration.

The proposed action calls for the incineration of 2,338,900 gallons of Orange (including Orange II) herbicide over a 468-day period at either Deer Park, Texas or Sauget, Illinois.

We concur that the process of incineration if properly carried out under the appropriate conditions can effectively reduce the components of Orange to carbon dioxide and hydrochloric acid. However, these two gaseous effluents must be disposed of in such a way that they pose essentially no hazard to the environment. The final impact statement must provide additional information if we are to determine whether or not this project will be carried out in a way which is protective of public health and the environment.

We offer the following specific comments to assist you in the preparation of the final statement:

1. Special precautions should be taken to assure that efficient combustion conditions (product intake, temperature, and retention time) are maintained throughout the operation. These precautions are necessary to insure that the original material plus any intermediate pyrolysis products are burned completely and are not present in the stack effluent. Since the natural combustion properties of the herbicide will provide the fuel required, there should be no mixing of this herbicide with other combustible wastes as suggested for the incinerator in Deer Park, Texas.

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2. The estimate of 468 days for the complete incineration is based on a feed rate of 5,000 gallons a day. If incineration is carried out at Sauget, Illinois, this time period must be increased to over 810 days since the incinerator capacity is only 2,880 gallons per day. No calculations were presented for the total volume of the wash from 42,483 barrels and the time for incineration of that wash.

3. Proper disposition of the hydrochloric acid is necessary if there is to be no adverse effect on the environment. At the Sauget, Illinois, incinerator, the daily volume of hydrochloric acid discharge is not given. Consequently we cannot calculate the concentration of the acid and the pH of the waste water. To assess the ability of the municipal sewer system to handle such a discharge over a long period of time, consideration should be given to the disposal of this waste dilute acid by sale, or free of charge, to companies who have need for such acid rather than disposing of it by sewer system discharge.

On the basis of the documented calculation of $12.4 \times 10^6$ lbs. of sodium chloride produced in Texas, it was calculated for these comments that there will be $7.7 \times 10^6$ lbs. of hydrogen chloride carried off in the liquid effluent at Sauget. For each of the 810 days of operation, this is approximately 9500 lbs. of hydrogen chloride.

The document indicates that approximately 95% of the total hydrogen chloride evolved in the incineration will be scrubbed from the effluent gas, the remaining 5% being exhausted to the atmosphere. Based on the same calculations as were used in the preceding paragraph, this is approximately 500 lbs. per day hydrogen chloride emission. Since the Sauget source is slightly east of a line drawn directly south from downtown St. Louis, and because the document indicates a prevailing southeast wind, it appears likely that this daily emission of 500 lbs. would fall into the area of downtown St. Louis most of the time. Because the draft environmental impact statement has not provided enough operating data on the incinerator at the Illinois site to calculate the concentrations of the hydrogen chloride emissions, it is impossible to accurately determine the effect of this amount of emissions on the surrounding community. It is safe to say however, that such an amount of emissions over such a long period of time could present a potentially serious condition.

It is felt that a correctly sized and operated sodium hydroxide scrubber added to the Sauget system would eliminate the hydrogen chloride problem completely. The sodium chloride and sodium carbonate produced by the scrubber could be disposed of by controlled discharge into the sanitary sewer system or directly into the river. In Deer Park, Texas, the absorption solution will be discharged into Tucker Bayou. There is not enough information to compute the expected plant effluent concentration of salt or sodium carbonate produced by the reaction of sodium hydroxide and carbon dioxide. This is important because salt equilibrium can affect the biota of estuarine systems and especially that of Tucker Bayou which has a variable rate of flow. The release of carbon dioxide into the atmosphere should pose no danger to the environment. We emphasize the necessity and the importance of compliance with Federal, State, and local air and water pollution control regulations.

4. Proper monitoring of the incineration process must be put into effect by both the contractor and the U.S. Air Force. Frequent periodic analyses of the stack gases and liquid effluent for unburned Orange pyrolyses products, hydrogen chloride, carbon dioxide, and ash (if any) must be made to assure that complete combustion is taking place. A technical representative should be present at the incinerator facility throughout the operation to assure that all combustion controls and scrubbers are functioning properly and to check on the monitoring operation and proper operational practices. Any breakdown in control measures or devices must be cause for stoppage of the operation until the problem is corrected.

5. The empty drums should be decontaminated with kerosene and an alkaline detergent and should be allowed to dry before being handled further. The preferred treatment of the drums should be either salvaging for further shipping uses or for smelting as scrap metal. Their disposal in landfill is the least acceptable alternative. If, however, this method of disposal must be used, the landfill site should be located on property so that there is no chance of runoff into streams, lakes, or groundwater systems.

6. The physical movement of 2,338,900 gallons of Orange from its present locations to the ultimate site of disposal is potentially a serious threat to the environment and we feel the draft statement does not give sufficient information on movement details, such as mode of transportation, off-loading, storage at disposal site, spill containment, decontamination, etc. We recommend the following: (1) careful observance of Department of Transportation safety requirements in the transport of hazardous materials; (2) spelling out of specific modes and routes of transportation so as to plan for any contingency that might occur; (3) separate and individual contingency plans covering such items as immediate field detoxification, health and safety considerations of personnel who might be involved in cleanup; (4) a firm written commitment from the transportation contractor that containment equipment is located and available to the contractor during transportation; and (5) pre-designation of the on-scene coordinator prior to any shipment.

Off-loading areas should be equipped with materials and equipment necessary for rapid cleanup, and off-loading equipment should be checked thoroughly before the commencement of each loading or unloading in order to assure safe and dependable operation. Furthermore, responsible persons engaged in off-loading should be given complete instructions in cleanup techniques along with instructions on how to proceed in case of a spill.

While shipment by water is cheaper than land and there has never been a spill during water transport, it might be recognized that material spilled in a waterway would be distributed by the current. A land spill could be much more easily contained. If shipment is made by rail or truck, cleanup teams and equipment should accompany the transport vehicles.

7. If the drums are deteriorating, consideration should be given to either redrumming or transfer to tankcars. As some of the Orange will be held for up to 2 1/2 years at the disposal site, there is question as to the advisability of storing the Orange in drums at all. If the site has suitable bulk storage tanks available, these should be used. Shipping in bulk and building several storage tanks at the site might prove cheaper and safer than redrumming, shipping and storing drums.

Because of the extensive precautions which should be taken during transportation and the possibility of contamination of other cargo in the event of leakage, we feel the use of Orange drums as filler cargo is inadvisable.

8. In the matter of storage, whether in bulk or in drums, only those areas especially designed for storage of hazardous materials should be used. Such areas should provide (1) structures to prevent surface water runoff from entering the area, (2) pavement and gutters to collect surface water runoff within the area, (3) drains to channel contaminated runoff to a holding facility, (4) materials and equipment necessary for rapid cleanup of spills, and (5) fencing to control admission to the areas. In addition, storage areas should be located remotely from occupied dwellings.

9. The alternative of building a new incinerator in a remote region should be examined in detail.

We appreciate the opportunity to review this draft environmental impact statement.

Sincerely yours,

Sheldon Meyers

Sheldon Meyers
Director
Office of Federal Activities



D594

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
WASHINGTON, D.C. 20201

OFFICE OF THE SECRETARY

MAR 13 1972

Mr. Aaron J. Racusin
Acting Assistant Secretary
of the Air Force
(Installations & Logistics)
Washington, D. C. 20330

Dear Mr. Racusin:

The Department of the Air Force draft Environmental Statement for the Disposition of Orange Herbicide by Incineration dated January 1972 has been reviewed. The following comments are offered.

1. The proposal is to destroy 2,338,900 gallons of Orange I and II herbicides by incineration. Orange I is 50/50 (by vol.) butyl 2,4-D and butyl 2,4,5-T. Orange II is 50/50 (by vol.) butyl 2,4-D and Iso-octyl 2,4,5-T. Incinerators to be used are at Houston, Texas and Sauget, Illinois.

2. The project description implies that the herbicide orange must be considered a very hazardous chemical which it actually is not. On the other hand, the polychlorinated dibenzo-p-dioxins which are highly toxic are not given that much attention.

3. On page 6 of the project description a contradiction seems to exist: One sentence suggests that impurities in 2,4,5-T could account for the teratogenicity of that product. The next sentence suggests that both compounds are teratogenic or fetotoxic to experimental animals of various species. This discussion, of course, is very important and should have been clarified, particularly regarding the dose/response data which are available in the literature. It is necessary to have this information on the teratogenicity of the nearly pure 2,4,5-T in mice strains, hamsters and chicks and lack of such effects in rats and rabbits available for comparison with the fetotoxicity of the "dioxin" compound in all species in which it has been tested. The difference in the order of magnitude of toxicity of these chemicals is impressive.



SAFGS FOI,P

4. The major reason for concern exists in the first sentence on page 7 regarding the possible formation of dioxins during incineration. This is considered unlikely based on the acidic conditions and would in any case not lead to any emission into the environment because of the high incineration temperature. This judgment is unwarranted, because data exist on formation of dioxin from precursors (equivalent to breakdown products) during pyrolysis (Higginbotham, et al. Chemical and toxicological evaluations of isolated and synthetic chloro derivatives of dibenzo-p-dioxin. Nature 220: 702-703, 1968) which make it clear that the safety of the process depends entirely on the adequacy of the temperature control. The better known dioxins are stable up to a temperature of 700°C, but will break down at 900°C. Whether that is also true of more highly chlorinated dioxins is unknown. However, the chosen temperature of incineration is to be much higher to assure decomposition. No question is raised about the formation of other compounds, as, for instance, hexachlorobenzene during pyrolysis which may withstand the high temperature for some time. There is knowledge about the existence and persistence of other polychlorinated polycyclic compounds formed on combustion of hydrocarbon in the presence of chlorine. Their toxicity has not been investigated.

5. A combustion analysis program to be carried out in collaboration with the USDA is expected to have results on pyrolysis available by July 1972 to assure complete destruction of the herbicide. Considering the difficulties encountered in determining trace amounts of the dioxins, it seems hard to believe that this program will be able to assure anyone of "complete" destruction of all pyrolysis products. This research activity will also not pay adequate attention to formation and destruction of other so far undescribed polymerization products since the time for completion of the study is too short. As these studies will undoubtedly not utilize the large scale facilities for their research, no information on the function of the actual combustion facility will be available when the program gets started.

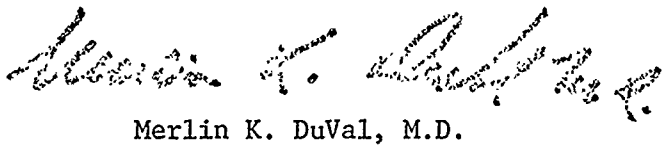
6. Free HCl (hydrochloric acid) should not go into the air and water as occurs at the Sauget, Illinois incinerator but should be converted to a salt such as sodium chloride before disposal.

7. The concern with the disposal of the drums is excessive. They need to be cleaned out as proposed and thereafter could be handled like other drums which contained pesticides and need not be crushed and buried. Their contents never were that toxic.

8. The alternatives to the proposed action are dealt with too quickly. Because a committee of experts has made its recommendations to EPA, alternative 2 and 3 should be re-evaluated. Alternative 8 is not an alternative to the problem since it considers only the disposal of the drums. Alternative 7 in conjunction with 2 and 3 appears to be the safest procedure. Use in the proper manner and degradation in soil, admittedly over an extended period of time, seems to be the best solution, based on the possible hazard of dioxin or other polychlorinated hydrocarbon production during pyrolysis compared to the known hazard of the herbicide which is relatively small.

The opportunity to review this draft environmental impact statement is appreciated.

Sincerely yours,



Merlin K. DuVal, M.D.
Assistant Secretary for
Health and Scientific Affairs

V

DIR CIVIL ENGR
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EXECUTIVE
ASST EXEC
Copy to PREL

# United States Department of the Interior

OFFICE OF THE SECRETARY
WASHINGTON, D.C. 20240

MAY 2 1972

Dear Mr. Racusin:

In response to your letter of January 20, 1972, we have reviewed the draft environmental statement for the proposed disposition of Orange Herbicide at Deer Park, Texas, and Sauget, Illinois.

On page 10, it is stated that the incineration plant is capable of burning Orange Herbicide. However, on pages 11 and 12, we find that a combustion analysis program is underway and that the results of the program will not be available until July 1972. Since municipal incinerators are generally incapable of properly handling materials such as Orange Herbicide, the results of these studies should be made available for comment prior to commencement of this program.

Only two incineration sites were presented in the statement. Some commentary and explanation are required. Of the two incineration plants, the one at Deer Park, Texas, has the advantages of distance from a major population center, larger capacity, and a caustic scrubber. The stack should be taller to permit greater mixing of effluent gases, which will include corrosive hydrogen chloride. About 800 pounds of hydrogen chloride will be emitted daily in stack gases. When combined with moisture of the atmosphere, the resultant hydrochloric acid will attack metals and metal finishes and increase acidity of surrounding waters. This could create a shift of aquatic organisms to more acid-tolerant but less attractive recreational species.

Disposal of the drums by sale as scrap or for reconditioning is not an alternative to the total proposed action; however, it is clearly one of several possible alternatives for disposal of the drums after they are emptied. We feel that every effort should be made to recycle as many drums, or the scrap metal, as possible. Disposal of over 42,000 steel drums in a land fill hardly seems acceptable in today's climate. Guidelines for preparation of drums for recycling or for scrap have been developed. Toxic waste disposal systems have also been developed. Information concerning these systems is available through the National Agricultural Chemicals Association.



D- 594

Finally, we must express concern in regard to the large amounts of sodium chloride (13 tons) and $CO_2$ (45 tons) which will be discharged daily. These discharges will place a considerable additional burden on the air and aquatic environment, and these potential impacts should be fully evaluated prior to issuance of discharge permits. The best available techniques for control of air and water pollution should be used.

The discharge of large amounts of sodium chloride may adversely affect the aquatic environment. At times of low water (drought), this discharge might increase the salinity so as to favor those aquatic species most tolerant to this change and so cause a shift of aquatic organisms. It is also possible that salinity will increase in parts of Galveston Bay so much that parasitism and predation in oyster beds will increase. These effects would be minimized with high dilution and discharge at a time of high water. Applicable State and Federal air and water quality standards should be included in the statement, and the methods used to meet these standards should be described.

The feasibility of processing the sodium chloride for chlorine, sodium, or alkali in a nearby chlor-alkali plant should be discussed, as well as the irretrievable loss of the herbicide, if burned.

We appreciate the opportunity to review this statement.

Sincerely yours,

Deputy Assistant Secretary of the Interior

Mr. Aaron J. Racusin
Acting Assistant Secretary
(Installations and Logistics)
Department of the Air Force
Washington, D. C. 20330

USAF ENVIRONMENTAL HEALTH LABORATORY

KELLY AFB, TEXAS 78241

# APPENDIX M

# BIOLOGICAL MONITORING AND TOXICITY STUDIES IN SUPPORT OF "ORANGE" HERBICIDE INCINERATION TESTS AT THE MARQUARDT COMPANY VAN NUYS, CALIFORNIA

June 1974

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## I. SUMMARY

A. This report describes ecological and toxicological studies performed in support of incineration tests conducted jointly by the United States Air Force and the Marquardt Company. The incineration tests consisted of technical evaluations of a series of eight burns designed to investigate the destruction of "Orange" herbicide by combustion in a full scale, commercial incineration system. This system provided for the scrubbing of effluent combustion gases with a sodium hydroxide or "caustic" solution. No auxiliary fuel was used to incinerate the herbicide. Each of the test burns lasted from 2.27 to 5.93 hours. The ecological and toxicological studies described in this report provided real-time biomonitoring to rapidly detect biologically detrimental effects of the test burns in the area surrounding the incinerator, and to compliment the chemical analyses of spent scrubber water as regards toxicity.

B. Atmospheric biomonitoring methods utilized plants in the area surrounding the incinerator. Observations were made of the local flora in the area in addition to test plants placed in sixteen locations around the incinerator. The 160 test plants used were young tomato plants. Tomato plants are known to be especially sensitive to chlorophenoxy herbicides. Meteorological data was recorded throughout each test burn. The biomonitoring studies revealed no herbicide or other chemical damage to the plants in areas downwind from the incinerator.

C. Biomonitoring of the eight spent scrubber waters consisted of bioassays performed on a representative sample of each test burn. Each sample was composed of numerous portions of spent scrubber water collected throughout the entire length of a test burn. Test animals used in the bioassays were 3-spine sticklebacks (Gasterosteus aculeatus) and brine shrimp (Artemia salina). No unexpected toxic effects were observed. The chlorine produced by incinerating the herbicide (a chlorinated hydrocarbon) was collected as free, available chlorine in the scrubber waters. As expected, free chlorine in the spent scrubber waters produced lethal effects on sticklebacks at 20-35 times the toxicity seen in scrubber waters in which the chlorine had been removed. The bioassays with the spent scrubber waters were compared to similar toxicity studies with artificial spent scrubber water. The "artificial" spent scrubber water was used to establish the toxicity to be expected when aquatic organisms are exposed to such a solution. Also, toxicity studies were performed to determine the effects of osmotic gradients on the test animals. The toxicities seen with the spent scrubber waters in which free chlorine had been removed were not significantly different from the toxicity found with artificial spent scrubber water. Osmotic toxicity studies indicated that unavoidable osmotic effects contributed largely to the toxic effects seen in the spent scrubber waters.

## II. INTRODUCTION

### A. SCOPE OF INVESTIGATION

#### 1. Description of Incineration Tests

a. The ecological studies described in this report were in support of a testing program conducted jointly by the United States Air Force and the Marquardt Company to investigate the destruction of "Orange" herbicide by combustion in a commercial incineration system. Results of the incineration tests were reported separately from the ecological studies. A brief description of the incineration tests is presented in the following paragraphs as background information to clarify the objectives of the ecological studies.

b. Incineration tests were conducted at the Air Force-Marquardt Jet Laboratory at Van Nuys, California between 8 October 1973 and 21 December 1973. A full scale, commercial (Marquardt) incineration system was used. This system contained a combustion gas scrubber which used a sodium hydroxide solution to remove potential air pollutants from the incinerator exhaust. Since "Orange" herbicide is composed of chlorinated hydrocarbons, efficient combustion was expected to produce mainly HCl, $CO_2$, $H_2O$, $Cl_2$, CO, and particulate carbon in the effluent gases. These materials were removed in varying proportions by the scrubber system. The spent scrubber water was stored in holding tanks until chemical analyses and bioassays could determine that release of the material would not result in a water pollution problem. No auxiliary fuel was used to incinerate the "Orange" herbicide. A small amount of natural gas was used to preheat the incinerator before the herbicide was injected into the combustion chamber.

c. The following two paragraphs are direct quotes from the summary of the published report of the incineration study entitled, "Report On The Destruction Of "Orange" Herbicide by Incineration," (April 1974). (Hereafter referred to as the "Incineration Report"). The report was written by the Marquardt Company and the USAF Environmental Health Laboratories at Kelly AFB and McClellan AFB. The two quoted paragraphs summarize the chemical analyses performed during the incineration tests and the final results of the tests.

d. "Extensive sampling and analyses were conducted to quantitate the constituents of the unscrubbed combustion gases, the liquid used to cool and scrub the combustion gases, scrubbed effluent gases, drum cleaning samples, and any solid residues deposited in the system. Samples were analyzed by mass spectroscopy, flame ionization, gas chromatography, and atomic absorption. Process system parameters and noise data were observed and recorded.

e. Test data demonstrated that the "Orange" herbicide was effectively and safely destroyed by incineration; no herbicide feed compounds were found (within the limits of detectability) in any combustion gas,

scrubbed effluent gas, spent scrubber water or combustion chamber deposit sample resulting from incinerator operation (four test burns) while using slot type fuel injection nozzles. Likewise, no herbicide feed compounds were found in samples resulting from incineration operations (four test burns) while using a central poppet type fuel nozzle except for one combustion chamber deposit sample and one spent scrubber water sample. This anomaly was attributed to the characteristics of poppet nozzle fuel injection. From sample analyses data, conclusions were made regarding possible undetectable discharge mass rates of herbicide constituents, effluent biological impact, formation of pyrolyzates and hydrolyzates, and possible criteria for drum cleaning operations. Criteria were also established regarding incinerator noise generation and incinerator process system functions."

2. Scope of Ecological Studies

The purpose of the ecological studies was to determine if the incineration of "Orange" herbicide could be accomplished without untoward effects on the plant and animal life in the vicinity of the incinerator. In addition, the ecological studies were designed to detect early symptoms of improper incinerator operation by real-time biomonitoring and to detect biologically harmful combustion byproducts should any escape detection in the chemical analyses of incinerator effluents. Environmental protection was provided by biomonitoring the two possible routes of contamination: a) spent scrubber water effluent, and b) air contamination downwind from the incinerator stack.

a. Biomonitoring for Contamination of the Spent Scrubber Waters from Each of the 8 Test Burns

The sodium hydroxide solution used in the incinerator's scrubber was expected to efficiently trap the acid gas products of combustion and any undestroyed herbicides or their incomplete combustion products. Bioassays were performed on spent scrubber water from each burn to insure that there was no unusual toxicity caused by the presence of unexpected chemicals in the SSW that might prove harmful to aquatic biota. The spent scrubber water from each individual burn was stored in a holding tank until completed bioassays with fish and brine shrimp together with chemical analyses indicated that it could be safely released into the Marquardt Company's 1.4 million gallon waste water holding reservoir.

b. Ecological Studies to Determine if Biologically Active Emissions Were Produced

Biota in the area of the incinerator was closely observed to provide early detection of downwind air contamination with corrosive chemicals or unoxidized herbicides should the scrubber system not remove

all toxic materials. Records of wind speed and direction were kept for the time period of each burn. The presence of animal life on the Marquardt property was observed and recorded. Condition of native and decorative plants on the Marquardt property and its perimeter was observed and recorded. Also, the condition of 160 tomato plants positioned in 16 stations surrounding the incinerator was closely observed for any damage. These plants were placed in their stations prior to the first burn and then observed for changes in the days following each burn. After the completion of the eight burns, plants selected from areas of highest potential exposure were observed for an additional two week period.

B. METHODS OF SPENT SCRUBBER WATER TREATMENT FOR AQUATIC BIOASSAYS USING STICKLEBACKS AND BRINE SHRIMP

1. Artificial Spent Scrubber Water

a. Aquatic bioassays were utilized as a means of screening for unusually toxic factors that might possibly contaminate the used or "spent" scrubber waters of the 8 test burns. Unexpected toxicity of the scrubber waters could have been caused by a single toxic chemical or by combinations that are synergistic or contain potentiating factors. The results of the aquatic bioassays were reported as an "$LC_{50}$."*

b. To determine the relative toxicity that would normally be expected with a spent scrubber solution, an artificially "spent" scrubber solution (Art. SSW) was used for comparison or "control" bioassays. This artificial spent scrubber water was formulated by using the calculated quantity of hydrochloric acid that would be produced by Orange incineration in relation to other scrubber and incinerator parameters. These parameters were predicted by computer systems analysis for the Marquardt burner when incinerating "Orange" herbicide. Hydrochloric acid, in quantities representing the chlorine disposition from "Orange" herbicide, was added to fresh scrubber water. Then, the pH was adjusted to 7.0 using commercial grade sulfuric acid before this Art SSW was used in bioassays.

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*$LC_{50}$, or Lethal Concentration 50%, is a concentration value statistically derived from the establishment of a dose-related response of experimental organisms to a toxicant. The $LC_{50}$ represents the best estimation of the dose required to produce death in 50% of the organisms. Note that a more toxic chemical has a smaller $LC_{50}$. The time period for which the 50% response was derived must also be indicated. In these tests with SSW, 48 hours was the time of exposure except as noted.

2. Spent Scrubber Water Collection and Treatment

Spent scrubber water from each burn was proportionally sampled and collected in a 55 gallon drum throughout the entire period of each burn. At the end of a burn, a forklift transported the drum to the toxicity testing laboratory. Enough SSW for the bioassays was immediately drawn from the drum and acidified to a pH of 3.5. The SSW was acidified to minimize the potential for alkaline hydrolysis of the relatively toxic herbicide esters should unoxidized herbicides have been present as contaminants. In addition, the acid pH promoted the escape of $Cl_2$ and $CO_2$ as gases. (See Appendix B for discussion of relative toxicity and hydrolysis.) Nitrogen was bubbled through the acidified SSW until tests indicated that available chlorine* was less than 0.2 ppm. Just before use in the bioassays the SSW was adjusted back to pH 7 with unused scrubber water.

C. METHODS AND MATERIALS FOR ON-SITE ANIMAL BIOASSAYS

1. Aquatic Test Animals

a. Fish and crustaceans were used as indicator species in the bioassays of the scrubber waters from the eight test burns. The 3-spine stickleback (Gasterosteus aculeatus) was used as the major bioassay test animal. This species of fish is classed as "moderately sensitive" to pollutants.(5) However, sticklebacks can survive in a remarkable range of salinity extremes.(3) This characteristic made the stickleback an ideal species for use in assaying for toxic materials in the high specific gravity scrubber water. Thus, toxic action due to osmotic effects was de-emphasized, allowing a more concentrated solution of SSW to be used. Further, the sticklebacks were good monitors for "Orange" herbicide components since they were found to be very sensitive to the N-butyl ester of 2,4-D. In toxicity studies at the Environmental Health Laboratory at Kelly AFB, Texas (EHL/K), the 48 Hr, $LC_{50}$ was found to be 0.54 ppm.

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*Free available chlorine. The $LC_{50}$ of the first bioassay using spent scrubber water from burn I (SSW I) was compared with the $LC_{50}$ from the artificial SSW. The material from the actual burn was 20 times more toxic than the reference bioassay using Art SSW. (Art. SSW 48 Hr, $LC_{50}$ = 10.4% vs. SSW I 48 Hr, $LC_{50}$ = 0.53%). This unexpected toxicity was found to be due to free chlorine dissolved in the SSW. Since toxicity of the chlorine could conceal the toxic effects of more pertinent contaminants, the above method was utilized to remove it.

b. The sticklebacks were collected from San Antonio Creek at Vandenberg AFB CA. San Antonio Creek is a pristine stream originating by the base and emptying into the Pacific Ocean. It has clear, cold water with a specific gravity of 1.001. The sticklebacks were collected by seining. Only the smaller, sexually immature fish were retained for use so as to eliminate possible sexually-related metabolic differences that could produce added variations in response to toxicants. Mean fish weight was 245 mg. Mean fish length was 3.1 cm. (See Fish Statistics, Table A-1)

c. The fish were acclimated to the laboratory environment a minimum of 5 days before being used. They were held in 30 gallon all-glass tanks equipped with charcoal and dacron-fluff filters. The fish adapted to captivity very rapidly and in two days were reacting with anticipation whenever anyone approached the tanks with food. The fish were fed Tetramin® flakes twice a day.

d. Brine shrimp (Artemia salina) were hatched at EHL/(K) and transported to Van Nuys in insulated containers oxygenated with battery-operated air pumps. They were fed brewers yeast. Brine shrimp were 15-20 days old when used in the bioassays. The culture medium used for the shrimp was made by adding artificial sea salts* to the conditioned tap water to adjust the specific gravity to 1.022. The resulting brine solution was aerated at least 24 hours before it was used.

2. Animal Bioassay Exposure Procedures

a. Dynamic Bioassays

(1) "Dynamic" or continual-flow bioassays were performed on all the assays which used fish to detect toxicants in the spent scrubber water. A proportional diluter (8),(9) was used to provide five logarithmically-spaced concentrations of each spent scrubber solution. A sixth exposure chamber received 100% diluent water as the control. Two proportional diluters were used for these studies. Appendix Table A-2 shows the resultant dilutions of each.

(2) Bioassays were performed in accordance with principles described in Standard Methods (12) and Sprague (10). Test animals were not fasted prior to testing. However, food was withheld during the actual assay period. Ten fish were used in each of the five concentrations and in the control (60 fish total for each assay). Exposure chambers were plastic rat cages modified to contain 4 liters of diluted toxicant. This provided a ratio of 0.6 gm of fish per liter of water. This is a more favorable ratio

*Marine Land Sea Salts®, Aquatic Systems Inc., East Lake, Ohio

than recommended in Standard Methods (12). The flow of diluted toxicant into each chamber was adjusted to a retention time of 2 hours which was equivalent to a 6 hour, 95% replacement time. This provided a better flow rate than the 8 to 12 hours, 90% replacement time recommendations of Sprague (10) and insured adequate maintenance of the dissolved oxygen concentrations.

(3) Response of test animals was recorded throughout a 48 hour test period except for selected runs in which a 96 hour exposure period was used to confirm the absence of cumulative effects. The quantal response measured was death. A fish was counted as dead when all gill movement ceased. Dissolved oxygen and pH were monitored to insure that the cause of death was not lack of oxygen or changes in pH. Water temperature was maintained at 20°C. Probit analysis was performed on the data recorded at 1, 2, 24 and 48 hours of exposure to evaluate quantal response to graded doses. Replicates were not performed due to time limitations and other material considerations.

b. Static Bioassays

Bioassays with brine shrimp were "static" types in which the experimental concentrations were not replenished during the exposure period. Five brine shrimp were placed in 200 ml of each concentration of spent scrubber water. The SSW was diluted with the same artificial sea water that was used to culture the shrimp. Two replicates of each concentration were used. Graded concentrations ranged from 40% to 100% spent scrubber water.

3. Dilution Water

a. Conditioned tap water was used as the diluent in all of the assays using fish. The water was conditioned in a plastic-lined 55 gallon drum. Initially the drum was filled with hot tap water. Water in the drum was aerated continuously to drive off chlorine gas and maintain a high dissolved oxygen level. Temperature was adjusted to 20°C by pumping the water through a stainless steel coil immersed in a refrigerated water bath. The water was then passed through a charcoal filter before it was pumped to the proportional diluters. The dilution water was repeatedly checked to insure that no chlorine residual remained. The resulting conditioned tap water was a fairly soft water (hardness = 56 mg/l) with a pH of 8.1. Comprehensive analytical characterization of the conditioned water is listed in Table A-3 of the Data Appendix.

b. Dilution water for the brine shrimp static assays was prepared in the same manner as the culture medium used for the shrimp. Artificial sea salts were added to the conditioned tap water to adjust the specific gravity to 1.022. The resulting brine solution was aerated at least 24 hours before it was used.

4. Chemical and Physical Monitoring Techniques

a. Each concentration in each exposure chamber was monitored for several parameters throughout the exposure period. Temperature was measured to insure that it remained at 20°C as dictated by the waterbath temperature control system. pH and dissolved oxygen were monitored to insure that these parameters played no part in the fish mortality. Specific gravity and free available chlorine were also measured in all exposure chambers.

b. The methodology used to measure these parameters is described as follows:

(1) pH: An indicating, recording type pH meter (Analytical Measurements, Model 30WP) was used throughout the study. pH standards of 4.7 and 10 were prepared in the laboratory at EHL/K and used for calibration prior to each period of use.

(2) Temperature: Large scale, laboratory thermometers were placed in the water bath and in each bioassay for a continuous monitoring of the desired 20°C. Readings were taken at least 6 times per day to insure proper operation of the bath and bioassay systems.

(3) Dissolved Oxygen: A Yellow Springs Instrument Company, Model 51A Dissolved Oxygen Meter was used in the survey. Calibration was accomplished prior to each use. Measurements of each concentration were taken at 0 time, 24 and 48 hours, during each bioassay. Dissolved oxygen measurements were taken of holding and acclimation aquaria repeatedly throughout the study.

(4) Chlorine: A Prism Viewing, Color Comparator, Federal Stock #6630-087-1838 (O.T. Kit) was used throughout the survey. This test uses a color reaction produced with Orthotolidine to measure the presence of free available chlorine in concentrations larger than 0.2 ppm. Concentrations smaller than 0.2 ppm were detectable as a slight color change.

(5) Specific Gravity: A Urinalysis Hydrometer was used to measure specific gravity of each dilution in the test chambers. The highest value measurable with this hydrometer is 1.060. The more dense, undiluted solutions of spent scrubber water were weighed to determine specific gravity.

5. Treatment of Data

$LC_{50}$'s were determined by the probit analysis method of Litchfield and Wilcoxon. (6) Confidence limits for the $LC_{50}$ were not calculated because each assay for each individual spent scrubber water was not replicated, nor was it possible to repeat each assay for more balanced

and statistically satisfying partial responses on each side of the $LC_{50}$ point. Each of the dynamic assays resulted in definitive dose-related responses. With the dynamic assays, no deaths occurred in the control fish so that no weighted correction factors were used. $LC_{50}$'s and the slopes of the dose response curves are listed in Table A-4 in the Data Appendix. Other statistical treatments such as variance and standard error of the mean used standard formulas. (4)

## D. METHODS AND MATERIALS FOR ON-SITE ECOLOGICAL OBSERVATIONS

### 1. Ecological Biomonitoring

a. The species of each animal sighted on Marquardt property was noted in the logbook used to maintain all observations. Plant life on the Marquardt property and the surrounding perimeter was monitored before, during and after the burns. The plant life was observed in order to detect any symptoms of auxin-like changes should chlorophenoxy herbicides contaminate the incinerator exhaust. Damage that could result from air contamination with corrosive chemicals such as chlorine or hydrochloric acid was also closely looked for during the observation period.

b. In addition to native and decorative plants, young tomato plants (which are sensitive to highly chlorophenoxy herbicides) were used as bioassay organisms during the monitoring period. One hundred and sixty young plants (2 months old) were divided into groups of 10 and placed at 16 different stations around the test incinerator. The condition of the indicator plants was carefully recorded. Special care was taken to look for auxin-like and corrosive chemical damage. The height of each plant was periodically measured. During each of the eight burns the area around the incinerator was observed to determine which tomato plants were most exposed to the exhaust of the incinerator. On some occasions the steam from the incinerator exhaust was observed to be condensing and the droplets of moisture were falling out onto the tomato plants. After completion of the entire study, plants from six of the stations that received the most exposure were transported back to EHL/K. These plants were observed for two weeks to allow time for any latent damage to appear.

### 2. Meteorological Monitoring

Wind speed, wind direction, and temperature readings were obtained every half hour during the incineration periods by calling Van Nuys Airport Weather Information.

## III. RESULTS AND DISCUSSION

### A. RESULTS OF SPENT SCRUBBER WATER STUDIES

#### 1. General Characteristics of the Spent Scrubber Waters

a. The spent scrubber waters (SSW) from the eight burns had a temperature of 164°F at the scrubber outlet collection point. Their pH values ranged from 10.5 to 11.8 and the average specific gravity was 1.057. Available chlorine concentrations ranged from 250-500 mg/l. Available chlorine existed completely as the "free" chlorine moity and none as "combined" available chlorine (12) Table A-5 in the Data Appendix lists other parameter ranges. Sample collection procedures and detailed analytical results are described in the incineration report.

b. The major characteristics described above could reasonably account for severe detrimental effects on aquatic organisms should the scrubber effluent empty directly into a natural body of water. In actual industrial operations some form of treatment is usually used to reduce or eliminate the effects of thermal pollution and acid-base shifts. Free available chlorine can also be removed. However, chlorine is so reactive that its effects are transitory and, in a limited "mixing zone", are often considered acceptable. In most of the bioassays in this study, chlorine was physically removed. The chlorine removal process and pH adjustment increased the average specific gravity of the SSWs from 1.057 to 1.068.

#### 2. Sensitivity of Aquatic Bioassays

a. The general characteristics of SSW mentioned above produced inherent toxic effects on the aquatic test animals that, in effect, reduced the sensitivity of the assays for unknown toxicants. Therefore, the assays could only be expected to reveal the presence of acute, relatively highly toxic contaminants or combinations of contaminants. Based on previous aquatic studies with 2,4-D 2,4,5-T and their esters, the realistic assumption was that toxic effects of significantly toxic contaminants would be additive with the toxic effects normally expected from the high specific gravity scrubber waters. Therefore, the presence of a relatively highly toxic contaminant was expected to result in an obviously smaller $LC_{50}$ (increased toxicity) when compared to uncontaminated scrubber waters. The pessimistic assumption would be that no additive effects occurred so that the presence of low concentrations of toxicants such as the N-butyl ester of 2,4-D would not be detected by an obviously lower $LC_{50}$.

b. Assuming no additional effects (the pessimistic assumption) the low level of detectability for the N-butyl ester of 2,4-D was calculated to be 3 ppm in the scrubber waters (available chlorine removed). This detection limit was calculated using the dilution range of 5% to 50% for each assay,

the high toxicity of the ester to Sticklebacks (48 Hr. $LC_{50}$=0.54 ppm), and a mean 48 Hr. $LC_{50}$ of 17.9% for all 8 SSWs.

3. Effect of Available Chlorine on Toxicity

a. In the bioassays of the SSW, temperature and pH were held constant. Available chlorine was removed as described in Part II B of this report. However, a few assays were run without chlorine removal. The comparison of toxicities resulting from the absence or presence of chlorine is striking as shown in Table 1 below.

TABLE I: EFFECT OF AVAILABLE CHLORINE REMOVAL ON TOXICITY OF SSW USED IN BIOASSAYS WITH STICKLEBACK.

| | CHLORINE REMOVAL | 24 Hr. $LC_{50}$ | 48 Hr. $LC_{50}$ |
|---|---|---|---|
| BURN I SSW | Yes | 12.8% | 12.8% |
| BURN I SSW | No | 0.53% | 0.53% |
| BURN III SSW | Yes | 28.8% | 28.8% |
| BURN III SSW | No | 0.84% | 0.84% |
| BURN VI SSW | Yes | 29.5% | 20.5% |
| BURN VI SSW | No | 0.75% | 0.63% |

b. Scrubber waters not bubbled with nitrogen were 20-35 times more toxic. The conclusion that this toxicity was due to available chlorine and not some other factor was based on chlorine measurements of SSW dilutions taken from the exposure chambers. Measurements of 0.4 ppm or greater available chlorine coincided with death in 100% of the fish in those exposure chambers. The 0.4 ppm value for toxic effects is in general accord with chlorine effects observed by other workers. (3),(7)

4. Toxicity of Scrubber Waters (Chlorine Removed)

a. In each bioassay, sticklebacks were exposed to serial dilutions of each scrubber water that ranged from 5% to 50% SSW. The dose-related response of the fish to those concentrations were in the range expected from toxicity due mostly to osmotic effects. To demonstrate the relationship of specific gravity of the scrubber waters to toxicity, new $LC_{50}$ values were calculated based on the specific gravity of the serial dilutions rather than the concentration of SSW. Therefore, the toxicity of SSW from each burn could be considered jointly for dose-response relationships established on the basis of specific gravity and concentration expressed as percent SSW.

TABLE 2

RESULTS OF TOXICITY STUDIES

| MATERIAL TESTED | SP. GRAVITY OF TREATED SSW | 48 HR $LC_{50}$ | | SP. GRAVITY $LC_{50}$ AT 48 Hrs |
|---|---|---|---|---|
| Art. SSW | 1.1270 | 10.4% | | 1.017 |
| SEA SALTS | 1.011-1.032 | NA | | 1.019 |
| BURN I | 1.075 | 12.8% | | 1.014 |
| BURN II | 1.079 | 16.0% | | 1.016 |
| BURN III | 1.061 | 28.8% | | 1.019 |
| BURN IV | 1.063 | 16.5% | | 1.016 |
| BURN V. | 1.076 | 15.5% | | 1.013 |
| BURN VI | 1.060 | 24.4% | | 1.017 |
| BURN VII | 1.076 | 12.5% | | 1.014 |
| BURN VIII | 1.050 | 16.7% | | 1.011 |

b. A completely separate toxicity study was accomplished which established the dose-related response of the sticklebacks to pure differences in specific gravity. This study used a commercial marine salt mixture to compose saline concentrations that produced serial specific gravities ranging from 1.011 to 1.032.

c. The results of all of these studies are summarized in Table 2, "RESULTS OF TOXICITY STUDIES". Comparing the 48 Hr. $LC_{50}$ values shown on Table 2, all 8 SSWs had higher concentrations than the reference "artificial SSW" (Art. SSW). However, the fact that the actual SSWs are less toxic than the Art. SSW is because the Art. SSW has a higher specific gravity than the 8 SSWs. The computer-predicted Art. SSW contained more solutes than the actual SSWs. Had the prediction been more accurate, less dilution would have been required, and the Art. SSW $LC_{50}$ value would probably have fallen somewhere in the range of the $LC_{50}$ of the actual burns.

d. The specific gravity "$LC_{50}$" (S.G. $LC_{50}$) in Table 2 shows that the specific gravity expected to kill 50% of the sticklebacks in 48 hours is 1.019 when the solutes are sea salts. When the solutes are more similar to those found in actual scrubber water, as in Art. SSW, the specific gravity $LC_{50}$ drops to 1.017. Therefore, it is reasonable to assume that the toxicity of the SSWs with S.G. $LC_{50s}$ around 1.017 are primarily due to their osmotic effects. BURNS II, III, IV and VI had SSW S.G. $LC_{50s}$ ranging from 1.016 and 1.019.

e. The specific gravity does-response curve of Art. SSW indicates that a 10% death rate would be expected in sticklebacks exposed to a specific gravity of 1.014 (S.G. $LC_{10}$). BURNS I, V, VII and VIII have S.G. $LC_{50}$ that range from 1.011 to 1.014. Compared to the Art. SSW, these 4 SSWs would be suspected to containing chemicals that contribute an additive effect to the expected osmotic toxicity. However, these studies were not sensitive enough to positively detect such mild effects.

f. The slopes* of the 48 Hr. dose-response curves are similar to the slopes of the dose-response curves for Art. SSW and sea salts. The mean 48 Hr. slope = 1.16 ($\sigma$ = 0.04) for all 8 SSWs plotted on a percent SSW to percent response curve. The slope value for Art. SSW = 1.14. When the responses were replotted against specific gravity, the 48 Hr. slopes of the SSW were still indistinguishable from those of Art. SSW and sea salts. (See Table A-4 Data Appendix)

5. Results of Brine Shrimp Studies

Brine shrimp survived in 100% SSW and all serial dilutions of all 8 SSWs for 24 hours. Beyond 24 hours of exposure, death was sporadic and not relative to concentration so that an $LC_{50}$ could not be calculated.

*Slope of the dose-response function. (6) (Litchfield and Wilcoxon, 1949).

B. RESULTS OF BIOMONITORING STUDIES

1. Results of Local Flora and Fauna Observations

a. The Marquardt Company property is a very large industrial site surrounded by other industrial and aircraft industry operations. A large Air National Guard Base lies on the northwest perimeter of the Marquardt property (See Figure 1). The northern property line is bordered by aircraft hangars. The eastern perimeter is bordered by the Van Nuys Airport runways.

b. All of these industries had sparse or no vegetation on their property. There were a few conifers in front of a hangar just outside the northeast corner of the Marquardt property. The company's unused strip of land on the northern border had little vegetation. The plants present were mainly tumbleweeds and bermuda grass which were mostly dormant. The tumbleweeds had matured and their seeds were apparently the food source for the blackbirds, house finch and mourning doves that fed in the area. The only other animals sighted were numerous domestic cats which had become feral. Other vegetation that was observed during the test burns included a few shrubs on the east perimeter and a variety of decorative plants and trees buildings on the southwest quarter of the Marquardt property. Trees and some shrubbery in a trailer park outside the southwest corner were also observed. Almost all deciduous plants were dormant or becoming dormant because of the late fall season. No effects of chemical damage were observed throughout the period of the test burns on the few plants that were still green.

2. Results of Tomato Plant Biomonitoring Studies

Figure 1 shows the relationship of each station to the incinerator. There were 16 stations; each with 10 tomato plants. Table 3 is a compilation of weather data taken during each burn. During the periods of low wind velocity the wind direction varied considerably. On these occasions the steam plume from the incinerator drifted from one direction to another and would disappear about 200 feed from the stack. An observer standing underneath the plume could feel droplets of moisture falling from the plume. The condensed moisture sometimes fell directly onto the tomato plants of Station 5. On the two days that the wind velocity was 19 mph, the wind remained constant in speed and direction throughout the burns. None of the tomato plants in the downwind areas exhibited symptons of auxin-like effects as would be expected from chlorophenoxy herbicide contamination. Also, no corrosive chemical damage occurred as would be expected had chlorine or hydrochloric acid been an air contaminant (Appendix B). All the plants from Station 5 and five other stations were shipped to EHL/K'after the study. No deleterious effects were noted during the two weeks these plants were held for observation.

FIGURE 1: RELATION OF TOMATO PLANTS TO INCINERATOR

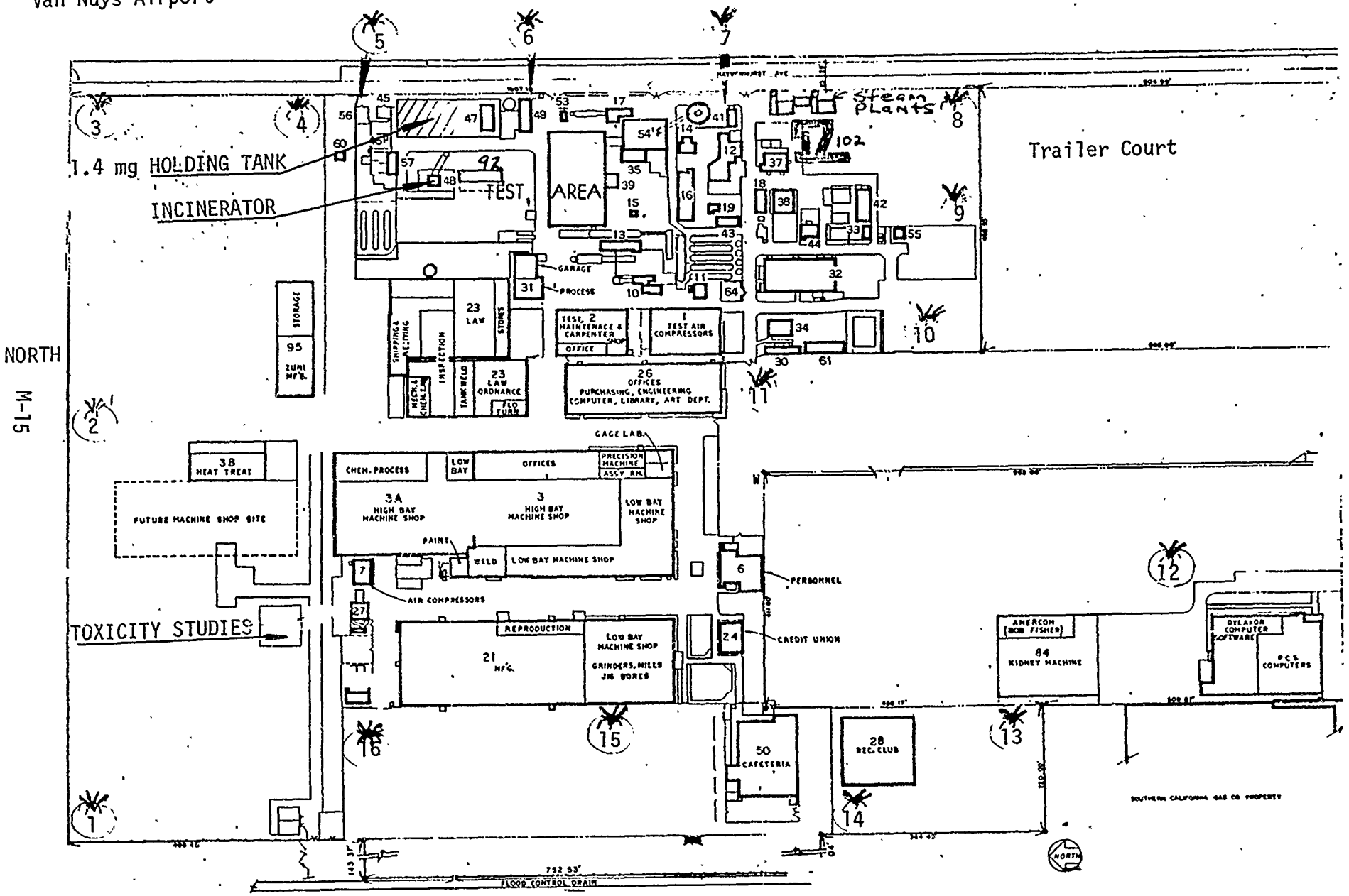


TABLE 3

WIND CONDITIONS DURING TEST BURNS

| BURN NUMBER | DATE | RANGE OF WIND DIRECTION | AVERAGE WIND VELOCITY | TEMPERATURE RANGE F |
|---|---|---|---|---|
| I | 13 Nov | 130°-155° | 7 MPH | 55-64 |
| II | 16 Nov | 120°-180° | 5 MPH | 55-56 |
| III | 19 Nov | 340°-NC° | 19 MPH | 58-NC |
| IV | 20 Nov | 120°-160° | 9 MPH | 62-NC |
| V | 27 Nov | 310°-350° | 6 MPH | 63-69 |
| VI | 28 Nov | 350°-NC | 19 MPH | 60-NC |
| VII | 29 Nov | Calm-varied | 0 | 62-NC |
| VIII | 30 Nov | Calm-150° | 0-12 | 60-62 |

## IV. CONCLUSIONS

a. Sticklebacks, when exposed to graded dilutions of spent scrubber waters from each of the eight test burns, sustained mortalities that were directly related to concentration or dose. Acute mortality was maximal at 12 to 24 hours of exposure so that there was little change in $LC_{50}$ values at times beyond 24 hours. In cases where exposure was extended to 96 hours, there was no increase in mortality with the increase in time of exposure.

b. The acute toxicity studies with sticklebacks indicated that when free available chlorine was removed, the toxicities of the spent scrubber waters were not higher than toxicities expected for solutions with similar osmolality. Therefore, no significant concentrations of acutely toxic contaminants were detected in the spent scrubber waters from the 8 test burns. Also, no effects from synergistic or potentiating combinations of chemicals were observed.

c. Osmotic toxicity studies indicated that unavoidable osmotic effects contributed largely to the toxic effects exhibited by the spent scrubber waters.

d. Free chlorine in the spent scrubber waters produced lethal effects on sticklebacks at 20-35 times the toxicities seen in scrubber waters in which the chlorine had been removed. Free available chlorine in the spent scrubber waters is a highly toxic factor that can be removed by proper treatment of such an industrial waste.

e. Observations of local plant life and sensitive biomonitor tomato plants demonstrated that the 8 test burns produced no herbicide or chemical damage to plant life surrounding the incinerator.

## V. BIBLIOGRAPHY


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# APPENDIX A
# (TO APPENDIX M)

# DATA APPENDIX

TABLE A-1

FISH STATISTICS

| | | Weight in Gms | Length* in Cm |
|---|---|---|---|
| | Arithmetic Mean | 0.246 | 3.1 |
| | Standard Deviation | 0.1013 | 0.442 |
| | Variance | 0.01026 | 0.196 |
| | Standard Error of Mean | 0.0320 | 0.140 |
| (95%) | Upper Confidence Limit | 0.31816 | 3.42 |
| (95%) | Lower Confidence Limit | 0.17326 | 2.80 |
| | Maximum Value | 0.433 | 3.9 |
| | Minimum Value | 0.115 | 2.5 |
| | Range | 0.318 | 1.4 |
| | Number of Values | 10 | 10 |

*Fork Length as reported by Carlander[3] indicates a size typical of Sticklebacks 3-4 months old.

TABLE A-2

SERIAL DILUTIONS PRODUCED BY PROPORTIONAL DILUTERS
{Mount & Brungs(8),(9)}

| DILUTER NO. 4 | CONCENTRATION EXPRESSED AS PERCENT OF THE STOCK SOLUTION* |
|---|---|
| 1 | 0% Control |
| 2 | 14% |
| 3 | 19% |
| 4 | 32% |
| 5 | 58% |
| 6 | 100% |

| DILUTER NO. 5 | |
|---|---|
| 1 | 0% Control |
| 2 | 11% |
| 3 | 19% |
| 4 | 32% |
| 5 | 58% |
| 6 | 100% |

*Stock Solution for SSWs with Chlorine removed consisted of 50% SSW.

TABLE A - 3

RESULTS OF ANALYSES OF DILUTION WATER

(units in mg/L unless noted)

| ITEM | LAB ANALYSIS (mg/l unless noted) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1. COLOR | | 0 | 1 | 5 | • | Units | | | |
| 2. TURBIDITY | | 0 | 0 | 5 | • | Units | | | |
| 3. CHEMICAL OXYGEN DEMAND | 0 | 0 | 0 | 1 | 1 | • | | | |
| 4. DISSOLVED SOLIDS | | 0 | 1 | 8 | 8 | • | | | |
| 5. TOTAL SUSPENDED MATTER | | | | | | • | | | |
| 6. VOLATILE & FIXED SUSP MATTER | | | | | | • | | | |
| 7. OILS & GREASES (Infrared Method) | | | | 0 | 0 | • | 5 | | |
| 8. SURFACTANTS (As mg/L LAS) | | | | 0 | 0 | • | 1 | | |
| 9. PHENOLS | | | | | < | • | 0 | 0 | 1 |
| 10. CHLORIDES | | | 0 | 2 | 0 | • | | | |
| 11. FLUORIDES | | | | | 0 | • | 4 | | |
| 12. NITRATES | | | | < | 1 | • | | | |
| 13. PHOSPHATES | | | 0 | 0 | 1 | • | 0 | | |
| 14. SULFATES | | | 0 | 2 | 6 | • | | | |
| 15. CADMIUM | | | | | | • | 0 | 4 | |
| 16. CHROMIUM (HEXAVALENT) | | | | | < | • | 0 | 1 | |
| 17. CHROMIUM (TOTAL) | | | | | < | • | 0 | 5 | |
| 18. COPPER | | | | | < | • | 0 | 2 | |
| 19. CYANIDES | | | | | < | • | 0 | 1 | |
| 20. IRON | | | | | < | • | 1 | | |
| 21. LEAD | | | | | < | • | 0 | 5 | |
| 22. MANGANESE | | | | | < | • | 0 | 5 | |
| 23. SILVER | | | | | < | • | 0 | 1 | |
| 24. ZINC | | | | | < | • | 0 | 5 | |
| 25. Mercury | | | | | < | • | 0 | 0 | 5 |
| 26. Total Organic Carbon | | | | < | 1 | • | | | |

27. Hardness (EDTA as Mg/L $CaCO_3$)=64
28. pH=8.3
29. Specific Gravity=1.005

TABLE A-4 RESULTS OF TOXICITY STUDIES

| MATERIAL TESTED | SP. GRAVITY OF $CL_2$RxED SSW | 24 HR $LC_{50}$ | 48 HR $LC_{50}$ | SLOPE of 48 HR | SP. GRAVITY $LC_{50}$ AT 24 HRS | SP. GRAVITY $LC_{50}$ AT 48 HRS | SLOPE OF 48 HR | SP. GRAVITY OF SOL THAT 100% DEATHS IN 48 HRS | SP. GRAVITY OF SOL THAT NO DEATHS IN 48 HRS |
|---|---|---|---|---|---|---|---|---|---|
| Art. SSW | 1.1270 | 11.5% | 10.4% | 1.14 | 1.018 | 1.017 | 1.0018 | 1.023 | 1.012 |
| SEA SALTS | 1.011-1.032 | NA | NA | - | 1.019 | 1.019 | 1.0018 | 1.025 | 1.015 |
| BURN I | 1.075 | 17.5% | 12.8% | 1.15 | 1.014 | 1.014 | 1.0016 | 1.019 | 1.009 |
| BURN II | 1.079 | 17.4% | 16.0% | 1.21 | 1.017 | 1.016 | 1.0027 | 1.027 | 1.010 |
| BURN III | 1.061 | 28.8% | 28.8% | 1.16 | 1.019 | 1.019 | 1.0014 | 1.024 | 1.015 |
| BURN IV | 1.063 | 26.5% | 16.5% | 1.15 | 1.016 | 1.016 | 1.0018 | 1.021 | 1.011 |
| BURN V | 1.076 | 15.5% | 15.5% | 1.18 | 1.013 | 1.013 | 1.0023 | 1.023 | 1.008 |
| BURN VI | 1.060 | 29.5% | 24.4% | 1.14 | 1.021 | 1.017 | 1.0020 | 1.024 | 1.008 |
| BURN VII | 1.076 | 12.5% | 12.5% | 1.10 | 1.014 | 1.014 | 1.0022 | 1.016 | 1.009 |
| BURN VIII | 1.050 | 24.3% | 16.7% | 1.22 | 1.013 | 1.011 | 1.0023 | 1.016 | 1.005 |
| | | | | X=1.16 | | | X=1.0020 | | |
| | | | | 6 = 0.04 | | | 6 = 0.004 | | |

TABLE A-5: RANGE OF SSW PARAMETERS FOR ALL 8 BURNS

| Parameter (mg/l unless noted) | Range of Quality |
|---|---|
| Temperature ($^{\circ}$F) when collected | 164 |
| pH | 10.5 - 11.8 |
| Specific Gravity | 1.044 - 1.073 |
| Specific Conductances (pmho/cm) | 11.3 -15.8 |
| Total Solids or Total Dissolved Solids (x $10^3$) | 61-87 |
| Suspended Solids | 56-97 |
| Chlorides (x$10^3$) | 16.5 -28.0 |
| Free and Total Chlorine Residuals | 250-500 |
| Sodium (x $10^3$) | 32-38 |
| Iron, Total | 3.0 - 5.0 |
| Total Alkalinity (x $10^3$ as $CaCO_3$) | 32.0 - 52.5 |
| Carbonate Alkalinity (x $10^3$ as $CaCO_3$) | 22.4 - 36.4 |
| Hydroxyl Alkalinity (x $10^3$ as $CaCO_3$) | 9.6 - 16.1 |
| Bicarbonate Alkalinity (x $10^3$ as $CaCO_3$) | 0 |

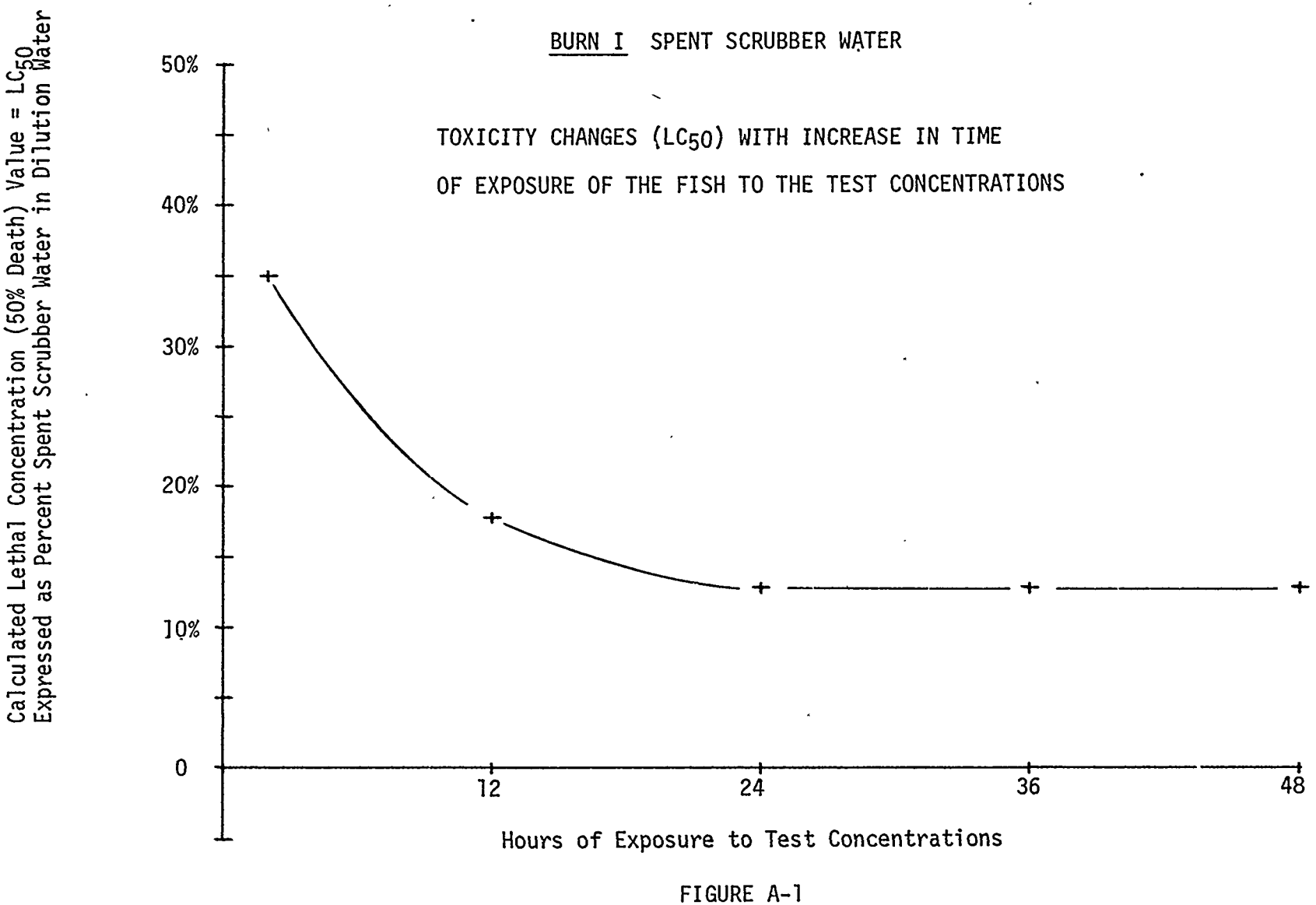

BURN I SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-1

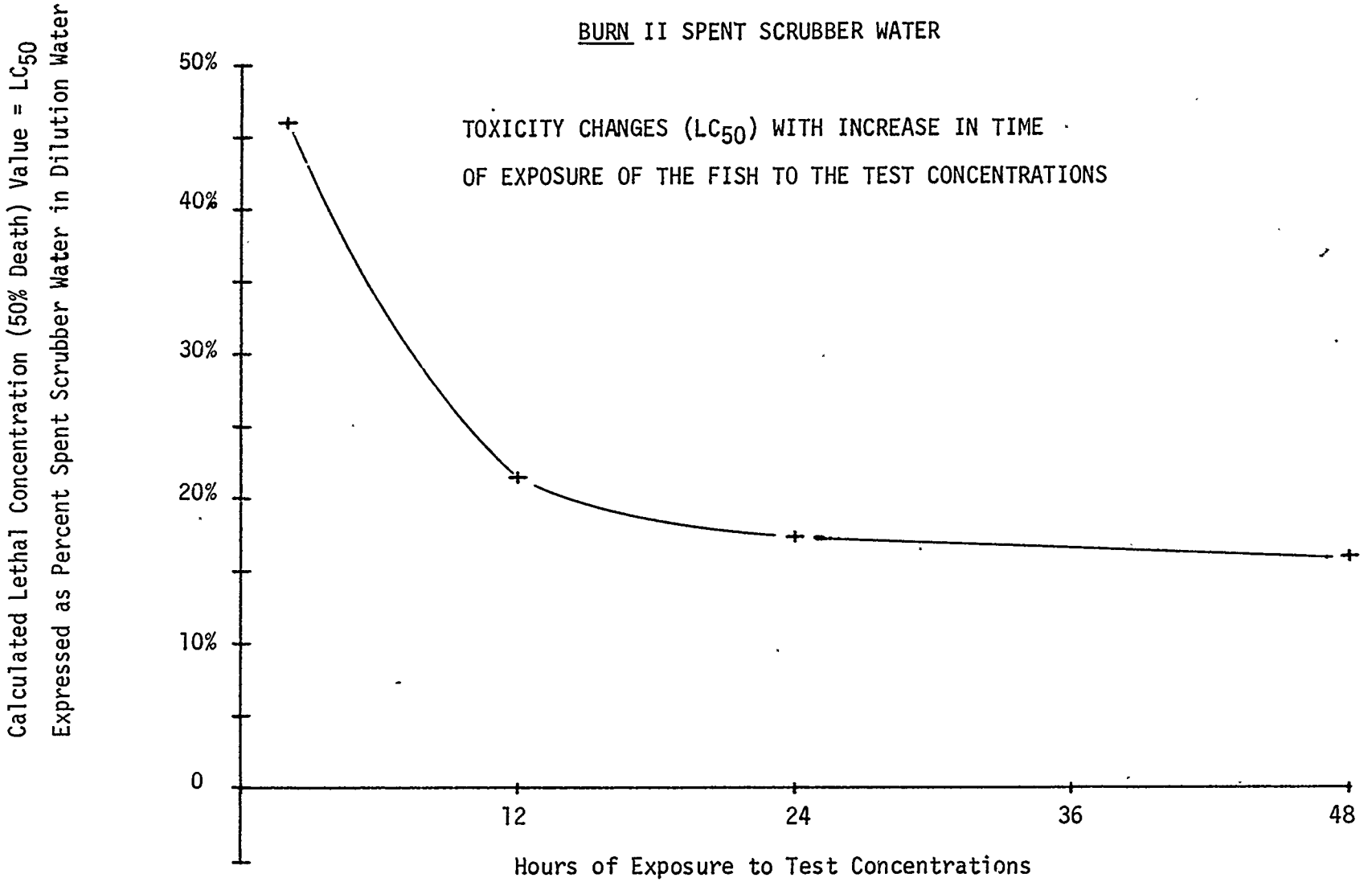

BURN II SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-2

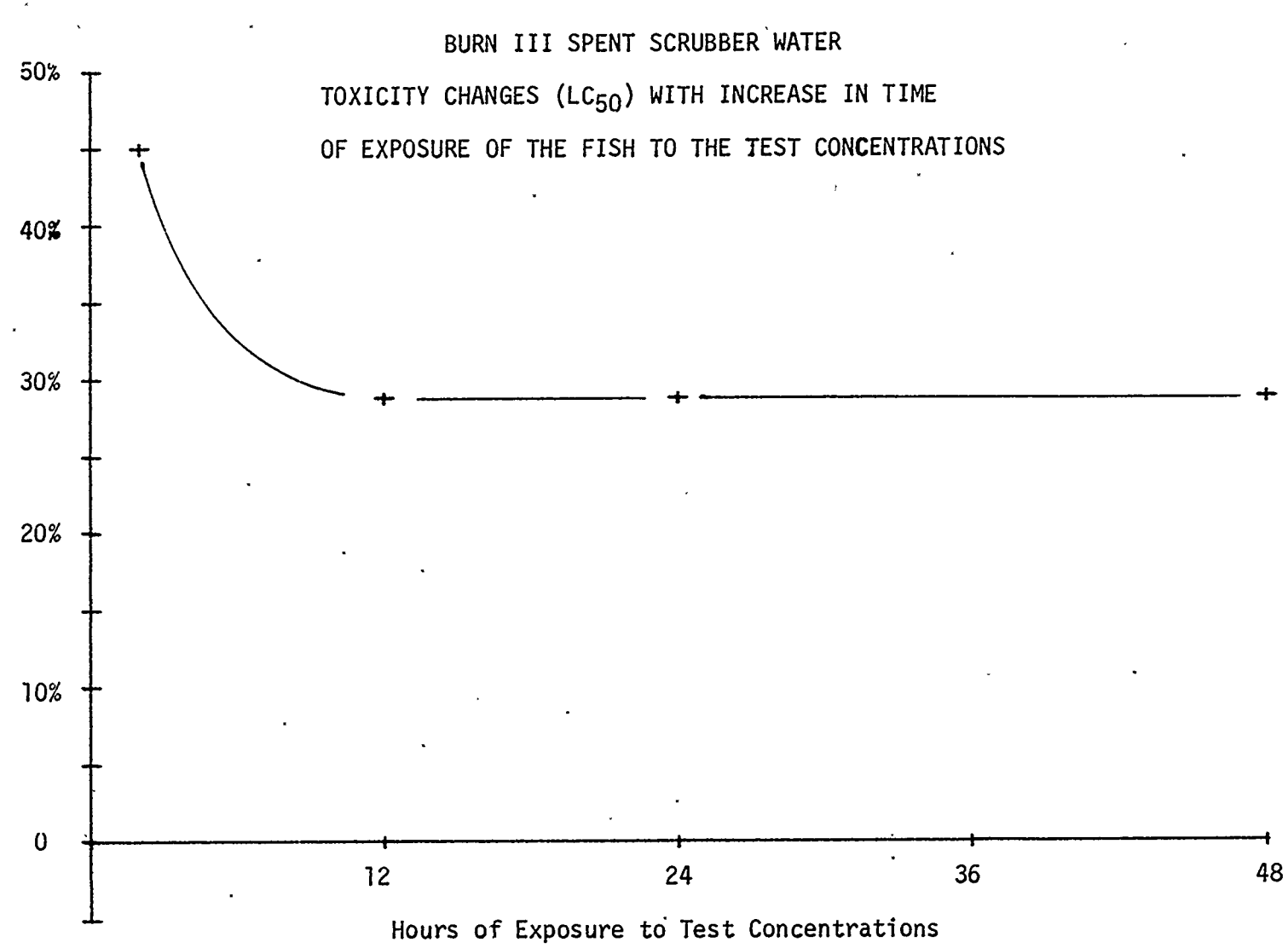

BURN III SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-3

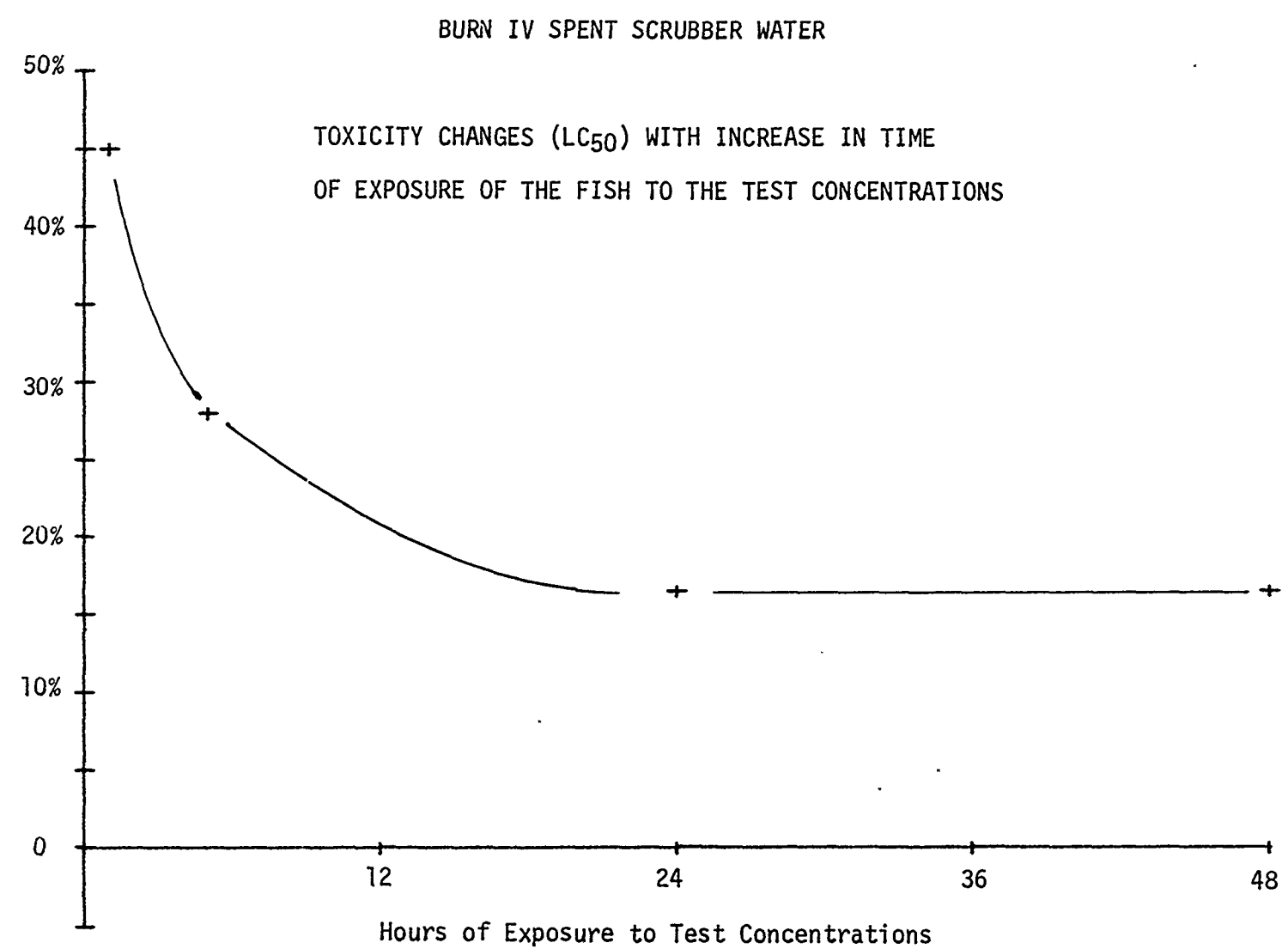

BURN IV SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-4

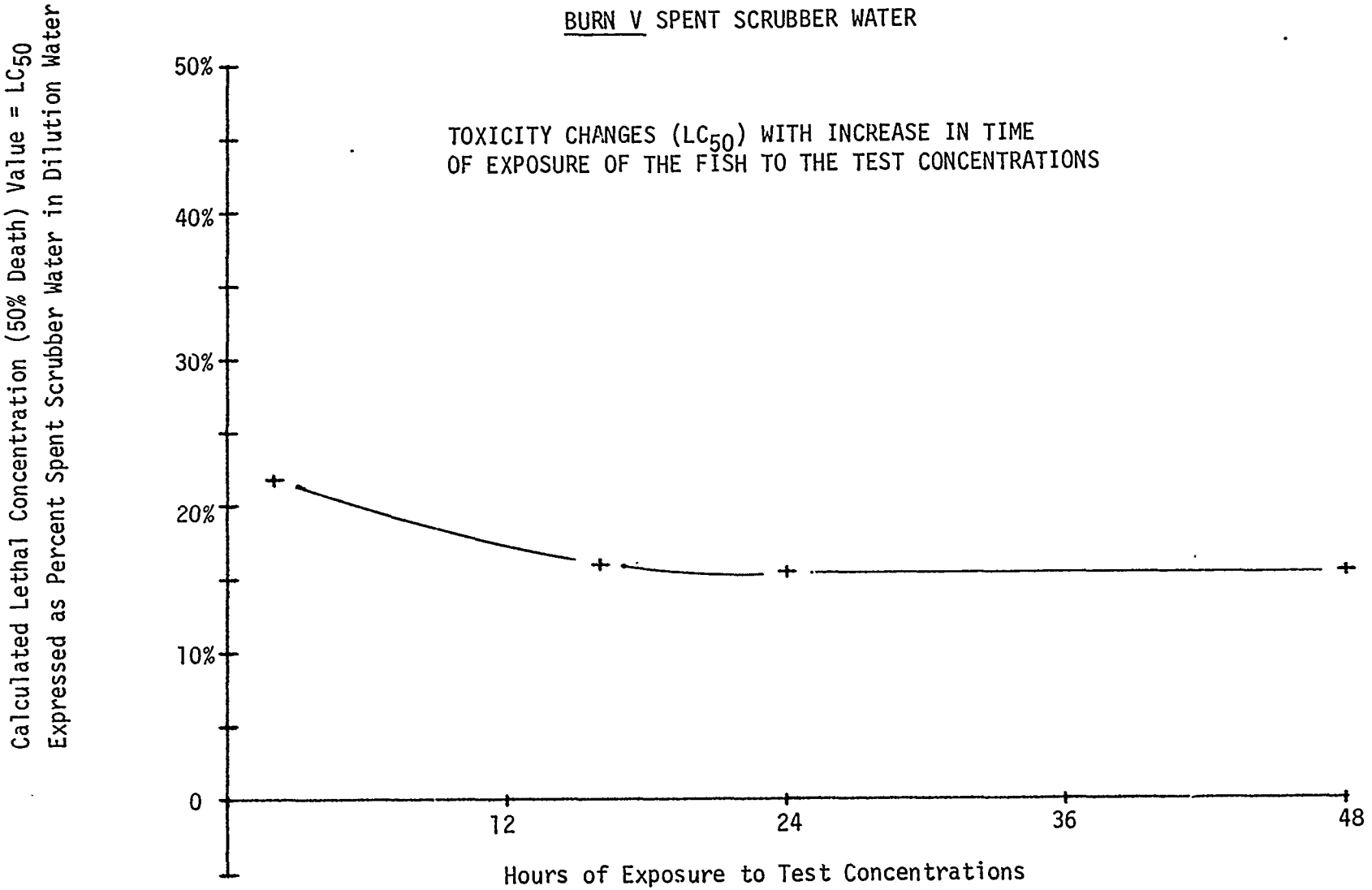

BURN V SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-5

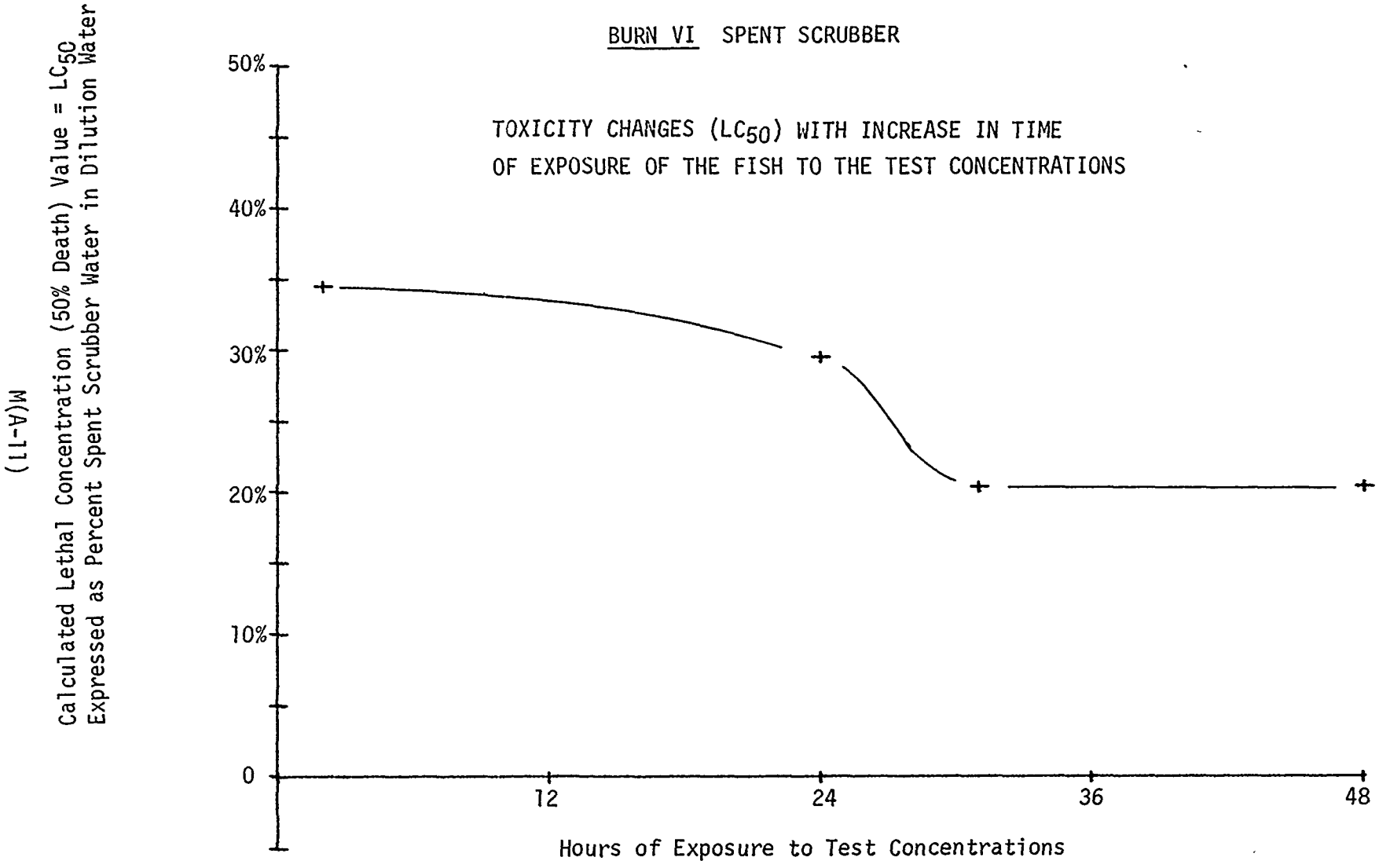

BURN VI SPENT SCRUBBER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
M(A-11)
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-6

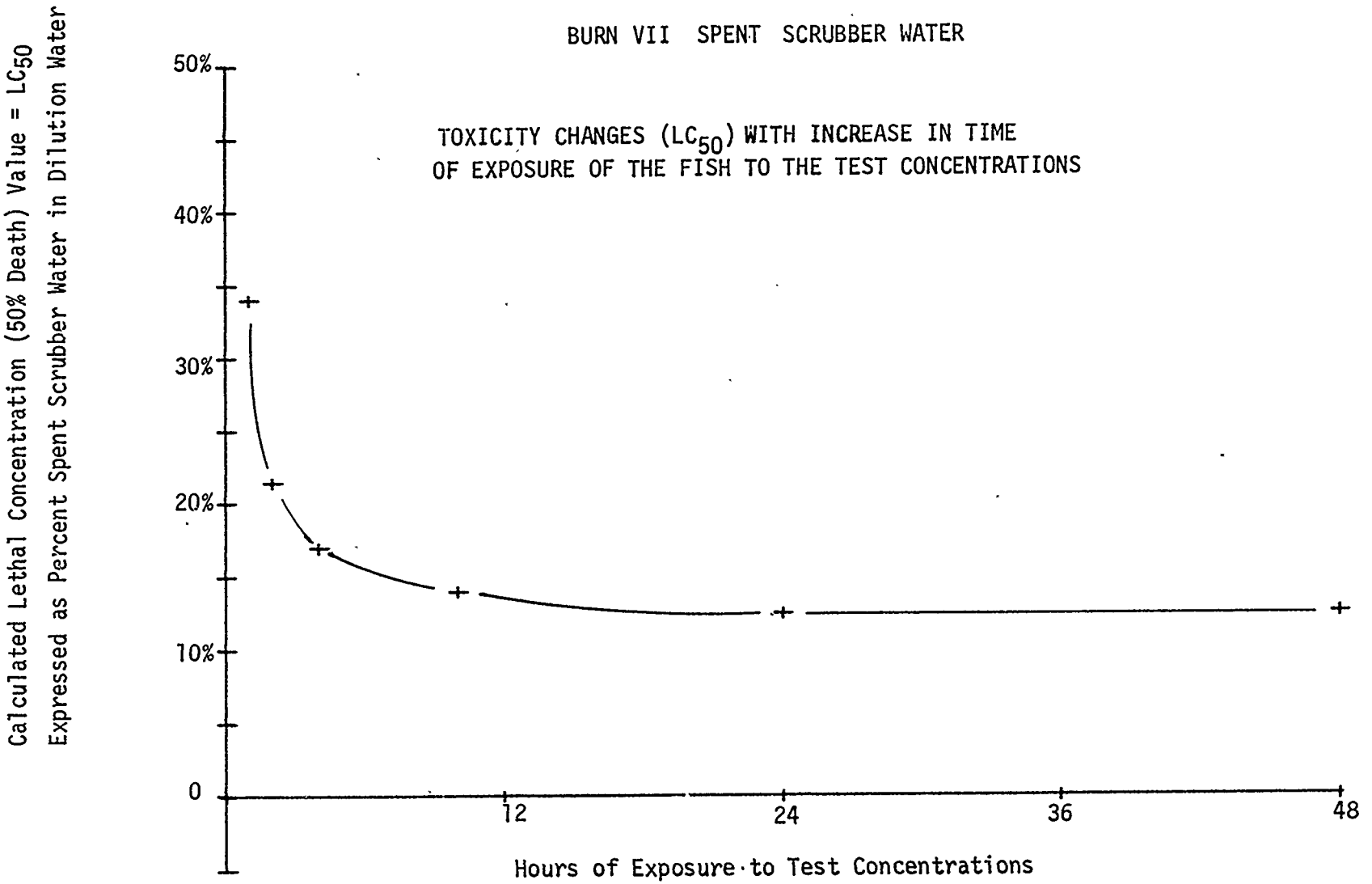

BURN VII SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-7

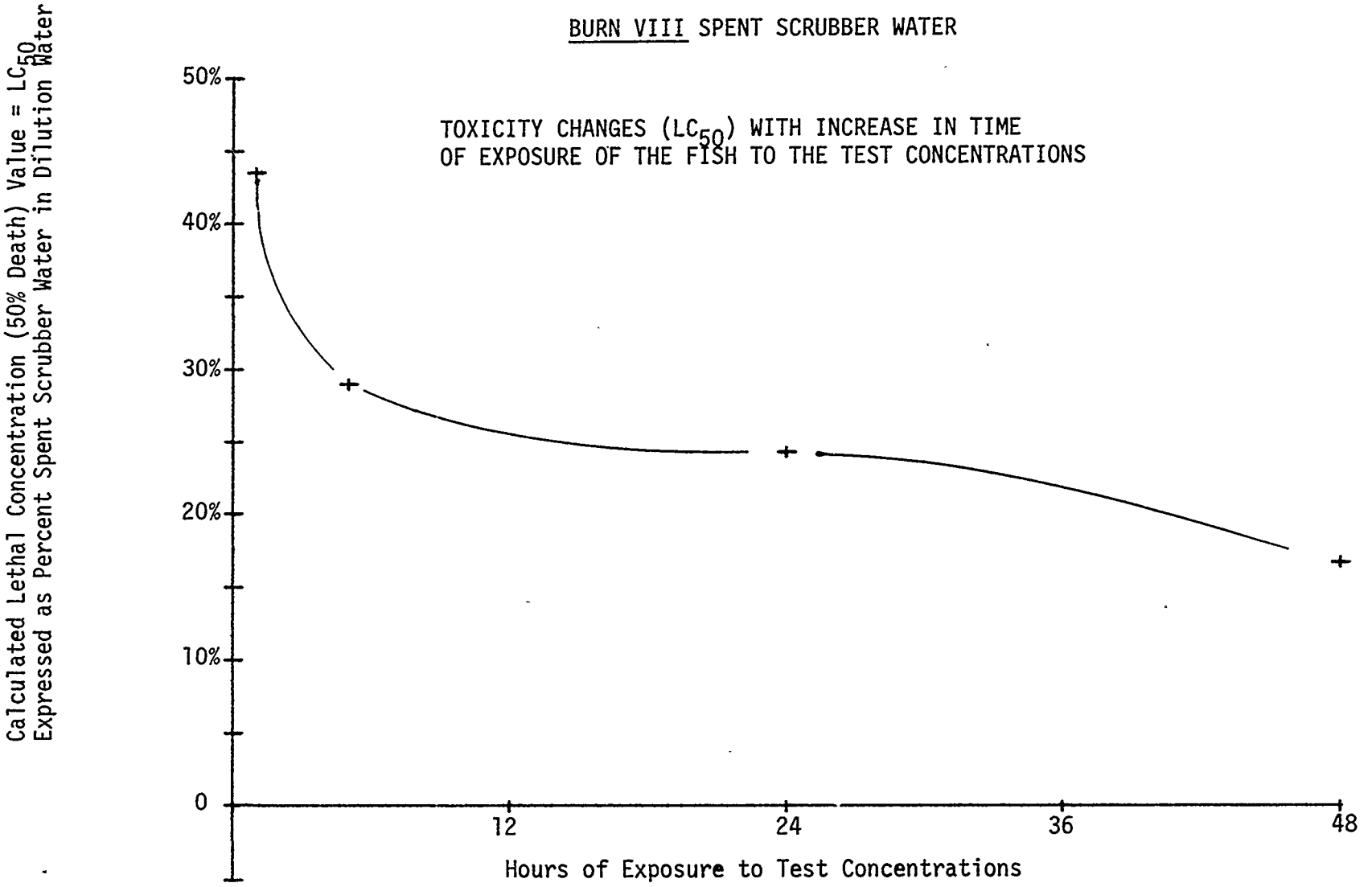

BURN VIII SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-8

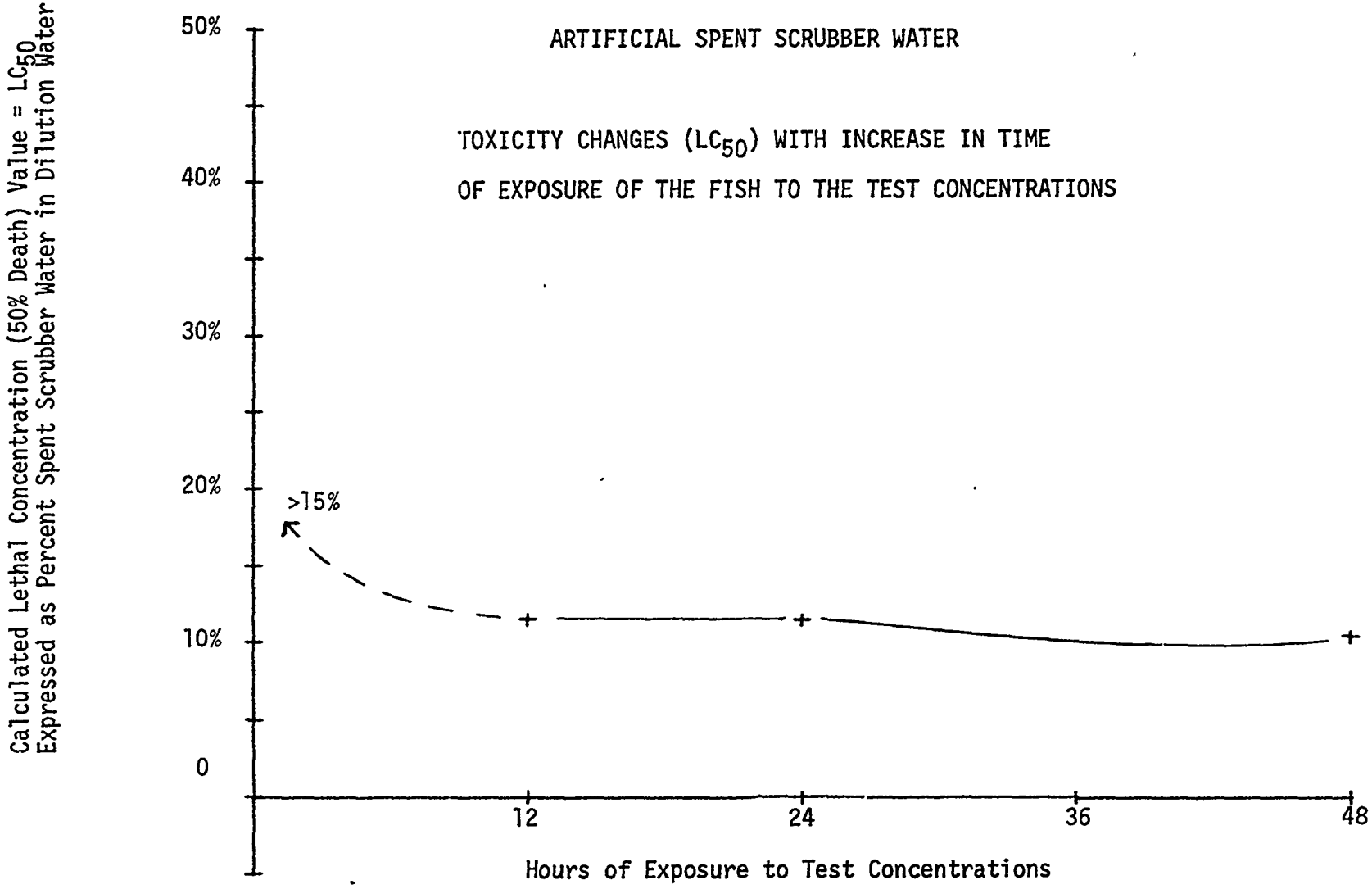

ARTIFICIAL SPENT SCRUBBER WATER
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
Calculated Lethal Concentration (50% Death) Value = $LC_{50}$
Expressed as Percent Spent Scrubber Water in Dilution Water
50%
40%
30%
20%
10%
0
>15%
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-9

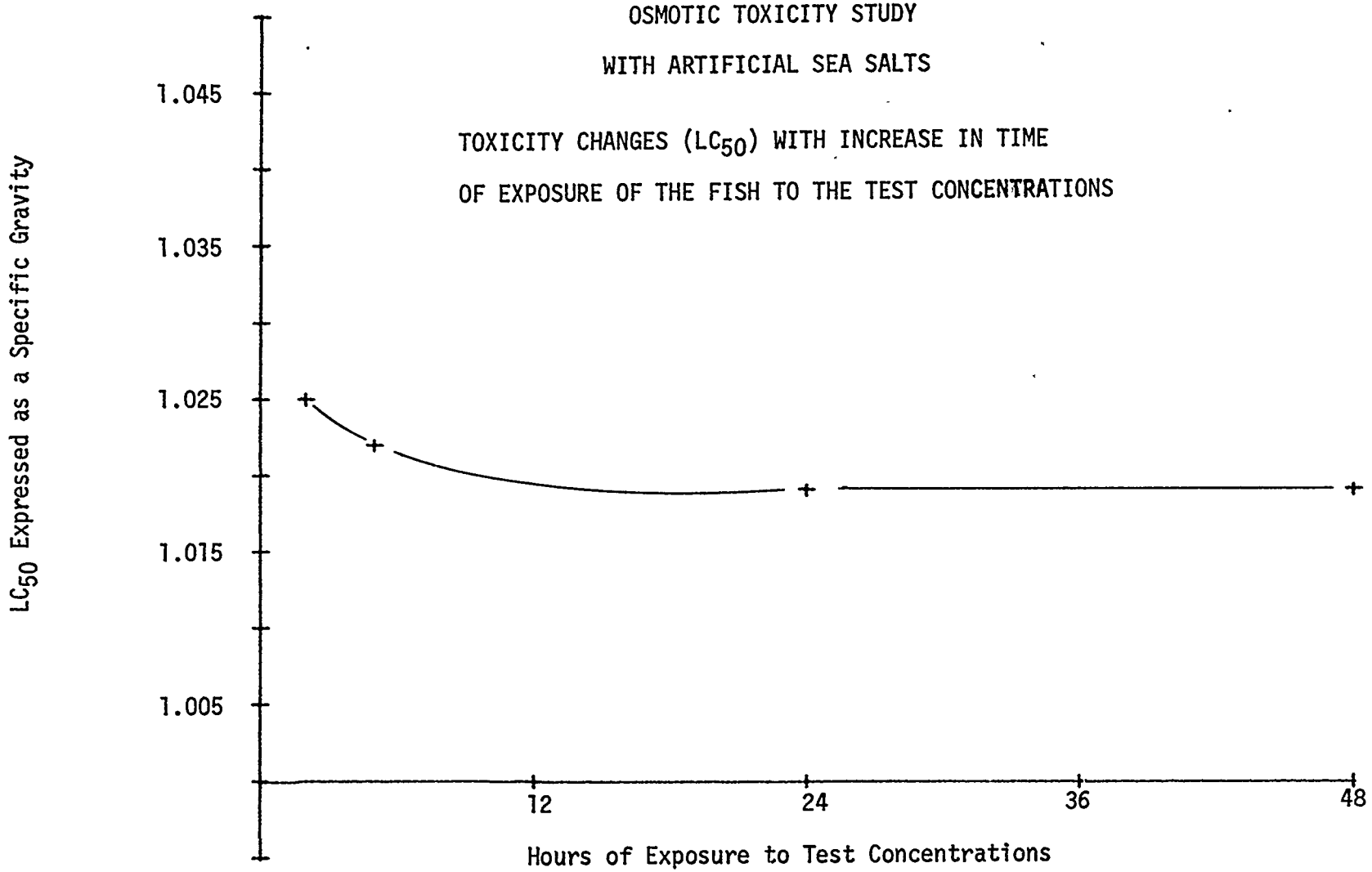

OSMOTIC TOXICITY STUDY
WITH ARTIFICIAL SEA SALTS
TOXICITY CHANGES ($LC_{50}$) WITH INCREASE IN TIME
OF EXPOSURE OF THE FISH TO THE TEST CONCENTRATIONS
$LC_{50}$ Expressed as a Specific Gravity
1.045
1.035
1.025
1.015
1.005
12
24
36
48
Hours of Exposure to Test Concentrations

FIGURE A-10

APPENDIX B (TO APPENDIX M)

HERBICIDE TOXICITY DISCUSSION

This Appendix consists of information pertinent to this report which describes the effects of chlorophenoxy herbicides on plants and aquatic animals. The material quoted was written by Major Inman for the "Candidate Environmental Statement for Disposition of Orange Herbicide by Incineration", March 1974, USAF Environmental Health Laboratory, Kelly AFB, Texas.

(1) Metabolism and Distribution

(a) General Comparisons: The behavior of the chlorophenoxy herbicides in non-mammalian aquatic animals is quite different than the behavior described for terrestrial mammals and birds. The herbicides have a greater toxic potential for aquatic animals. First, the route of entry is different in most instances. The aquatic animal absorbs the herbicide which is distributed throughout his total environment (absorption is mainly via gills in fish). Then, the differences in renal function must be considered. Generally, non-mammalian aquatic animals do not have highly developed kidneys. Thus, once the herbicide is in the aquatic animal's body, some metabolic changes must occur in the molecule to make it more polar if it is to be excreted. Toxicity testing is also necessarily different with aquatic animals. Usually, aquatic animals are placed in a concentration of the toxicant to gradually absorb the material at a rate depending on the animal's physiology and the behavior of the toxicant in the particular water conditions. Therefore, the actual dose to each animal is not known in most studies with aquatic animals. In contrast, toxicity studies with terrestrial animals usually allow calculation of a known dose per unit weight of each animal. Thus, toxicities are often reported as "$LD_{XX}$" (Lethal Dose) for terrestrial animals and "$LC_{XX}$" (Lethal Concentration) for aquatic animals.

(b) Metabolism in Fish: Donald P. Schultz (Fish-Pesticide Research Laboratory, Bureau of Sport Fisheries and Wildlife, 1973) studied the uptake, distribution, and dissipation of $^{14}C$-labled dimethyl amine salt of 2,4-D (DMA-2,4-D). Three species of fish were exposed to 0.5, 1.0 or 2.0 mg/l concentrations of herbicide for up to 84 days exposure period. No mortalities occurred, nor were adverse biological effects observed at these exposure levels. The highest radioactive residue found in muscle tissue occurred in Bluegills exposed to 2.0 mg/l for 84 days (1.065 mg/kg). However, gas-liquid chromatography indicated that over 90% of the radioactive residues consisted of metabolites of 2,4-D. The major metabolite in the fish was found to be 2,4-D glucuronic acid conjugate. Current investigations have found at least six metabolites of 2,4-D in fish. Thus, in contrast to many of the organochlorine pesticides which undergo biomagnification through the food chain, DMA-2,4-D is metabolized in fish without accumulation of the parent compound.

(2) Behavior in Aquatic Systems

(a) Solubility Limits and Rates Vs. Hydrolysis Rates: The esters of 2,4-D or 2,4,5-T found in Orange herbicide have a very limited solubility in water. Because of this very low solubility, the actual concentrations of esters produced in a body of water by accidental contamination would likely be much less than the "expected value" calculated from the volumes involved. The USAF EHL(K) is in the process of studying the behavior of Orange herbicide in aquatic systems especially sea water. In one study using artificial sea water*, Orange herbicide was mixed into the water in an amount equal to 150 mg/l. Had all components gone right into solution, by computation, ester concentrations would have been 64 mg/l (2,4-D NBE) and 61 mg/l (2,4,5-T NBE). The actual, measured concentrations were 2 mg/l (2,4-D NBE) and 1.8 mg/l (2,4,5-T NBE) immediately after mixing. These increased to 18 and 22 mg/l of 2,4-D NBE and 2,4,5-T NBE, respectively, at 24 hours and then started a rapid decline to 7.5 and 9.5 mg/l at 48 hours after mixing. The rate of disappearance of the ester of 2,4-D was fairly rapid and was assumed to be mainly a result of hydrolysis. The half-life of the ester was 15 hours. The addition of natural biota such as bacteria, algae and fish would be expected to produce an even faster disappearance of 2,4-D NBE. Evidence that this occurs was observed in studies EHL(K) is conducting with marine animals at the National Marine Fisheries Laboratory in Port Aransas, Texas. In one of these studies, shrimp were exposed in five different concentrations of 2,4-D NBE and natural sea water. The average half-life of the ester in the five concentrations was 5 hours. This was 1/3 of the half-life observed in the situation where no biological systems existed.

(b) Circulation of Water in Relation to Availability of Herbicide for Absorption: Some of the toxicity studies completed so far indicate the complexity of trying to predict the ecological results of a planned or accidental contamination of a body of water with phenoxy herbicides. At EHL(K), Orange herbicide was mixed in a fish tank at a concentration that would theoretically produce a 200 ppm (v/v) concentration if such a high concentration were possible. Most of the herbicide rapidly sank to the bottom of the tank after mixing. Fathead minnows placed in the tank showed no ill effects during two weeks of exposure. Yet in a toxicity study under the same conditions but with continuous agitation of the water by aeration, all of the fish died in a "20 ppm concentration" of Orange herbicide water in 24 hours. Subsequent studies revealed that some circulation of the water was essential if a dose-related response was to be established in toxicity studies with the N-butyl esters of 2,4-D and 2,4,5-T. Thus, the actual effect seen in nature might well depend on a factor such as the degree of mixing in the affected body of water.

(c) Importance of Hydrolysis: It is important that when the esters of 2,4-D and 2,4,5-T hydrolyze, their toxicity to aquatic animals is decreased by almost a factor of 10 (paragraph (3)(b) below). In the static situation described in the paragraph above (no aeration), the rate of hydrolysis was probably faster than the rate that the ester went into solution so that lethal concentrations were never attained. Toxicity studies with fresnwater and saltwater animals at EHL(K) have been the so-called "Static Bioassay" in which no attempt is made to maintain a constant concentration of the herbicide ester in each test chamber. "Concentrations" are theoretical and based on volumes of herbicide and water mixed together rather than from analysis of water to quantitate the herbicide. Most studies reported from literature are of the same type. The toxicity tests at EHL(K) revealed that in both freshwater and saltwater, most of the test organisms had responded at twelve hours of exposure. There was rarely any increase in mortality past 24 hours.

(d) Other Factors Affecting Actual Concentration: Many other factors can influence the concentration of N-butyl esters of 2,4-D and 2,4,5-T in a body of water. In studies where large amounts of Orange herbicide were placed in water, the globules of the herbicide appeared to become coated with an opaque material that may have inhibited the ester from going into solution. Cope (1970) treated ponds with 0.5 ppm to 10 ppm propylene glycol butyl ether ester (PGBE) of 2,4-D. He was able to measure residues of herbicide absorbed or adsorbed in vegetation and bottom sediment for 6 weeks after treatment in the 10 ppm treated pond. Crosby (1966) reported that 2,4-D decomposes rapidly in the presence of water and ultraviolet light.

(3) Toxicity

(a) Factors Affecting Toxicity: The toxicity of the chlorophenoxy herbicides to aquatic animals varies considerably with many factors such as water chemistry variables, temperature, and the particular salt, ester or amine form of the herbicide considered. Species susceptibility varies greatly. For example, the 96-hour $TL_{50}$* for fathead minnows exposed to DMA-2,4-D was found to be 335 mg/l. Yet, for bluegills and channel catfish the $TL_{50}$ values were 177 and 193 respectively. A temperature increase from 17°C to 20°C increased the relative toxicity to the catfish from a $TL_{50}$ of 193 mg/l to 125 mg/l (Schultz, 1973).

(b) Toxicity Comparisons by EHL(K): The USAF EHL(K) (1974), performed static toxicity studies with Orange herbicide. Also, toxicity studies were performed using each individual N-butyl ester of 2,4-D and 2,4,5-T. Freshwater bioassays using the fathead minnow (Pimephales promelas) resulted in a 48 hr $LC_{50}$ of 3.4 ppm for Orange herbicide containing 14 ppm TCDD. The 48 hr $LC_{50s}$ for esters of 2,4-D and 2,4,5-T were 2.8 ppm and 5 ppm respectively. The 48 hr $LC_{50}$ for 2,4-D in the minnows was 270 ppm. The 2,4,5-T 48 hr $LC_{50}$ concentration was 333 ppm. Note that the toxicity of ester formulations were considerably more toxic than the respective acid. Also, EHL(K) found the N-butyl ester of 2,4-D to be more toxic than the N-butyl ester of 2,4,5-T.

In salt water studies by EHL(K), the 48 hr $LC_{50}$ values in the shrimp (Penaeus sp.) were 5.6 ppm for 2,4-D NBE and 33 ppm for 2,4,5-T NBE. Oysters (Crassostrea virginica) were exposed to "potential concentrations" of 2,4-D NBE ranging from 0.5 ppm to 85 ppm. The only acute effect observed was the death of one of the oyster (10%) in the highest concentration at 48 hours.

(c) Other Animals and Other Effects: Many other aquatic animals besides fish can be affected by phenoxy herbicides. Saunders (1971) studied the effects of the propylene glycol butyl ether (PGBE) form of 2,4-D on six freshwater crustaceans. He found the following 48 hr $TL_{50}$ values: Daphnia magna = 0.10 ppm, seed shrimp = 0.32 ppm, scud = 2.6 ppm, sowbug = 2.2 ppm, glass shrimp = 2.7 ppm, and crayfish had an unknown value larger than 100 ppm. Cope (1970) studied the chronic effects of PGBE ester of 2,4-D on the bluegills. Survivors of ponds treated with high concentrations (10 and 5 ppm) had a 2 week delay in spawning. For pathologic lesions, high-treatment fish had earlier and more severe effects than did low-treatment fish. The pathology involved the liver, vascular system and brain. Remarkably, growth of the fish was faster in the ponds receiving the high-treatment than in the lower-treatment ponds. Tables B-1 and B-2 were extracted from a U.S. Forest Service Environmental Impact Statement (EIS-OR, 1973). The tables indicate the effects of herbicides on other aquatic species and point out some toxic effects that can be measured other than death of the organisms.

d. Behavior in Plants

(1) Distribution and Metabolism: Orange herbicide is a systematic herbicide that affects plants by a hormonal type of action usually described as "auxin-like" or "auxin-type". Auxins are any of a group of substances which promote plant growth by cell elongation, bring about root formation, or cause bud inhibition or other effects. 2,4-D and 2,4,5-T are compounds of this type. When applied to leaves of a plant, chlorophenoxy herbicides are absorbed through the cuticle into the plant system. The N-butyl ester forms of 2,4-D and 2,4,5-T found in Orange herbicide are usually more effective than more polar forms because of better absorption into the plant. This is also demonstrated in Yamaguchi's work (1965) in which he found that 2,4-D moves into plant leaves better from acidic solutions than from alkaline solutions. Approximately ten times as much 2,4-D was abosorbed from a medium having pH 3 than one with pH 11. 2,4-D has a $pK_a$ of 2.8 and would be highly disassociated at pH 11. Once the herbicide is in the plant it is translocated to areas where food is being stored as in rapidly growing new roots and shoots. The chlorophenoxy herbicides can be stored in certain cells of the plant. Also, metabolism occurs through degradation of the acetic acid side chain, hydroxylationof the aromatic ring, or conjugation.

(2) Toxicity: Once in the plant, herbicides act by interfering with the photosynthetic, respiratory, and other plant processes causing the plant to lose its leaves and ultimately die. Plant susceptability to sublethal exposures of 2,4-D is markedly influenced by the growth condition of the plant and by environmental factors. Since most of the injury is expressed by growth response, the plant must be growing in order to show injury. In

TABLE B-1

ACUTE EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

| DERIVATIVE | ANIMAL | CONCENTRATION | EFFECT | REFERENCE |
|---|---|---|---|---|
| Isooctyl esters (From 3 manufacturers) | Bluegill | 10-31 ppm | 48 TLm | Hughes & Davis (1963) |
| PGBE ester | Bluegill | 17 ppm | 48 TLm | Hughes & Davis (1963) |
| Butoxyethanol ester | Bluegill | 1.4 ppm | 48 TLm | Hughes & Davis (1963) |
| PGBE ester | Shrimp | 1 ppm (48 hrs.) | 20% mortality or paralysis | Butler (1965) |
| PGBE ester | Fish (salt water) | 0.32 ppm | 48 hr TLm | Butler (1965) |
| Alkanolamine Salt | Bluegill | 435-840 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Dimethylamine Salt | Bluegill | 166-458 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Isooctyl ester | Bluegill | 8.8-59.7 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Dimethylamine Salt | Fathead Minnow | 10 ppm | 96 hr $LC_{50}$ | Lawrence (1966) |
| Acetamide | Fathead Minnow | 5 ppm | 96 hr $LC_{50}$ | Lawrence (1966) |
| Oil soluble amine salt | Bluegill, Fathead Minnow | 2 ppm | 4 mo. $LC_{10}$ | Lawrence (1966) |
| PGBE Ester* | Bluegill, Fathead Minnow | 2 ppm | 4 mo. $LC_{10}$ | Lawrence (1966) |
| Butoxyethyl ester | Bluegill & Fathead | 2 ppm | 72 hr $LC_{50}$ | Lawrence (1966) |
| Butyl and isopropyl esters, mixed | Bluegill | 1.5 - 1.7 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| N,N-Dimethyl coco-amine salt | Bluegill | 1.5 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Ethyl ester | Bluegill | 1.4 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Butyl Ester | Bluegill | 1.3 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |
| Isopropyl ester | Bluegill | 1.1 ppm | 48 hr $LC_{50}$ | Lawrence (1966) |

*Propylene Glycol Butyl Ether

TABLE B-2

NON-LETHAL EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

| DERIVATIVE | ANIMAL | DOSE | EFFECT | REFERENCE |
|---|---|---|---|---|
| Butoxyethanol ester | Oyster | 3.75 ppm (96 hrs) | 50% decrease in shell growth | Butler (1965) |
| Butoxyethanol ester | Shrimp | 1 ppm (48 hrs) | No effect | Butler (1965) |
| Butoxyethanol ester | Fish (salt water) | 5 ppm | 48 hr. TLm | Butler (1965) |
| Butoxyethanol ester | Phyto-plankton | 1 ppm | 16% decrease in $CO_2$ fixation | Butler (1965) |
| Dimethylamine | Oyster | 2 ppm (96 hrs) | No effect on shell growth | Butler (1965) |
| Dimethylamine | Shrimp | 2 ppm (48 hrs) | 10% mortality or paralysis | Butler (1965) |
| Dimethylamine | Fish (salt water) | 15 ppm (48 hrs) | No effect | Butler (1965) |
| Dimethylamine | Phyto-plankton | 1 ppm (4 hrs) | No effect on $CO_2$ fixation | Butler (1965) |
| Ethylhexyl ester | Oyster | 5 ppm (96 hrs) | 38% decrease in shell growth | Butler (1965) |
| Ethylhexyl ester | Shrimp | 2 ppm (48 hrs) | 10% mortality or paralysis | Butler (1965) |
| Ethylhexyl ester | Fish (salt water) | 10 ppm (48 hrs) | No effect | Butler (1965) |
| Ethylhexyl ester | Phyto-plankton | 1 ppm (4 hrs) | 49% decrease in $CO_2$ fixation | Butler (1965) |
| PGBE 1/ ester | Oyster | 1 ppm (96 hrs) | 39% decrease in shell growth | Butler (1965) |
| PGBE 1/ ester | Shrimp | 1 ppm (48 hrs) | No Effect | Butler (1965) |
| PGBE 1/ ester | Fish (salt water) | 4.5 ppm | 48 hr TLm | Butler (1965) |

1/ PGBE is propylene glycol butyl ether.

addition, plants in shaded areas respond more slowly than those exposed to direct sunlight. Because of these various factors which affect plant response to the 2,4-D type herbicide, differences in lists showing plant susceptability should be expected. Orange herbicide is effective on a wide variety of woody and broadleaf plant species. Other lower plant forms can also be affected by auxin-type herbicides. Even unicellular algae exhibit toxic effects or die when exposed to 2,4-D or 2,4,5-T (Walsh, 1972). However, much higher doses of the herbicides are required than for plants with a more complex structure.

(3) Herbicides as Air Pollutants: Although herbicides have long been accepted as environmental pollutants which affect sensitive vegetation, the air pollution aspects of volatile herbicides have not been widely explored. However, there is growing evidence that some 2,4-D compounds may be present in the ambient atmosphere in some parts of the United States at levels sufficient to cause adverse growth effects on sensitive vegetation. During 1962 through 1964, Vernetti and Freed measured 2,4-D concentrations in air samples taken in an agricultural area of eastern Oregon. Concurrently, they surveyed for auxin-like plant damage in the areas where the air samples were taken. In the spring of 1962, measured concentrations of the isopropyl ester of 2,4-D in the air ranged from 0.015 ppm to 0.64 ppm. This was during the time of year when the huge wheat fields of the area were being treated for weeds by aerial application of the isopropyl ester. Plant damage to tomato crops appeared to coincide with periods of highest measured concentrations of the isopropyl ester. Other plants, especially locust trees, also showed growth regulator symptoms. Legislation in the state curtailed the use of the isopropyl ester and decidely reduced the contamination and resulting plant damage. Laboratory studies by Vernetti and Freed indicated that 0.015 ppm would be the threshold concentration of isopropyl ester that tomato plants could be exposed to and still survive under the conditions of the experiment. Volatility studies by the same workers demonstrated that the isopropyl ester was three times more volatile than the butyl ester. In fact, complex analyses of the air samples ruled out butyl and other esters of 2,4-D as principal contaminants.

(4) Relative Species Sensitivity: Different researchers vary in their results of relative plant sensitivity to phenoxy herbicides. From field observations, grapevines and box elder appear to be among the most sensitive since they respond to 2,4-D air pollution when other plants showed no evidence of injury. Injury to grapevines may result from exposure to levels in the ppb range. Other workers report tomato plant damage in the ppt range. Walsh (1972) reports a 50% reduction in growth of unicellular marine algae exposed to phenoxy herbicide concentrations of 50 to 300 ppm. Other relative sensitivities are indicated in Table B-3.

TABLE B-3 Sensitivity of selected plants to 2,4-dichlorophenoxyacetic acid*

**Sensitive**

Apple
*Malus*, sp.
Birch
*Betula*, sp.
Boxelder
*Acer negundo*, L.
Dogwood
*Cornus*, sp.
Elderberry
*Sambucus*, sp.
Forsythia
*Forsythia*, sp.
Grape
*Vitis*, sp.
Hickory
*Carya*, sp.
Lambs-quarters
*Chenopodium album*, L.
Linden
*Tilia*, sp.
London plane tree
*Platanus acerifolia* (Ait.) Willd.
Maple, Norway
*Acer platanoides*, L.
Oak, black
*Quercus velutina*, Lam.
Sorrell
*Rumex*, sp.
Sumac
*Rhus*, sp.
Tobacco
*Nicotiana*, sp.
Tomato
*Lycopersicon esculentum*, Mill.
Treeofheaven
*Ailanthus altissima*, Mill.
Wisteria
*Wisteria*, sp.
Yellow wood
*Cladrastis lutea*, Koch
Zinnia
*Zinnia*, sp.

**Intermediate**

Aster, wild
*Aster*, sp.
Cedar
Cherry
*Prunus*, sp.
Cherry, choke
*Prunus virginiana*, L.
Corn
*Zea mays*, L.
Gladiolus
*Gladiolus*, sp.
Hemlock
*Tsuga*, sp.
Mulberry
*Morus*, sp.
Oak, pin
*Quercus palustris*, L.
Oak, red
*Quercus palustris*, L.
Peach
*Prunus persica*, Sieb. & Zucc.
Potato
*Solanum tuberosum*, L.
Privet
*Ligustrum*, sp.
Ragweed, giant
*Ambrosia trifida*, L.
Rhododendron
*Rhododendron*, sp.
Rose
*Rosa*, sp.
Spruce, Colorado blue
*Picea pungens*, Englm.
Sweetgum
*Liquidambar styraciflua*, L.
Yew
*Taxus*, sp.

**Resistant**

Ash
*Fraxinus*, sp.
Bean, bush
*Phaseolus vulgaris*, L.
Cabbage
*Brassica oleracea*, L.
Eggplant
*Solanum melongena*, L.
Pear
*Pyrus communis*, L.
Peony
*Paeonia*, sp.
Rhubarb
*Rheum rhaponticum*, L.
Sorghum
*Sorghum vulgare*, Pers.

* FROM AIR POLLUTION CONTROL ASSOCIATION REPORT NO. 1

# APPENDIX N
# INFORMATION ON INCINERATOR SHIPS

Documents included in this appendix are listed in the order of appearance.

*1. Extract from Prof. Dr. Klaus Grasshoff of Kiel University's report on: Possible effects of burning chlorinated hydrocarbons at sea.

*2. Burning of chlorine containing liquids on the incineration ship Matthias. Investigations on combustion gases: 26 August 1971.

*3. Effect on the Marine Environment of the Combustion at Sea of Some Industrial Waste.

**4. L'Incineration in Haute Mer de Residus Industriels Chlores.

**5. Incineration on the High Seas of Chlorinated Industrial Wastes.

6. Testimony by Mr. H. Compaan at the Ocean Incineration Hearing, Houston TX, 4 Oct 74 (Data on Vulcanus incinerator efficiency)

* From a number of documents submitted by Antillian Incinerating Company N.V.

** Original French document provided by Ocean Combustion Services.

Extract from Prof.Dr.KLAUS GRASHOF of Kiel University's report on:

Possible effects of burning chlorinated hydrocarbons at sea.

Page 2, line 27:

By means of extensive controlled measurements, the BAYER Company of Leverkusen, Germany, has established that if the burning of chlorinated hydrocarbons is carried out at temperatures higher than 1,000° C, more than 99.9% of the materials are completely burnt. A combustion of 12 ts per hour of material containing an average of 30% of chlorine will result in 3.6 ts hydrochloric acid and about 19 ts carbon dioxide. (Part of the carbon will also be transformed into carbon monoxide) About 12 kg per hour of chlorinated hydrocarbon will be destroyed only partially or not at all.

The hydrochloric acid condenses quickly with the water vapour contained in the air. In moderate wind conditions, the smoke plume will spread over a sea area of at least 250,000 $m^2$ before the hydrochloric acid falls into the water. This means that about 15 g hydrochloric acid would fall on a square metre per hour. The sea water has a considerable capacity to neutralize acids, which can be expressed as its total alkalinity, i.e., the sum of all the weak alkalies contained in sea water. Of these, the most important are the acid carbonates (about 76%), the carbonates (20%) and the borates (4%). Other alkalies, due to their small volume, play only a minor role and are therefore not discussed here.

1.

$$A = C_{HCO_3^-} + 2\,C_{CO_3^{--}} + C_{B(OH)_4^-}$$

With a salt content of about 34‰ (dependent on conditions at the place of combustion) the total alkalinity of the surface sea water will average 2.3 milli equivalents per litre. In other words, 1 $m^3$ sea water can neutralize about 80 g hydrochloric acid. This neutralization reaction will result in carbon dioxide, boric acid and chlorine ions, as shown below:

$$HCO_3^- + HCl = CO_2 + H_2O + Cl^-$$

$$CO_3^{--} + 2HCl = CO_2 + H_2O + 2\,Cl^-$$

$$B(OH)_4^- + HCl = B(OH)_3 + H_2O + Cl^-$$

The water of the North Sea contains an average of 19 g chlorine ions ($Cl^-$) per litre, or 19 kg per $m^3$. The 15 g chlorine ions per $m^2$ resulting from the combustion mentioned above, represents an increase in the chlorine ions content of 0.08 ‰. In fact, in the North Sea there is a turbulent mixing which produces vertical water exchanges, which extend even to very deep water. In addition, there are fast horizontal movements due to the tides. Consequently, the quantities of hydrochoric acid which fall each hour on the surface of the sea spread in at least 100 times more water. As a result, the increase in chlorine ions content is smaller than 0.001‰, and thus too small to be determined by the normal measuring methods. This is also valid for the temporary decrease in total alcalinity, which is probably about 0.4 milli equivalents per litre. After the mixing mentioned above has taken place, this decrease will be about 0.004 milli equivalents, which is not measurable either.

2.

In addition, a new equilibrium is restored, as the resulting carbon dioxide escapes into the atmosphere, and the calcium carbonate, from the particles of materials contained in the sea water, is dissolved.

The disturbance of the carbonic acid system through the neutralization of the falling hydrochloric acid appears, in realistic terms, much less than the disturbance brought about by the assimilation (intake of carbon dioxide) or the respiration (output of carbon dioxide) through the natural biological processes.

The possibility of ecological disturbance caused by the small increase of the chlorine ions content can be discarded.

As mentioned earlier, 12 Kg/hour of chlorinated hydrocarbon are not completely burnt. However, these products do not condense immediately with the water vapours, but are spread by atmospheric movement over considerably larger areas. In this way, the quantities of chlorinated hydrocarbons which reach the sea are negligeable compared with those re ching it through the rivers or in other ways, as well as through evaporation of insecticides in the atmosphere.

date: June 22nd.73

BAYER CORPORATION

# MEMORANDUM

Plant: Leverkusen
Management Office

Division: AWALO-Airlaboratory

Subject: Burning of chlorine containing liquids on the incineration ship Matthias.
Investigations on combustion gases : 26 august 1971.

In order to establish the combustion efficiency, analyses were made of the organic components and the hydrochloric acid contained in the combustion gases resulting from the burning of three different mixtures: a mixture of solvents, belonging to the category of inflamable fluids classified as K 1 (3100 Kg/h); a mixture of liquids classification K 2 (3450 Kg/h) containing Dichlorpropane; and a mixture of liquids classification K 3 (3750 Kg/n) containing Chloronitribenzene as the main component.
The combustion temperature was kept between 1400 and 1500°C. The combustion time length was 3-6 hours for each product.
During each combustion, the following samples were taken:

5 instant samples
3 adsorbtion samples on silica-gel
2 concentration samples in n-Butanol

All the combustion gas samples were taken by using a 2 m long cuartz glass tube, penetrating in the furnace about 0.4m below and at 1 meter distance from the furnace's edge. From this cuartz glass tube, the gases first had to go through a condensate separator.
The following methods were used for the identification and the quantitative analyses of the organic components:
UV analyses, gaschromatography combined with mass spectrography, gaschromatography combined with selective detectors, especially flame ionization and electrons capture detection, the silica gel process for establishing the organic linked carbon.

Summary of results

The gas chromatogram of the instant samples, which were taken in 0.5 l evacuated gas sampling pipes, retained in the zone of higher boiling hydrocarbons, between 2 and 6 components. Their concentration of about 1 vol ppm for each sample, was too low for their identification, even when making full use of the highly resilience ability of the mass spectrography.

The UV-analyses of the 100 l samples of combustion gases concentrated in n-Butanol, did not permit either the identification of the only slightly suggested absorbtion strips.

Volumes between 30 and 100 l of combustion gases absorbed on silica gel, were taken, to determine the organically linked carbon; the total carbon content of 10 to 25 $mg/m^3$ that was found, corresponds to the concentration established in the gaschromatograms.

For a combustion gas volume of 45,000 $m^3/h$, the unburnt percentage, calculated from the total content in carbon, respectively from the sum of the higher boiling components, is between 0.02 and 0.08 w %. Consequently, the combustion efficiency is for all 3 burned mixtures higher than 99.9%.

The condensates caught for each of the three mixtures (2-10 ml/100 l combustion gas) were neutralized with NaOH and diluted to 1:50 with aired town water. The toxicity of this liquid was tested in laboratory by using golden orfe (Idus melanotus). Two golden orfe were kept in this liquid for each condensate. After 4 days exposure in these liquids, no harmfull effect whatsoever on the golden orfe could be established.

CENTER OF BIOLOGICAL STUDIES AND
RESEARCH AND OF OCEANOGRAPHIC MEDICINE
(C.E.R.B.O.M.)

The national institute for health and medical research

Parc de la Côte
Avenue Jean Lorrain
NICE (A.M.)
Telephone 89.32.92

Foundation of the town of NICE

INCIMER
ROTTERDAM
(The Netherlands)

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# EFFECT ON THE MARINE ENVIRONMENT OF THE COMBUSTION AT SEA OF SOME INDUSTRIAL WASTE

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GENERAL REPORT

Project leader : Dr. M. Aubert

Collaborators : A. Fruchart; J. Ph. Breittmayer, G. Flatau;
D. Puel; F. Laumond; M. Perrin; B. Chabanne;
M. Collet-Planas

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## 1. INTRODUCTION AND THE OBJECTIVE OF THE STUDY

C.E.R.B.O.M. was requested by the Company INCIMER to study the consequences that a method of incinerating various liquid chlorinated waste at sea, has on the marine environment. This technique is used at present in the North Sea, with the agreement of the Dutch official authorities. Consequently, based on the measurements performed in the North Sea and the samples taken, which were submitted to various laboratory tests, we tried to predict the effect of this incineration in the Mediterranean Sea, where the Company intends to extend its activities.

The studies which we show, had to be performed at short notice, which explains why they are not completed. Nevertheless, they make possible a good approach of the problem and especially, it allows a comparison between the incineration method and the straight throwing into the sea, which is the more frequently used method.

## 2. MEASUREMENTS AND SAMPLING "IN SITU"

During two days we attended the burning of chlorinated waste, supplied from various sources, in the North Sea, in the zone assigned for this operation by the Dutch official authorities.

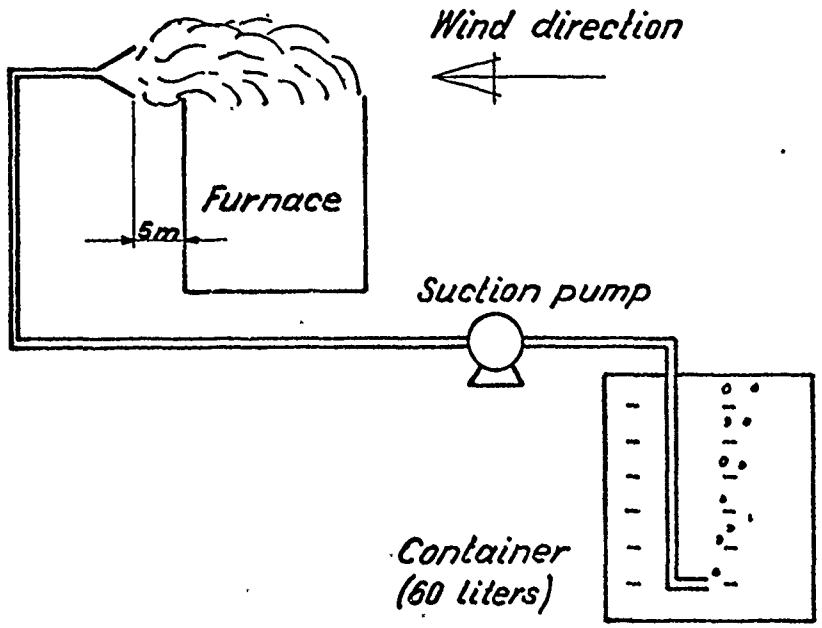
After a preheating with fuel, the waste is injected into the furnace, where it burns by itself at a temperature of about 1300°C. The resulting smoke, although immediately beaten down by the wind blowing at 25 to 40 knots, is very rapidly diluted: it is possible to move in the smoke plume as near as ten meters from the furnace, without feeling any discomfort, so much the more, there is no danger whatsoever for the ships that we saw crossing the plume at a distance of few cable lengths.

The measurement of the pH of the sea water under the plume, showed that the increase in acidity is measurable only on a distance of about 50m from the furnace: we took advantage of a moment when the ship faced head wind, for taking measurements along its side, which gave the following results.

| Distance to the Furnace | 10 m | 30 m | 50 m | Control samples |
|---|---|---|---|---|
| p.H. | 7.6 | 7.8 | 8 | 8.1 to 8.2 |
| Saltness 0/00 | 34.31 | 34.33 | 34,47 | 34 to 34.20 |

Moreover, this minimal acidification is only temporary, because all measurements made during the ship's sailing, before and after the burning within as well as outside the incineration zone, gave pH's of 8.1 to 8.2. Moreover, this acidification has a bearing only on the superficial layer. However, it could be somewhat more pronounced when the sea is totally calm, because then, less diffusion takes place. Anyway, in the Mediterranean Sea, where the pH is 8 to 8.2, one can expect that figures below 7, would be rare. Consequently, these conditions are acceptable. One notes also a slight increase of the saltness, without important consequences.

However we were interested in the smoke falling out in the sea and in its possible toxicity: for this, we took suction in the plume and let the combustion mixture bubble-up in a container filled with sea-water. This container has a very small opening and it is high enough to make the contact between the smoke and the water last as long as possible (see illustration here below).




In the experiment, the capacity of the suction pump was 1 litre/m. The suction took place during thirty-four hours, i.e.: 2040 litres gas at about 40°C, i.e. about 1800 litres at 0°C. During this handling, the pH of the sea water contained in the 60 l container, went down with one unit, which corresponds more or less to a contribution of 0.16 mole of hydrochloric acid. If the sucked gas would not have been diluted, one would have recuperated about 20 acid moles.

Consequently, one must admit that the smoke is diluted 100 times at 5m distance from the furnace. Of course, this dilution was enhanced by the very strong wind. However, it is thinkable that with a slight wind, the smoke is not blown down immediately on the sea's surface, and in this way it will be similarly diluted (with air) by the time it reaches the water.

Any way, the concentration we obtained in the 60 l container, is higher than what one can actually find in the sea. This is important, because this concentrate was used for establishing a laboratory nutrition chain.

Further, we took samples of the plancton, the sea water and of the fish, within and outside the incineration area. Unfortunately we did not find the same kind of fish in both places, which makes the comparisons difficult.

The counting of the phytoplanctonic populations, does not show significant differences between the burning area (samples 1 to 4) and the neighbouring areas (samples 5 and 6). The content in diatomae in all the samples is low, but one could not say that this is caused by the incineration.

Plancton
Sampling Place : Incineration Area
Samples 1 to 4

| Sampling Number | Diatomae (per ml) | Dinoflagellates (per ml) | Other flagellates, among which also Nanoplancton (per ml) |
|---|---|---|---|
| 1 | 14 | 1 | 570 |
| 2 | 70 | - | 240 |
| 3 | 4 | rare | 360 |
| 4 | 8 | - | 2850 |

Plancton
Sampling Place : Off Rotterdam
Samples 5 and 6

| Sampling Number | Diatomae (per ml) | Dinoflagellates (per ml) | Other flagellates, among which also Nanoplancton (per ml) |
|---|---|---|---|
| 5 | 31 | rare | 630 |
| 6 | 21 | rare | 5760 |

## 3. BIOLOGICAL TESTS

1) Unburnt liquid effluent

We investigated the toxicity of the unburnt effluent, with respect to various marine and estuary species:

- cyprinides
- crabs
- nereids
- mussels

For all these organisms, death resulted within less than ten hours, for dillutions up to 1/10,000.

As for the phytoplancton, even for a dillution of 1/10,000 one notices a stop in the growth and the mortality of Asterionella japonica and Diogenes sp.

The zooplancton Artemia salina did not live more than one day in a dillution of 1/10,000.

We did not push further these tests, which were made only for allowing some comparisons, and which show that throwing of chlorinated hydrocarbons into the sea, can be catastrophical for the marine environment.

2 The concentrate of smoke in sea water

The same toxicity investigations were carried out during thirty four hours, with the sea water in which the smoke had bubbled-up. Concentrations of 1; $\frac{1}{2}$; $\frac{1}{4}$; 1/8; 1/16; 1/32; 1/64; 1/128; 1/256; 1/500 were used, for the following marine or estuary species:

- cyprinides
- rascassides
- crabs
- nereides
- mussels

No mortality or any physical disturbance was experienced, even when the undilluted "bubbled-up" water was used. The length of the observation periods was seven days.

For the zooplancton Artemia salina no differences were found between the control samples and those living in the bubbled-up water, whatever its concentration was. The observation period was 15 days.

For the phytoplancton, the undiluted bubbled-up water causes to the Diogenes sp. a facing of the colour, indicating a change of the chloroplasts, thus a loss of the photo-synthesis function. Diluted bubbled-up water have no effect within 12 days. With Asterionella japonica a delay of the growth was noticed after the 5th day, whereas normally this takes place only the 8th day, this phenomenon being sensitive mainly for dilutions up to 1/8. Beyond the 11th day, one notices for all the cases a higher mortality than the normal.

This smoke concentrate was then used in a 1/4 dilution to investigate the inducted toxicity.

This dilution was chosen in order to avoid disturbances with the Diogenes sp. and because the Cyprinides used, cannot put up with the strong saltnesses (for this species, fresh water must be added to the sea water).

The tested nutrition chain, has the following components:

phytoplancton —— Zooplancton —— fish —— mamals

(Diogenes sp.) (Artemic salina) (Cyprinides) (Mus musculus)

This chain was chosen because, being of the pelagique type, it fits well to the given problem and because we did not have time for other tests.

The poisoning periods were 8 days for the marine species and 12 days for the mice.

Neither mortality, nor physical disturbance, nor abnormal behaviour was observed at any level.

## 4. CHEMICAL ANALYSES

### A. Nature and composition of the gases: released by the combustion at 1,300°C.

These measurements were performed at the analytical laboratory of C.N.R.S. (National Company of Scientific Research). The samples were taken in a pan made of silicon, placed in a silicon tube, fixed in the upper part of a tubular electrical furnace and heated to 1300°C.

The tube is moved very slowly, in order to have as much as possible a complete combustion. Despite this precaution, the combustion has an explosive characteristic which results in the formation of very fine particles of soot (little quantitative importance).

Under these conditions, the gases are composed of carbon dioxyde and monoxyde, steam, undefined traces of hydrocarbons, and of hydrochloric acid released at a rate of 123 litres per kilogram of chlorinated waste. As explained here above, these gases are very much diluted before falling into the sea and do not represent a danger for the marine environment. Work is being carried out for trying to determine the composition of the soot.

### B. Investigation of the chlorinated waste:

This investigation was performed:

- on two samples of sea water from the incineration area
- on two samples of sea water from outside the incineration area
- on four samples of mackerel caught in the incineration area
- on two herrings, caught outside this area
- on one poisoned mouse from the nutrition chain
- on one control mouse

1) Water samples

After extractions are performed on a 250 ml sample, with three times 100 ml petrol-ether, the solvent is dried up by evaporation, retaken in 10 ml hexane, and analyzed by chromatography in vapour phase (Carlo Erba 2200 - column OV101 2m, temperature: 150°C - flow ($N_2$00)$\pm$30 ml/mn, injected amount 2 µl - detection by capture of the $^{63}$Ni electron). A solution of the straight effluent at various concentrations is used as standard solution.

2) Fish and mice samples

After pounding a known amount of the sample (muscle for fish, lever, kidney, hart, lungs, muscle for mice) this is purified by being passed through a column of 40g of florisil (200 ml of an extracting solution made of 65% petrol-ether and 35% methylene chloride).

The solution containing the extract is concentrated until it is dry and retaken with 10 ml hexane. A solution of the straight effluent is passed through a similar florisil column and used as standard solution.

Results

We were unable to determine the presence of chlorinated waste in the samples provided for analysis. The solutions standard used for the water analyses being 1.62 ppb, one can estimated in a first approximation that the concentration in effluent is lower than 1.62 ppb, which, when reported to 1 g water sample, it corresponds to a concentration lower than 0.023 mg/g.

We did not find any noticeable difference in the pace of the chromatograms of the control mouse and the poisoned mouse. The chromatograms of the caught fish, show peaks, but these peaks could not be identified with those of the chromatogram of the straight effluent solution.

C. Investigation of heavy metals

This investigation was made for mercury and lead:

- in the fish and plancton caught in the North Sea
- in the waste before the combustion
- in the bubbled-up water
- in the different links of the nutrition chain

The following table gives a summary of the results of these analyses:

| | | Hg ppm (humid weight) | Pb ppm (humid weight) |
|---|---|---|---|
| Incineration area | Mackerel (1) | 1.03 | 0.69 |
| | " (2) | 0.33 | 3.52 |
| | " (3) | 0.66 | 0.64 |
| | " (4) | 0.80 | 0.36 |
| | Plancton (1) | 3.54 | 64.8 |
| | " (2) | 1.58 | 10.5 |
| | Effluent before burning | 0.114 mg/1 | |
| North Sea outside the incineration area | Herring (1) | 0.35 | 0.50 |
| | " (2) | 0.34 | 0.24 |
| | " (3) | 0.14 | 0.62 |
| | Plancton (3) | 1.47 | 13.2 |
| | " (4) | 5.27 | 52.7 |

| | | Hg (ppm) (humid weight) | Pb (ppm) (h. wt.) |
|---|---|---|---|
| Laboratory Nutrition Chain | Bubbled-up water | 0.72 g/1 | |
| | micro-seaweed + control specimen | 0.14 | 0.81 |
| | micro-seaweed + poisoned zooplancton | 0.22 | 4.09 |
| | Control cyprinides (1) | 0.04 | 0.71 |
| | " (2) | 0.04 | 0.63 |
| | " (3) | 0.05 | 0.27 |
| | Poisoned cyprinides (1) | 0.04 | 0.50 |
| | " (2) | 0.07 | 0.44 |
| | " (3) | 0.10 | 0.65 |
| | " (4) | 0.10 | 0.92 |
| | Control mouse (1) | 0.09 | 1.- |
| | " (2) | 0.05 | 1.- |
| | " (3) | 0.04 | 1.- |
| | Poisoned mouse (1) | 0.09 | 1.- |
| | " (2) | 0.09 | 1.- |
| | " (3) | 0.08 | 1.- |

From these figures it appears:

1) That the waters receiving the fall out of the incineration, show no difference with the rest of the sea. It is evident that in such changeable environment, the pollutions come from many places and can be found everywhere. The contribution of the burned waste appears negligible, any way short term. It is impossible to follow "in situ" the long term consequences.

2) That no mercury or lead accumulation takes place in the organisms of the nutrition chain living in an environment clearly more concentrated in burned gas than the sea surface during the incineration.

3) That despite all, there are traces of mercury in the effluent. This mercury seems not to be in the form of methyl-mercury, because it is not accumulated in the nutrition chain. However one should make sure that a longer period of exposure to poisoning has no other consequences and that the receiving environment does not contain micro-organisms capable of methylating the mercury.

The measurements concerning cadmium, another dangerous metal, are being carried out.

## 5. CONCLUSIONS

The purpose of our experiments was to give an answer on the biological and sanitary aspect of the process of incineration at sea of chlorinated liquid waste. These experiments are by no means exhaustive, but they are sufficiently significant for guiding and allowing the taking of immediate decisions, based on the knowledge one has on the short term consequences. Thus, it appears to us:

1) that the process does not seem to bring about changes in the biological mass

2) that smoke entering the marine environment does not seem to have an effect on the productivity. However, if this smoke comes into the sea in large volumes, there are some indications, such as the discolouration of the Diogenes sp., showing that the neutrality is not perfect.

3) that no phenomenon of accumulation through the nutrition chain takes place, neither for the mercury, nor for the lead, nor for the chlorinated hydrocarbons. We did not yet investigate the possible presence of other toxic materials such as cadmium or benzopyrenes, which could exist in the soots, but anyway, they have not caused any disturbance in the various links of the nutrition chain we have studied.

In the present state of our knowledge, it seems that the process of incineration does not cause, certainly not short term, any special harm to the oceanic environment.

It appears anyhow very superior to the method of straight throwing these industrial (waste) into the waters, as it is practiced usually. This straight throwing, causes a complete and immediate destruction of the sealife, even in very low concentrations, much inferior to 1/10,000. Moreover, even lower concentrations than these, will have results with

dangerous consequences for the consumer of marine products.

Naturally, this favourable advice for the burning, must be confirmed by the long term continuation of the measurements, as a certain number of points have still to be determined. It is evident that this advice concerns only the tested products and that any change in the nature of the burned waste would reopen the question. Exact measurements would be necessary to evaluate the possible harmfulness of these products.

January 1974.

# L'INCINERATION EN HAUTE MER DE RESIDUS INDUSTRIELS CHLORES

-:-:-:-:-:-:-:-:-:-:-:-:-:-.

Le Ministère chargé de l'Environnement (Direction de la Prevention des Pollutions et Nuisances) a été, courant 1973, saisi de deux demandes d'autorisation d'incinération formulées par deux sociétés étrangères spécialisées dans la destruction en mer, à partir de navires spécialement équipés, des résidus chlorés (hydrocarbures et solvants clorés) produits par l'industrie chimique.

Les Sociétés Incinératrices et leurs moyens.

La première demande a été formulée par le canal de la Direction générale des services maritimes de la Compagnie Maritime et Charbonnière WORMS par la Société "OCEAN COMBUSTION SERVICE" de Rotterdam.

La S.A.R.L. " INCIMER " de Marseille a été à l'origine de la seconde.

Chacune des sociétés concernées dispose d'un ou de plusieurs navires incinérateurs spécialement équipés : les Mathias I et Mathias II pour INCIMER, le VULCANUS pour l'O.C.S. dont le tableau ci-après (Tableau I) résume les caractéristiques essentielles.

Ces navires ont, sur le plan de la conception, en commun :

- une capacité de stockage de volume variable.

- un ou deux fours circulaires à ciel ouvert, revêtus intérieurement de briques réfractaires.

- un ensemble de brûleurs spécialement adaptés au type de produits à incinérer et fonctionnant avec atomisation d'air comprimé.

- un système d'alimentation du four en air assurant un excès d'air nécessaire à la combustion complete des produits. Cette alimentation est assurée par un ou plusieurs ventilateurs.

Produits incinérés - Nature et Volume.

Les produits pour lesquels les deux sociétés "INCIMER" et "O.C.S." ont sollicité une autorisation d'incinération sont des produits résiduaires de l'industrie chimique en grande partie constitués d'hydrocarbures chlorés, ayant pour formule chimique générale la formule :

$$C_x H_y Cl_z \ (o).$$

dans laquelle x peut être égal à 1,2,3 ou 4, y à 0,1,2,3, ou 4, z à 2,3,4,5 ou 6.



.../...

## TABLEAU N° 1

| Sociétés | INCIMER | | O.C.S. |
|---|---|---|---|
| Navires | MATHIAS I - MATHIAS II | | VULCANUS |
| **Caractéristiques des navires** | | | |
| Type | | Cargo transformé | cargo transformé |
| Longueur hors tout | 40 m | 72,80 m | 101,95 m |
| Largeur | ±8 m | 10,85 m | 14,40 m |
| Tirant d'eau en charge | | 5,20 m | 7,40 m |
| Jauge brute | | | 3.089 tx |
| Vitesse | | 11 noeuds | 13 noeuds |
| Equipage | | 12 hommes | 16 hommes |
| Capacité de stockage | 550 t | 1350 t | 3.505 m3 |
| Double fond (hauteur) | | 0,80 m environ | 0,90 m minimum |
| Nombre de citernes | 6 | 12 + 2 cuves en pontée | 15 |
| Ballast | | Ne se leste jamais | 4 capacités à l'avant + cofferdans et double fond |
| **Installation d'incinération** | | | |
| Incinérateurs - Nombre | 1 | 1 | 2 |
| Ø extérieur | 5 | | 5,50 m |
| Ø intérieur | | | 4,80 m |
| hauteur | 6 m | | 10,45 m |
| Alimentation air | | | 90.000 m3/h |
| Brûleurs - Nombre | 6 | 8 | 3/incinérateur (type Saack |
| Débit unitaire | 0,8 t/h | 1 t/h | |
| Capacité d'incinération totale | 3,6 t/h ou 5 t/h | 8 à 10 t/h | 20 à 22 t/h |
| **Technique d'incinération** | | | |
| T° minimale | 1000°C | 1000°C | 1400°C |
| T° maximale | 1450°C | 1500° C | 1650°C |

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Ces produits dont la composition n'est pas stable et qui ne peuve donner lieu à aucune réutilisation émanent essentiellement des chaines fabrication de matières plastiques, de chlorure de vinyl monomère à partir d'éthylène, de nombreux produits pharmaceutiques, d'insecticides, de pesticid utilisant toutes les hydrocarbures chlorés comme produit de base.

Comme la formule l'indique, la teneur en chlore de ces résidus peut varier dans de notables proportions, ce que traduisent les chiffres avancés par les industriels et spcialistes qui ont été confrontés aux problèmes d'incinération.

Dans un article consacré à l'"Incinération de rejets liquides et récupération de produits chimiques" et paru dans "Informations Chimie" (*) M. Hidemasa Tsuruta évalue à 65-70 % la quantité de chlore contenue normalement dans les résidus chlorés rejetés par les installations de VCM à partir d'éthylène.

Le Professeur Dr Klaus Grasshof, chef du Département "Chimie des Mers" à l'Institut d'Etudes Maritimes" de l'Université de Hiel, estime, quant à lui, à 30% le pourcentage moyen de chlore contenu dans les rejets brûlés en mer à partir du port de Rotterdam.

D'autres documents enfin font état de teneurs variant de 20 à 80 %, la moyenne se situant aux environs de 50%.

On possède peut de données sur le volume global de ces rejets.

Selon le Professeur Docteur Klaus Grasshoff, cité précédemment, la quantité de tels produits résiduaires atteindrait 100 à 130.000 tonnes/an en Europe Occidentale (dont 50 à 70.000 tonnes en Allemagne Fédérale). La Société SOLVAY évalue, quant à elle, à 200 000 tonnes la quantité d'hydrocarbures et de solvants chlorés rejetés par l'industrie chimique de l'Europe de l'Ouest.

En ce qui concerne la France, les estimations font preuve de la même incertitude et varient selon les sources d'information de 25 à 60 000 tonnes/an, quantités essentiellement en provenance des industries chimiques SOLVAY/PECHINEY - UGINE KUHLMAN/RHONE PROGIL.

Traitement actuel des rejets en France.

Ces produits résiduaires sont actuellement éliminés de façons très diverses légales ou illégale . Au nombre de ces dernières, le rejet de quantités généralement peu importantes transportées en fûts ou par citernes dans les cours d'eau, d'anciennes carrières desaffectées ou décharges d'ordures non surveillées doit être raisonnablement retenu.

* Information Chimie, n°124, Oct. 1973, pp. 179-186

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Sur le plan légal, il existe actuellement deux stations privées de destruction de liquides organiques chlorés, appartenant respectivement aux sociétés UGINE KUHLMANN et RHONE-PROGIL.

Ainsi cette dernière société dispose-t-elle à Saint Auban (Alpes de Haute Provence) en fonctionnement avec Chloé 1 et les ateliers de trichloréthylène et de divers solvants chlorés d'une unité expérimentale de 0,7 t/h en usage depuis 4 ans et d'une unité industrielle de 1,4 t/h en fonction depuis 3 ans selon le procédé breveté RHONE PROGIL.

La Société Solvay dispose également d'une unité de traitement mais hors de France au niveau du Groupe.

Leur capacité réduite est sans doute le reproche majeur que l'on peut leurs faire.

Dans ces installations il est procédé à la destruction des résidus chlorés par pyrolyse ou combustion en atmosphère oxydante avec récupération d'acide chlorydrique par lavage à eau vive.

En général les liquides résiduaires, à la différence des carburant brûlent mal. Leur incinération pose donc de nombreux problèmes, en particulier ceux liés à la faible chaleur de combustion, à leur viscosité élevée, à la présence de particules solides et dans certains cas à la polymérisation ou à la décomposition des produits.

D'une façon générale une augmentation de la teneur en chlore rend plus difficile leur incinération. De même agissent les fortes teneurs en eau et en cendres. Cependant l'utilisation de brûleurs à haute efficacité permet de brûler, sans carburant auxiliaire, des rejets ayant des pouvoirs calorifiques relativement faibles se situant entre 2.500 et 3.500 K cal/kg.

Cependant pour des teneurs en chlore supérieures à 70 % (pouvoir calorifique inférieur à 3.000 K cal/kg) il s'avère nécessaire pour assurer une bonne combustion, soit d'utiliser un carburant auxiliaire, soit d'ajouter aux produits incinérés un carburant de pouvoir calorifique plus élevé.

Ceci étant et de façon théorique, dans des conditions de combustion optimales, les gaz sortant du four contiennent essentiellement de l'Azote du gaz carbonique, du chlore et de l'acide chlorydrique.

Ces constituants obéissent à plusieurs réactions dont notamment :

$$H_2O + Cl_2 \rightleftharpoons 2\,HCl + \tfrac{1}{2}\,O_2$$

.../...

Cette réaction d'équilibre est déplacée vers la droite quand la température croit - Ainsi la quantité de chlore libre diminue :

- si on augmente la température (les hautes températures sont également utiles pour réaliser une combustion complète des composés organiques, cependant la résitance des matériaux réfractaires limite cette température à environ 1.500° C).

- si on augmente la quantité de vapeur d'eau.

- si on diminue autant que possible la quantité d'oxygène.

Principe de l'Incinération en Mer.

L'incinération en haute mer à partir de navires spécialement équipés fait appel au procédé de pyrolyse évoqué précédemment mais s'en distingue par l'absence d'installations de lavage et de récupération d'acide chlorydrique.

Technique de l'incinération.

Le four est tout d'abord préchauffé au fuel jusqu'à une température de 1000 degrés environ dans le cas des MATHIAS I et II et de 1400 - 1500° C dans le cas du VULCANUS avant que les résidus à incinérer ne soient introduits.

Lorsque ces températures sont atteintes, l'injection des déchets dans la ou les chambres de combustion est entreprise par le moyen de pompes d'injection pouvant être branchées soit sur une seule citerne de stockage, soit simultanément sur plusieurs ou la totalité des citernes.

L'utilisation de brûleurs doubles permet d'introduire directement dans la flamme produite par la combustion du fuel des quantités croissantes de liquides résiduaires et de moduler les apports en fonction de la température qui doit toujours se maintenir au dessus d'un certain seuil conditionnant la complète pyrolyse des produits traités. L'afflux de fuel peut être ainsi réduit , sinon arrêté totalement. Dans le cas où la température tombe en dessous du seuil de complète pyrolyse, un sytème automatique rétablit l'injection de fuel.

Dans le cas de produits dotés d'un pouvoir calorifique inférieur à 3000 K cal/h, une injection continue de fuel peut s'avérer nécessaire et être rendue effective . Dans les cas extrêmes, l'incinération de résidus aqueux est ainsi possible, moyennant une consommation évidemment très accrue de fuel.

En l'absence d'installations de lavage et de récupération d'acide chlorydrique, la totalité des gaz de combustion se répand dans l'atmosphère puis après condensation par la vapeur d'eau contenue dans l'air est précipitée sur la surface de la mer.

.../...

Cette précipitation a été présentée par les industriels comme sans inconvénient pour la faune et la flore marines. En particulier il a été considéré que l'acide chlorydrique produit serait très rapidement neutralisé du fait des teneurs élevées en éléments basiques que présentent les eaux marines.

Lors de la neutralisation il y aurait production de gaz carbonique d'acide borique et de chlorure.

Il s'établirait en outre après un laps de temps très court un nouvel équilibre du fait que le gaz carbonique dégagé s'échappe dans l'atmosphère, et que le carbonate de calcium présent dans l'eau passe à l'état de solution. Ces réactions auraient ainsi pour effet de rétablir le degré d'alcalinité antérieur.

En fait la complexité des phénomènes qui se déroulent dans le milieu marin dont l'équilibre est souvent précaire ont incité l'Administration à une approche prudente du problème et à demander aux industriels qu'avant tout examen de leur demande, un dossier scientifique et technique aussi complet que possible soit constitué sur les procédés d'incinération en mer et sur les risques de nuisances qui leur sont associés.

A cet effet le Ministère chargé de l'Environnement a proposé aux industriels qu'indépendamment de l'étude des documents ayant trait aux observations et analyses faites par des laboratoires étrangers ou français à l'occasion de campagnes d'incinération au large de la Hollande , une expérimentation grandeur nature portant sur des produits chlorés rejetés par l'industrie chimique française soit réalisée sous le contrôle des Administrations et Organismes concernés par la protection et la défense du milieu marin.

# L'EXPERIMENTATION PORTANT SUR L'INCINERATION EN MER ET SES RESULTATS

-:-:-:-:-:-:-:-

**But.**

L'expérimentation se proposait de recueillir toutes informations sur :

- la qualité des effluents à la sortie des incinérateurs (gaz de combustion et imbrûlés).
- la dispersion et la qualité des effluents gazeux dans l'atmosphère.
- les phénomènes associés à la retombée des effluents gazeux sur la surface de la mer (mesures de pH...)
- l'incidence de ces rejets sur le milieu marin au point de vue écologie.

en partant de produits incinérés ayant, sur le plan des caractéristiques physico-chimiques, valeur de référence pour toute éventuelle autorisation d'incinérer que pourrait ultérieurement délivrer l'Administration.

**Moyen mis en oeuvre.**

On participé à l'expérimentation qui s'est déroulée du 19 au 22 Avril 1974 au large de ROTTERDAM, à l'intérieur du permis octroyé par les autorités néerlandaises aux navires incinérateurs :

Industriels.

* le navire incinérateur Vulcanus de l'"Océan Combustion Service" pour le compte de la Société Maritime et Charbonnière WORMS
* le navire incinérateur MATTHIAS II, de la société allemande Stahl-Und-Blech-Bau, Bochum pour le compte de la société INCIMER.

.../...

TABLEAU II

Etude des charges - Mesures physicochimiques

-:-:-:-:-:-:-:-:-:-

| | Charge du Matthias II | Charge du Vulcanus |
|---|---|---|
| Mesures physiques | | |
| Densité à 20° C | 1,061 | 1,267 |
| Viscosité à 20° C | 1.085 cs | 0,787 cs |
| Intervalles de distillation entre 52 et 190 ° | 97,5 % | 97 % |
| Analyse élémentaire (% pondéral) | | |
| C | 43,2 | 25 |
| H | 7,15 | 4 |
| N | Non détecté | Non détecté |
| S | Non détecté | Non détecté |
| Cl | 47 | 71 |
| Métaux lourds -(p.p.m.) | | |
| Cr | 0,3 | 0,4 |
| Cu | 0,3 | 0,5 |
| Fe | 3 | 6,5 |
| Hg | 0 | 0 |
| Mn | 2,5 | 2 |
| P | 7 | <0,3 |
| Pb | 3,4 | 0,9 |
| Si | 3 | 2 |
| Zn | 0,3 | 1,2 |

## ETUDE DES CHARGES - MESURES SPECTROGRAPHIQUES

**Charge du MATTHIAS II ( en % poids )**

| | | |
|---|---|---|
| Hexènes | $C_6 H_{12}$ | 2,47 |
| Propanal | $CH_3 - CH_2 - C(=O)H$ | 14,16 |
| Acétone | $CH_3 - C(=O) - CH_3$ | 2,92 |
| 1-2 Dichloropropane | $CH_2Cl - CHCl - CH_3$ | 28,17 |
| Epichlorhydrine | $CH_2 - CH - CH_2Cl$ (O) | 4,24 |
| 2-3 dichloropropène | $CH_2 = CCl - CH_2Cl$ | 3,02 |
| di (chloroisopropyl)ether | $(CH_2 - Cl - CH(CH_3))_2 O$ | 28,54 |
| 3 chloropropylether | $(CH_2Cl - CH_2 - CH_2)_2 O$ | 5,49 |
| 2 chloropropylether | $(CH_3 - CHCl - CH_2)_2 O$ | 6,47 |
| autres corps | | 4,52 |

**Charge du VULCANUS ( en % poids )**

| | | |
|---|---|---|
| Chloroforme | $CHCl_3$ | 1,01 |
| + 1-1 dichloroethane | $CH_2Cl - CH_2Cl$ | |
| Tetrachlorure de C. | $CCl_4$ | 2,35 |
| 1-2 dichloroethane | $CH_2Cl - CH_2Cl$ | 73,03 |
| Tetrachlorethylène | $CCl_2 = CCl_2$ | 6,60 |
| 1-1-2 trichlorethane | $CHCl_2 - ClH_2Cl$ | 11,05 |
| autres corps | | 6,96 |

Il convient de noter les différences de composition qui séparent ces deux produits provenant respectivement de l'industrie chimique allemande et anglaise et considérés par les industriels comme representatifs de la production française en matière de rejets industriels chlorés.

Analyse des effluents à la sortie des incinérateurs.

Deux dosages, celui du chlore et du phosgène, ont été effectués à bord des navires incinérateurs. Leurs résultats figurent ci-après (en p.p.m.)

| | Matthias II | Vulcanus * | |
|---|---|---|---|
| Chlore | 250 | 2000 | 1100 |
| Phosgène | 2 | <1 | |

* 2 mesures.

Ces mesures ont été complétées de recherches sur les imbrûlés liquides, solides ou gazeux pouvant provenir d'une combustion incomplète des charges.

Les recherches effectuées sur les produits piégés lors de la combustion des résidus chlorés chargés à bord du Vulcanus ne mettent en évidence dans le gaz de combustion que des quantités négligeables (0,5 p.p.m.) de composés correspondant aux produits les plus lourds de la charge.

On peut donc estimer que la pyrolyse est pratiquement complète dans le cas du Vulcanus.

Des recherches identiques effectuées sur les produits piégés lors de la combustion des résidus chargés à bord du Matthias II donnent des résultats pratiquement identiques quant aux quantités d'imbrulés (de l'ordre de 0,5 p.p.m.).

Cependant il faut noter que parmi ces imbrulés figurent :

- des composés légers type acétone - également présents dans la charge.
- des "goudrons" insolubles dans l'eau, de nature encore indéterminée (recherche d'éventuels cancérigènes en cours).

Le premièr point implique que dans le cas du Matthias II la température de combustion n'est pas uniformément maintenue aux environs de 1000/1100° - comme paraissaient l'indiquer les enregistrements de t° effectués

.../...

Administrations.

* le Ministère chargé de l'Environnement (Direction de la Prévention des Pollutions et Nuisances - Service des Problèmes de la Mer et des Océans) représenté par Monsieur Jean Marie MASSIN, Chef de Mission.

* l'Institut Scientifique et Technique des Pêches Maritimes (I.S.T.P.M.) représenté par :

  - le navire océanographique Thalassa.

  - Messieurs ALZIEU et MAGGI

* le Centre National pour l'Exploitation des Océans (C.N.E.X.O.) représenté par Monsieur MOURLON, coordinateur des actions en mer et Mademoiselle JULLIEN.

* l'Institut français du pétrole (I.F.P.) représenté par Messieurs ROUSSEL et BUZON (Branche Chimie Raffinage - Division physico-chimie appliquée).

* le Commissariat à l'Energie Atomique (C.E.A.) représenté par :

  Monsieur PLATZER, Coordination de l'Analyse, C.E.A. Fontenay aux Roses.

  Monsieur VAVASSEUR et Monsieur LE BRONEC, Département de protection, Service Technique d'Etudes de protection et de pollution atmosphériques C.E.A. Saclay.

  Monsieur HAULET, Département de protection, Service technique d'Etudes de protection et de pollution atmosphériques C.E.A. Fontenay aux Roses.

  Monsieur BLAIN, Département de Recherches et d'Analyses - Service Etude des Analyses, C.E.A. Fontenay aux Roses.

Analyse des charges.

Un seul type de produit a donné lieu à incinération, sur chacun des navires concernés. Les analyses effectuées sur les prélèvements réalisés à bord des navires ont donné les résultats suivants (Tableaux II et III).

.../...

à partir des thermo-couples montés sur les parois du four - mais localement, tombe en dessous du seuil de dissociation des composés légers (400°).

La présence de goudrons pourrait être quant à elle préoccupante dans la mesure ou des éléments cancérigènes seraient mis en évidence. Il faut noter à ce propos que compte tenu des débits de gaz de combustion mis en jeu (de 100 à 140 000 $m^3/h$), 50 à 70 kg de résidus solides ou goudronneux sont rejetés par heure par le Matthias II.

Etude du panache.

Il a été procédé au dosage de l'acide chlorydrique au voisinage et dans le panache émis par les deux navires incinérateurs. A l'issue de ces dosages, il convient de retenir que les concentrations maximales d'acide chlorydrique dans les panaches, à quelques mètres au dessus du niveau de la mer sont du même ordre de grandeur (quelques v.p.m.) pour le Matthias et le Vulcanus.

Etude de l'eau de mer.

Les mesures de pH effectuées de façon continue à la surface de la mer au cours de l'expérimentation n'ont pu mettre en évidence aucune variation sensible de la qualité du milieu superficiel marin.

Par ailleurs les analyses effectuées sur les prélèvements d'eau de mer réalisés au point d'impact maximum des rejets gazeux sur le milieu marin n'ont décelé aucune trace d'hydrocarbures.

## CONCLUSIONS ET OBJECTIFS

-:-:-:-:-:-:-:-:-:-

Des premiers résultats obtenus à l'issue de l'expérimentation il résulte que :

1) En ce qui concerne les charges à incinérer.

- les caractéristiques physico-chimiques des rejets de l'industrie chimiques susceptibles d'être éliminés par incinération sont compte tenu des premiers résultats essentiellement variables.

  La notion de produit (s) testé (s) lors de l'expérimentation et ayant valeur de référence pour toute éventuelle autorisation à incinérer que pourrait délivrer l'Administration doit donc être écartée jusqu'à plus ample information.

  Ceci implique, que si le principe de l'incinération en mer est admis par l'Administration, toute autorisation sera subordonnée à un contrôle rigoureux de la qualité des chargements.
  Ce contrôle pourrait comporter :
  - une analyse relativement sommaire du produit embarqué (en vue de déceler, le cas échéant, la présence de métaux lours en quantités prohibitives).
  - un essai d'incinération à l'échelle réduite afin de déter miner la qualité des effluents de combustion.

2) En ce qui concerne la pyrolyse des charges.

- si la pyrolyse parait complète dans le cas du Vulcanus, quelques réserves peuvent être faites sur la combustion qui s'opère à bord du Matthias II (présence d'imbrulés légers et goudronneux).

  Le facteur température de combustion doit être en conséquence considéré comme primordial.

  Ceci implique que le contrôle des températures au cours de la combustion doit faire l'objet de dispositions spéciales et que toutes les parties du ou des fours puissent être contrôlées en service pour vérifier leur température.

.../...

3) En ce qui concerne l'incidence des retombées des gaz de combustion.

- exception faite des imbrulés solides ou goudronneux (en particuli des imbrulés non miscibles à l'eau dont la nocivité reste à montrer (étude en cours)), l'émission de chlore et d'acide chlorhydrique ne parait avoir aucune action sur le milieu marin.

Compte tenu de ce qui précède le Ministère chargé de l'Environnement propose que :

- une législation appropriée pour l'incinération en mer soit élaborée et que des décrets d'application tiennent compte sur le plan technique, en particulier :

  * de la nécessité de contrôler la nature de chaque chargement avant incinération en se référant, le cas échéant, aux indications fournies par un "incinérateur de contrôle" reproduisant en laboratoire les conditions reelles de l'incinération en mer.

  * de la nécessité de disposer de fours et de brûleurs assurant une pyrolyse complète des produits traités.

  * de la nécessité de contrôler de façon continue et en tous points la température du ou des fours de combustion.

- dans l'immédiat un certain nombre de dispositions seront prises pour que les navires incinérateurs puissent exercer leur activité à partir de ports français et à l'intérieur de zones maritimes qui leurs seront spécialement affectées, moyennant toutes précautions relatives à la protection du milieu marin.

FTD-HC-23-14-75

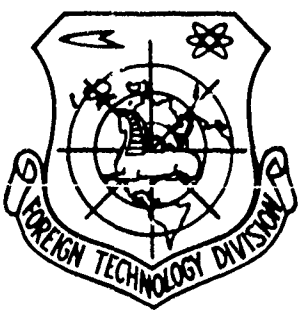
# FOREIGN TECHNOLOGY DIVISION




INCINERATION ON THE HIGH SEAS OF CHLORINATED INDUSTRIAL WASTES

by

Author Unknown



# EDITED TRANSLATION

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PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

## U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|---|---|---|---|---|---|
| А а | *А а* | A, a | Р р | *Р р* | R, r |
| Б б | *Б б* | B, b | С с | *С с* | S, s |
| В в | *В в* | V, v | Т т | *Т т* | T, t |
| Г г | *Г г* | G, g | У у | *У у* | U, u |
| Д д | *Д д* | D, d | Ф ф | *Ф ф* | F, f |
| Е е | *Е е* | Ye, ye; E, e* | Х х | *Х х* | Kh, kh |
| Ж ж | *Ж ж* | Zh, zh | Ц ц | *Ц ц* | Ts, ts |
| З з | *З з* | Z, z | Ч ч | *Ч ч* | Ch, ch |
| И и | *И и* | I, i | Ш ш | *Ш ш* | Sh, sh |
| Й й | *Й й* | Y, y | Щ щ | *Щ щ* | Shch, shch |
| К к | *К к* | K, k | Ъ ъ | *Ъ ъ* | " |
| Л л | *Л л* | L, l | Ы ы | *Ы ы* | Y, y |
| М м | *М м* | M, m | Ь ь | *Ь ь* | ' |
| Н н | *Н н* | N, n | Э э | *Э э* | E, e |
| О о | *О о* | O, o | Ю ю | *Ю ю* | Yu, yu |
| П п | *П п* | P, p | Я я | *Я я* | Ya, ya |

*ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ë in Russian, transliterate as yë or ë. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

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## GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

## RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

| Russian | English |
|---|---|
| sin | sin |
| cos | cos |
| tg | tan |
| ctg | cot |
| sec | sec |
| cosec | csc |
| sh | sinh |
| ch | cosh |
| th | tanh |
| cth | coth |
| sch | sech |
| csch | csch |
| arc sin | $\sin^{-1}$ |
| arc cos | $\cos^{-1}$ |
| arc tg | $\tan^{-1}$ |
| arc ctg | $\cot^{-1}$ |
| arc sec | $\sec^{-1}$ |
| arc cosec | $\csc^{-1}$ |
| arc sh | $\sinh^{-1}$ |
| arc ch | $\cosh^{-1}$ |
| arc th | $\tanh^{-1}$ |
| arc cth | $\coth^{-1}$ |
| arc sch | $\operatorname{sech}^{-1}$ |
| arc csch | $\operatorname{csch}^{-1}$ |
| rot | curl |
| lg | log |

# INCINERATION ON THE HIGH SEAS

# OF CHLORINATED INDUSTRIAL WASTES

During 1973, two requests authorizing the incineration of chlorine wastes (hydrocarbons and chlorinated solvents) in specially equipped vessels, were presented by two foreign Companies specialized in the destruction of wastes on the open sea, to the Ministry in charge of Environnement (Pollution and Nuisance Prevention).

## Companies of incineration and their equipment

The first request was presented through the Channel of the General Direction of Naval Services of the " Compagnie Maritime et Charbonniere WORMS", by the Society " Ocean Combustion Service" of Rotterdam.

The S.A.R.L. INCIMER of Marseille originated the second request

Both of these Companies own one or several incinerator-ships specially equipped : Mathias I and Mathias II for INCIMER, and the Vulcanus for O.C.S. ; the following table (Table I) will give a summary of their main characteristics.

From a basic point of view, those ships have in common :

- a storage capacity of expandable volume.

- one or two circular furnaces open to the atmosphere, lined with firebricks.

- a set of burners adapted specially for the type of product to incinerate, and functionning by atomisation of compressed air.

- an air-feeding system to the furnace providing air in excess so that the combustion of the products is complete. This air supply is provided by one or several fans.

## Incinerated products - Nature and Volume.

The products for which both Companies INCIMER and O.C.S. have applied for a permit to incinerate are the residual products

# TABLE No. 1

| COMPANIES | I N C I M E-R | O.C.S. |
|---|---|---|
| SHIPS | MATHIAS I - MATHIAS II | VULCANUS |
| **Caracteristics of the ships** | | |
| Type | Transformed freighter | transformed freighter |
| Overall length | 40 m — 72,80 m | 101,95 m |
| Width | ±8 m — 10,85 m | 14,40 m |
| Draught | 5,20 m | 7,40 m |
| Gross gauge | | 3.089 tx |
| Speed | 11 knots | 13 knots |
| Crew | 12 men | 16 men |
| Storage capacity | 550 t — 1350 t | 3.505 m3 |
| Double bottom (height) | 0.80 m approx. | 0.90 m minimum |
| Number of tanks | 6 — 12 + 2 tanks on deck | 15 |
| Ballast | No ballast | 4 spaces at the front + cofferdams & double bottom |
| **Incineration Equipment** | | |
| Incinerators - Number | 1 — 1 | 2 |
| Exterior Ø | 5 | 5,50 m |
| Interior Ø | | 4,80 m |
| Height | 6 m | 10,45 m |
| Air input | | 90.000 m3/h |
| Burners - Number | 6 — 8 | 3/incinerators (Saack type) |
| Delivery per unit | 0,8 t/h 1 t/h | |
| Total incineration capacity | 3,6 t/h 8 à 10 t/h or 5 t/h | 20 à 22 t/h |
| **Technique of incineration** | | |
| T° minimum | 1000°C 1000°C | 1400°C |
| T° Maximum | 1450°C 1500° C | 1650°C |

of chemical industries, mostly chlorinated hydrocarbons having for their general formula the following :

$$C_x H_y Cl_z \quad (0)$$

where x can be equal to 1,2,3 or 4; y to 0, 1, 2, 3 or 4; z to 2,3,4 5 or 6.

These products of unstable composition and which cannot be re-utilized come essentially from the manufacture of plastics and monomers of vinyl chloride (VCM) from ethylene, and numerous pharmaceutical products, insecticides, pesticides, all using chlorinated hydrocarbons as a basic product.

As indicated in the formula, the chlorine contents of these wastes can vary a great deal, and this is reflected by the figures mentioned by manufacturers and specialists for the incineration problems.

In an article about the "Incineration of liquid wastes and regeneration of chemical products" published in "Information Chimie"* (Chemical Information), Mr Hidemasa Tsuruta estimates that the quantity of chlorine normally present in the chlorinated wastes as a reject from the plants producing VCM from ethylene is about 65-70%.

Professor Klaus Grasshof, head of the Department of "Chemistry of the Oceans" at the Institute fo Marine Studies at Hiel University gives an estimate of 30%, as an average percentage of chlorine content in the wastes burnt at sea off the Harbor of Rotterdam.

Other documents mention amounts varying from 20 to 80%, with an average of about 50%.

Few actual data are given on the total volume of these wastes.

For Dr Klaus Grasshof (mentioned above), the quantity of these residus would be 100 to 130,000 tons (metric tons) per year in Western Europe ( 50 to 70,000 for West Germany). The Company SOLVAY approximates as 200,000 tons the quantity of hydrocarbons and chlorinated solvents rejected by the Chemical industry of Western Europe.

For France, the estimates present the same inaccuracy and vary with different sources of information from 25 to 60,000 tons per year, amounts produced mainly by the Chemical Industries of SOLVAY-PECHINEY, UGINE-KUHLMAN, RHONE-PROGIL.

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* Information Chimie 124, October 1973; 179-186.

Actual treatment of the wastes in France.

These residues are actually disposed of by various means, legal or illegal. Among the latter group, the rejects of generally negligible amounts carried by barrels or tanks to streams, disaffected quarries, or un-patrolled dumps, must be reasonably accounted for.

Legally, there are now two privately owned stations of destruction of chlorinated organic liquids, belonging to, respectively, UGINE-KUHLMAN and RHONE-PROGIL.

In St Auban (Alpes of Haute-Provence), the Company RHONE-PROGIL disposes, functionning with Chloé 1 and the plants of trichloroethylene and various chlorinated solvents , of an experimental unit of 0,7 tons /hour now in use for 4 years; and of an industrial unit of 1.4 t/h using for 3 years a procedure patented by RHONE-PROGIL.

The Company SOLVAY owns also an unit of treatment at the Group level, but outside of France.

The major fault which can be formulated is their reduced capacity.

In those plants, the chlorinated wastes are destroyed by pyrolysis or combustion by oxidation with recovery of hydrochloric acid by running water washing.

In general, the liquid-waste, unlike the carburants, burns very poorly. Their incineration is bound to many problems, due in particular to their low temperature of combustion, their high viscosity, the presence of solid particles, and in certain cases to the polymerization or decomposition of the products.

Generally speaking, the higher the chlorine contents, the more difficult the incineration. The high water or ash content behave similarly. However, high efficiency burners can consume, without auxiliary carburant, some residue with the low calorific power of 2500 to 3500 Kcal/kg

When the chlorine content is higher than 70% (calorific power less than 3,000 K cal/Kg) it becomes necessary, in order to have a complete combustion, either to use an auxiliary carburant, or to add to the products to be incinerated a carburant with higher calorific power.

In those conditions of optimum combustion, theorically the gasses released by the furnace contain essentially: nitrogen , carbon dioxide, chlorine and hydrochloric acid.

These components follow several reactions such as:

$$H_2O + Cl_2 \rightleftharpoons 2\,HCl + \tfrac{1}{2}\,O_2$$

This equilibrium is displaced towards the right when the temperature increases, so that the amount of free chlorine decreases:

- if the temperature is raised (high temperatures are also useful to realize a complete combustion of organic compounds; however the resistance of the firebricks limits this temperature to 1500° C).
- if the amount of water vapor is increased.
- if the amount of oxygen is lowered as much as possible

Principle of Incineration at sea

The incineration on the high sea by specially equipped ships is based on the forementionned pyrolysis technique, but it does not include the equipment for washing and recovery of hydrochloric acid.

Technique of incineration

The kiln is preheated by fuel to a temperature of approximately 1000° C. for the ships Mathias I and II, and of 1400 to 1500°C. for the ship Vulcanus, before the residues are brought in.

When the above temperatures are reached, the wastes are injected into the combustion chamber (or chambers) by means of injection pumps which can be plugged on one storage tank alone, or simultaneously on several or all of the tanks.

The double burners make it possible to introduce, directly into the flame of the burning fuel, increasing quantities of liquid wastes and to modulate the input as a function of the temperature, which must be maintained above a certain threshold, as a necessary condition for the complete pyrolysis of the treated products. The flow of fuel can then be reduced, if not completely stopped. When the temperature falls below the threshold of complete pyrolysis, an automatic system reactivates the fuel injection.

In the case of the products having a calorific power inferior to 3000 K cal/h, a continuous fuel injection might be necessary, and be still efficient. In extreme cases, the incineration of aqueous wastes is possible, of course with an increased fuel consumption.

In the absence of equipment for washing and recuperation of hydrochloric acid, all the gas of combustion is released to the atmosphere, then after condensation by water-vapor of the air, is precipitated onto the surface of the sea.

This precipitate has been described by the manufacturers as being harmless to the marine fauna and flora. In particular, it is considered that the hydrochloric acid produced would be rapidly neutralized by the high contents of alkaline elements of sea water.

During the neutralisation process, carbon dioxide, boric acid and chlorides would be produced.

After a short time lapse, a new equilibrium would be established because the released carbon dioxide escapes to the atmosphere promptly, and the calcium carbonate present in the water is solubilized. The effect of these reactions would be to re-establish the previous degree of alkalinity.

In fact, the complexity of the impact on the precariously balanced marine media has incited a prudent approach to the problem by the Administration who requires from the manufacturers, before examination of their application, a scientific and technical documentation as complete as possible concerning the procedures for incineration at sea, and the risks of nuisances associated with them.

As a result, the Ministry in charge of Environment has proposed to the manufacturers that, independently of the study of documentations concerning the analysis performed by foreign or french laboratories on the incineration experiments off the coast of Holland, a full scale experiment, directed towards the chlorinated wastes rejected by the French Industry, be realized under control of the Administration and Commission for the protection and defense of marine life.

# EXPERIMENT ON INCINERATION AT SEA, AND RESULTS

-:-:-:-:-:-:-:-

## Purpose

This experiment proposed to collect data on:

- the quality of effluents released from incinerators (combustion gas and unburnt)
- the dispersion and quality of gaseous output to the atmosphere.
- the facts associated with the gaseous fall-outs on the surface of the sea (pH measurements etc..)
- the effect of these wastes upon the marine life from the point of view of the ecology.

beginning with incinerated wastes having standard physico-chemical characteristics which could be used as reference for an eventual permit of incineration to be granted by the adminsitration.

## Means of experiment employed

In the experiment carried out between the 19 and 22nd of April 1974, off Rotterdam, under a permit granted by the Dutch authorities to the incinerator ships:

### Manufacturers

* incinerator ship Vulcanus from "Ocean Combustion Service" representing the Société Maritime and Charbonnière WORMS
* incinerator ship MATTHIAS II, of the German Company Stahl-Und-Blech-Bau, Bochum for the Company INCIMER

### Administrations

* The Ministry in charge of Environment (Division of Prevention of Pollution and Nuisances - Department of the Problems of Sea and Oceans) represented by Mr Jean Marie MASSIN, Head of the expedition.
* the Scientific and Technical Institute of the Sea Fisheries (I.S.T.P.M.) represented by

  - the ocean going vessel Thalassa.

  Messrs ALZIEU and MAGGI

* the National Center for the exploitation of the Oceans (C.N.E.X.O.) represented by Mr. MOURLON, coordinator of the experiments at sea and Miss JULLIEN.

* The French Institute of Petroleum (I.F.P.) represented by Messrs ROUSSEL and BUZON (Section Chemical Refinery - Division applied physico chemistry)

* the Atomic Energy Commission (C.E.A.) represented by

Mr PLATZER, Coordinator of the Analysis, C.E.A., Fontenay aux Roses.

Mr VAVASSEUR and Mr LE BRONEC, Department of Prevention, Technical Services for the study of protection and air pollution C.E.A. Saclay.

Mr HAULET, Department of Prevention, Technical Services for the study of protection and air pollution, C.E.A. Fontenay aux Roses.

Mr BLAIN, Department of Research and Analysis, Section: Study of Analysis, C.E.A., Fontenay aux Roses.

Analysis of Loads

Only one type of product was incinerated on each ship concerned, Analysis of the samples collected on the ship gave the following results: (Tables II and III).

The difference in composition of the two products coming, respectively, from the german and the english chemical industry and considered by the manufacturers as representative of the french production of chlorinated industrial wastes should be noted.

Analysis of the effluent of the incinerators

Two quantitative analysis were performed aboard ships: the chlorine and carbonyl chloride (phosgene), Results in p.p.m.

| | Matthias II | Vulcanus * | |
|---|---|---|---|
| Chlorine | 250 | 2000 | 1100 |
| Phosgene | 2 | < 1 | |

* 2 measurements

TABLE II

Study of the loads
Physicochemical data

-:-:-:-:-:-:-:-

| | Load of the Matthias II | Load of the Vulcanus |
|---|---|---|
| Physical measurements | | |
| Density at 20° C. | 1.061 | 1.267 |
| Viscosity at 20° C. | 1.085 cs | 0.787 cs |
| Intervals of distillation Between 52 and 190° | 97.5 % | 97 % |
| Elementary analysis ( % by weight) | | |
| C | 43.2 | 25 |
| H | 7.15 | 4 |
| N | Not detected | Not detected |
| S | Not detected | Not detected |
| Cl | 47 | 71 |
| Heavy Metals-(p.p.m.) | | |
| Cr | 0.3 | 0.4 |
| Cu | 0.3 | 0.5 |
| Fe | 3 | 6.5 |
| Hg | 0 | 0 |
| Na | 2.5 | 2 |
| P | 7 | < 0.3 |
| Pb | 3.4 | 0.9 |
| Si | 3 | 2 |
| Zn | 0.3 | 1.2 |

## TABLE III

## STUDY OF THE LOAD - SPECTOGRAPHIC MEASUREMENTS

Load of the MATTHIAS II ( in % weight)

| | | |
|---|---|---|
| Hexanes | $C_6 H_{12}$ | 2,47 |
| Propanal | $CH_3 - CH_2 - C(=O)H$ | 14,16 |
| Acetone | $CH_3 - C(=O) - CH_3$ | 2,92 |
| 1-2 Dichloropropane | $CH_2Cl - CHCl - CH_3$ | 28,17 |
| Epichlorhydrine | $CH_2 - CH - CH_2Cl$ (O) | 4,24 |
| 2-3 Dichloropropane | $CH_2 = CCl - CH_2Cl$ | 3,02 |
| di (chloroisopropyl) ether | $(CH_2Cl - CH(CH_3))_2 O$ | 28,54 |
| 3 chloropropylether | $(CH_2Cl - CH_2 - CH_2)_2 O$ | 5,49 |
| 2 chloropropylether | $(CH_3 - CHCl - CH_2)_2 O$ | 6,47 |
| Other | | 4,52 |

Load of the Vulcanus ( in % weight)

| | | |
|---|---|---|
| Chloroform | $CHCl_3$ | 1,01 |
| 1-1 dichloroethane | $CH_2Cl - CH_2Cl$ | |
| Carbon Tet. | $CCl_4$ | 2,35 |
| 1-2 dichloroethane | $CH_2Cl - CH_2Cl$ | 73,03 |
| Tetrachlorethylene | $CCl_2 = CCl_2$ | 6,60 |
| 1-1-2 trichlorethane | $CHCl_2 - ClH_2Cl$ | 11,05 |
| other | | 6,96 |

These measurements were completed by research on the un-burnt fluids, solids, or gases coming from incomplete combustion of the loads.

The study of the products trapped during the combustion of the chlorinated wastes loaded on the Vulcanus shows only negligible amounts (0.5 p.p.m.) of the compounds corresponding to the heaviest products of the loads in the gas of combustion.

The pyrolysis is then practically complete in the case of the Vulcanus.

Similar studies performed on the products trapped during the combustion of the wastes on the Matthias II gave almost identical results for the unburnt quantities (about 0.5 p.p.m.)

However, one must remark that among those unburnt are:

- light compounds of the type acetone, also present in the load.
- "tars", insoluble in water, of indetermined nature (under study for eventual carcinogens)

The first point implies that in the Matthias II the temperature of combustion is not maintained uniformly at 1000 to 1100°C. as indicated by the temperature recording of the thermo-couples installed on the wall of the furnace, but locally falls below the threshold of dissociation of light compounds (400°C.)

The presence of tars could be worrysome to the extent where carcinogenic elements would be demonstrated. It must be mentioned that taking into consideration the output of gas of combustion (100 - 140,000 $m^3/h$), 50 to 70 kg of solid wastes or tar are emitted by Matthias II per hour.

Study of the mixture of gas

Hydrochloric acid titration was performed next and in the gas mixture emitted by the two incinerator ships. It must be noted that the maximal concentrationsof hydrochloric acid in the air mixture a few meters above the sea water surface are in the same range ( a few v.p.m.) for the Matthias and the Vulcanus.

Study of the sea water

The pH measurements performed continuously at the surface of the sea during the experiment could not reveal any variation in the superficial marine media quality.

Analysis of the samples of sea water obtained at the maximal impact point of the gaseous rejects on the marine surface showsno trace of hydrocarbons.

## CONCLUSIONS AND AIMS

-:-:-:-:-:-:-:-:-:-:-

From the first results obtained from the experiment, it is concluded that:

1) For the loads to incinerate

- the physico-chemical characteristics of the chemical industry wastes susceptible to be destroyed by incineration are taken into consideration in the first and essentially variable results.

A simple notion of product (s) tested by the experiment and usable as a reference for any eventual permit of intineration released by the Administration must be set aside till more information is provided.

This implies that, though the principle of incineration at sea is accepted by the Administration, all authorizations will be subject to a strict control of the quality of the loads. This control could imply:

- a brief analysis of the loaded products (in order to detect, if necessary, the presence of heavy metals in prohibitive amounts).

- a test of incineration on a small scale in order to determine the quality of the combustion effluents.

2) For the pyrolysis of the loads

- if the pyrolysis seems to be complete in the case of the Vulcanus, a few reservations could be made on the combustion aboard the Matthias II (light unburnt products and tars).

Consequently, the factor "temperature of combustion" must be considered as primordial.

This implies that the control of the temperature during the combustion must be the object of a special attention, and that all the parts of the furnace (s) should be controlled during use to check the temperature.

3) For the incidence of gas of combustion fall-outs

- with the exception of the unburnt solids or tars (in particular of the unburnt not miscible with water of which toxicity still has to be demo·strated [under study]), the release of chlorine and hydrochloric acid seemsto have no impact on the marine life.

In consideration of the facts above, the Ministry in charge of the Environment proposes that.

- an appropriate legislation for the incineration at sea be enacted and that the decrees of application consider the technical point of view, in particular:

  * The necessity of checking the nature of each load before incineration, referring, if necessary, to the indications provided by a test incineration, duplicating in laboratory the actual conditions of the incineration at sea.

  * The necessity of using furnaces and burners performing a complete pyrolysis of the treated products.

  * The necessity of checking continuously and at all points the temperature of the furnace (s) of combustion.

- very soon a number of arrangements will be made so that the incinerator-ships can operate from french ports, and inside a marine zone which will be specially designated for this use, with all precautions concerning the protection of the sea life.

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ABSTRACT

11

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WITNESS NO. : 4

NAME : H. COMPAAN

OCEAN INCINERATION HEARING

OCTOBER 4,. 1974

I am H. Compaan of the central laboratory TNO. TNO is the National Research Council of the Netherlands. It is a nonprofit, semi-governmental research organization, employing about 4,000 distributed over many laboratories, committees, and working-groups. The Central Laboratory TNO has the special task to carry out multi-disciplinary research. I am heading a research group of 11, working mainly on problems of marine pollution and partly on air pollution.

The department of the Dutch government that is responsible for the environmental control of the Dutch Continental Shelf in the North Sea, gave TNO orders to search for uncombusted organic chlorine compounds in the exhaust gases of the Vulcanus during normal practice.

The investigations on the Vulcanus were carried out on May 29, 1974, on the North Sea, 20 miles northwest of the Hague. During the incineration of VCM - production waste containing approximately 70% combined chlorine, we took a number of stack samples in different ways. The samples were taken by myself and one assistant. The samples were obtained from the top center of the left incinerator by suction through a cooled quartz tube. The exhaust gases were led through: a) an impinger filled with water (organic free),
b) an impinger filled with 1 N sodium hydroxide (organic free)
c) an absorption tube filled with chromosorb 102.
During the sampling, two colleagues from the Central Technological Institute, TNO were measuring the flame temperatures of the incinerator and the carbon monoxide, carbon dioxide and oxygen contents of the exhaust gases.

The organic chlorine compounds were obtained by extraction of the scrubber liquids with cyclohexane and by thermal desorption from the absorption tubes. The samples were analyzed by gas chromatography with 4 different detection methods:
a) flame ionization detection
b) electron capture detection
c) helium plasma detection
d) mass spectroscopy
Helium plasma detection and mass spectroscopy gave the most conclusive results. The helium plasma detector showed clearly the presence of small amounts of organic chlorine compounds. With the mass spectrometer evidence was obtained for the presence of some organic bromine compounds as well. The total amount of organic chlorine thus found corresponds to a concentration of about 3-5 ppm in the exhaust gases, or not more than 40 ppm on the basis of the feed. This corresponds to a combustion efficiency of 99.996 percent.

During the incineration a sample of the waste was taken at a point

near the burners. Gas chromatographic - mass spectroscopic analysis showed that the waste had the usual composition. The samples were taken from 10 A.M. to 2:40 P.M. At 12:30 P.M. the flame temperature was 1200 - 1300°C. At 2:00 P.M. the flame temperature was 1300 - 1400°C.

The final report will be ready in October 1974.

[The above complete testimony is retyped from material available during the public hearing conducted by the Environmental Protection Agency in Houston TX on 4 Oct 1974. The hearing was relative to a permit application (No. 730D008C) from Shell Chemical Company to discharge to ocean waters off the coast of Texas]

# APPENDIX O

COMMENTS TO:

REVISED DRAFT ENVIRONMENTAL STATEMENT
DISPOSITION OF ORANGE HERBICIDE
BY INCINERATION

April 1974--AF-ES-72-2D(1)

A. This section presents the letters of comments which were forwarded to the Air Force on the revised Draft Environmental Statement. All comments received are included and the Air Force reply follows each comment.

B. Comments were received from the following:

United States Government Agencies/Departments

- Atomic Energy Commission
- Department of Agriculture
- Department of Commerce
- Department of Defense (Health and Environment)
- Department of Health, Education and Welfare (2 letters of comment)
- Department of Interior
- Department of Transportation
- Environmental Protection Agency

State Governments

- Hawaii (3 letters of comment)
- Mississippi

Other interested Groups

- American Eagle Foundation
- Center for Law and Social Policy (Representing Friends of the Earth and the National Audubon Society)
- The Marquardt Company

UNITED STATES
ATOMIC ENERGY COMMISSION
WASHINGTON, D.C. 20545

JUL 5 1974

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
Office of the Assistant Secretary
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

[1] This is in response to your letter dated May 9, 1974, inviting the U. S. Atomic Energy Commission to review and comment on the revised Draft Environmental Statement entitled, "Disposition of Orange Herbicide by Incineration."

[2] We feel that the United States Air Force environmental statement is well prepared in almost all areas. Of particular concern is Johnston Atoll wildlife; however, the statement does elucidate the lack of hazards and adverse effects the proposed action will have on the wildlife. The statement also demonstrates that there should be no adverse environmental effects from incineration either on the special ship or Johnston Island, given proper equipment operation within specified safety constraints.

[3] We do have some concern in areas of the statement which do not seem to be covered with sufficient detail. These are:

1. Transfer of the herbicide to the incinerator, including "de-drumming," bulk storage, control of spills, etc.

2. Clean-up of emptied drums.

3. Disposal of emptied drums.

[4] With respect to item 1, our prime concern is for the health and safety of all involved in or in proximity to the Island operation. This should be the primary consideration in the planning, scheduling, funding, and execution of whatever method is employed. Sufficient advance notice of the method of choice should be provided to field agencies to allow for coordinated and orderly design and construction of the "de-drumming" and transfer facilities. If the schedule for emptying the drums is anticipated to exceed a year, early construction of a bulk storage facility should be considered to minimize re-drumming and expedite the ultimate transfer operation.

[5] As for drum clean-up, the statement documents that even with repeated rinsing of the emptied drum, which is not only expensive and time-consuming, all the residue cannot be removed and that the difference between rinsed and unrinsed drums probably may not be worth the effort.

[6] We presume that the problem of drum disposal is still under study and feel that more consideration should be given to salvaging the drums so they ultimately become ingots. In any event, the crushed drums should be shipped in a sealed container in order to prevent release of any residual herbicide during shipment.

[7] Another area in the statement which we feel has been given marginal consideration is the alternatives to incineration. The alternatives such as "use," "return to industry" are briefly covered and have not been costed out. We should like to suggest that additional review be made of the possibility to return this chemical to the economy, if such can be done. Possibly the chemical processing industry could use this chemical as a raw material in another process. If this alternative is not economically sound nor technically feasible, we feel that such fact should be documented and that incineration is truly the only alternative.

[8] In summary, we feel that this draft statement adequately shows that there will be no adverse environmental impact from proper incineration, if in fact this is the only alternative. We would prefer that the incineration be done at sea since this will minimize exposure of the chemical to the Island personnel and request that as the methods are selected and procedures written, the health and safety of this personnel be of primary concern.

[9] We do object to incineration on Johnston Island for several reasons, but primarily because of the excessive length of time required for construction of a facility for disposal and for the actual disposal. Additionally, incineration on the Island is certain to cause an obstruction to our readiness program that now exists. Our final objection is the high cost of construction and the continuing excessive environmental pollution which could occur by having leaking levels of herbicide around for a much longer period of time.

[10] Since facilities for incineration at sea are in existence (e.g., the ship Vulcanus) and total disposal could be accomplished in less than two months, we prefer this method of incineration. This mode will also eliminate the obstruction to our readiness effort at a minimized cost to the Government.

[11] We have appreciated the opportunity to review and comment on the statement.

Sincerely,

James L. Liverman
Assistant General Manager for
Biomedical and Environmental
Research and Safety Programs

cc: Council on Environmental Quality (5)

RESPONSE TO COMMENTS FROM THE ATOMIC ENERGY COMMISSION LETTER (5 Jul 74)

1. (Paragraph 2,3,4 AEC Ltr) A complete dedrumming and transfer operation has been planned and engineered for Johnston Island (Part II.E.) The health and safety of personnel and the maintenance of the environment are prime considerations in this plan. Sufficient notification will be provided for the orderly implementation of the "dedrumming/transfer" project.

2. (Paragraph 3,4,5,6 AEC Ltr) See Part II.E. for drum disposal information.

3. (Paragraph 7 AEC Ltr) See Part I for Air Force action toward EPA registration of Orange herbicide.

4. (Paragraph 7 AEC Ltr) See Part V.C for Air Force action on the return of Orange herbicide to manufacturers.

5. (Paragraph 9,10 AEC Ltr) The proposed disposal action is incineration at sea with incineration on Johnston Island as the principal alternative.

DEPARTMENT OF AGRICULTURE
OFFICE OF THE SECRETARY
WASHINGTON, D. C. 20250

June 19, 1974

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

We have reviewed the revised draft environmental statement on "Disposition of Orange Herbicide by Incineration"--AF-ES-72-2D (1), April 1974. The statement is well organized, well written, and significant research data are presented to support the effective and safe disposal of orange herbicide by incineration.

We concur in the proposal to dispose of orange herbicide by incineration in a remote area near or on Johnson Island in the Pacific Ocean. With proper concern for the environment as outlined in the revised draft environmental statement, we concur that incineration is the most environmentally safe and most effective method of the alternative procedures that could be considered for the disposal of orange herbicide.

Sincerely,

F. H. Tschirley

F. H. Tschirley
Coordinator
Environmental Quality Activities

RESPONSE TO COMMENTS FROM THE DEPARTMENT OF AGRICULTURE LETTER (9 JUN 74)

No reply required.

**UNITED STATES DEPARTMENT OF COMMERCE**
**The Assistant Secretary for Science and Technology**
Washington, D.C. 20230

July 10, 1974

Dr. Billy E. Welch
Special Assistant
for Environmental Quality
Office of the Assistant Secretary
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

The draft environmental impact statement for the proposed "Revised - Disposition of Orange Herbicide by Incineration," which accompanied your letter of May 9, 1974, has been received by the Department of Commerce for review and comment.

The statement has been reviewed and the following comments are offered for your consideration.

The accidental discharge of Orange Herbicide into the air, ground or under "worst case" conditions is discussed under various conditions in the environmental statement. Two "worst case" conditions, that are not discussed, however, are the fate and effect of Orange Herbicide under the "worst case" conditions of either (1) jettisoning of the cargo of the vessel Vulcanus or (2) accidental sinking of the Vulcanus. Consideration should be given to these possibilities, even though they may be remote.

Thank you for giving us an opportunity to provide these comments which we hope will be of assistance to you. We would appreciate receiving a copy of the final statement.

Sincerely,

Sidney R. Galler
by Jane Lewis

Sidney R. Galler
Deputy Assistant Secretary
for Environmental Affairs



AMERICAN REVOLUTION BICENTENNIAL 1776-1976

RESPONSE TO COMMENTS FROM THE DEPARTMENT OF COMMERCE LETTER (10 Jul 74)

Information on possible environmental impact resulting from the jettisoning of the Orange cargo or sinkage of the incinerator ship has been included in Part III.C.5.a.

ASSISTANT SECRETARY OF DEFENSE
WASHINGTON, D. C. 20301

HEALTH AND
ENVIRONMENT

1 JUL 1974

MEMORANDUM FOR Special Assistant for Environmental Quality, SAFILE

SUBJECT: Revised Draft Environmental Statement "Disposition of Orange Herbicide by Incineration"

[1] The following comments on the Draft Environmental Impact Statement, "Disposition of Orange Herbicide by Incineration," are provided in response to your memorandum of May 9, 1974.

[2] In view of EPA withdrawal of its legal motion seeking a ban on the use of 2-4-5-T, further consideration should be given to disposition of that portion of the material which corresponds to current commercial formulation through controlled use by DoD or other governmental agencies.

[3] With respect to disposal via ship incineration, we would suggest that the possibility of accidental release of the material as a result of uncontrolled shipboard fire or natural causes be discussed.

[4] The discussion on incinerating the herbicide on Johnson Island should include the possible effect of the HCl from the exhaust on space tracking equipmen t and on the aluminum housing of certain of the stored chemical munitions.

[5] The Office of the ASD(I&L) also noted that no fully satisfactory method of disposal of the drained drums is proposed in the statement. Incineration of the drums to remove herbicide residues should be considered. This could be included as a requirement in the service contract. After incineration, disposal of the drums by any number of environmentally acceptable methods is possible including salvage for reuse of the metal.

H. R. Smith
Acting Deputy Asst Secretary of Defense
(Environmental Quality)

RESPONSE TO COMMENTS FROM THE ASSISTANT SECRETARY OF DEFENSE FOR HEALTH AND ENVIRONMENT LETTER (1 Jul 74)

1. (Paragraph 2 SoD for H&E Ltr) See Part I for Air Force action toward EPA registration of Orange herbicide.

2. (Paragraph 3 SoD for H&E Ltr) Information on possible environmental impact resulting from the jettisoning of the Orange cargo or sinkage of the incinerator ship has been included in Part III.C.5.a.

3. (Paragraph 4 SoD for H&E Ltr) If the principal alternative of incineration on Johnston Island were used, meteorological constraints and ambient air monitoring would be utilized to insure that hydrogen chloride does not represent a health hazard to personnel. These precautions would also insure that structures and space tracking equipment are not affected. Additional information on the effects of hydrogen chloride has been included in Part III.B.2.c.

4. (Paragraph 5 SoD for H&E Ltr) See Part II.E. for drum disposal information.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
OFFICE OF THE SECRETARY
WASHINGTON, D.C. 20201

AUG 23 1974

Dr. Billy E. Welch
Special Assistant for Environmental
Quality
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

[1] We have reviewed the revised draft Environmental Impact Statement concerning the "Disposition of Orange Herbicide by Incineration."

[2] Of vital concern to this Department from the proposed action is the impact to the physical environment and subsequent potential contamination of food for man and animal. A related problem involves the transportation of the phenoxy compounds, the transfer of the chemical to the ship, and one of increasing magnitude is the handling and disposal of wastewater and used containers. The potential seriousness of health and environmental hazards due to accidental causes, improper disposal and handling of the chemical and containers must be treated in the final impact statement, if we are to determine whether or not this project will be fully protective of public health and the environment.

[3] Physical movement of 0.86 million gallons of Orange from its present location in Gulfport, Mississippi, to the ultimate site of disposal is a potentially serious threat to the environment and contributing factor to contamination of food for man and animal use. The draft statement, in our opinion, does not give sufficient information on movement and handling procedures. Another problem exists in the disposal of the empty 55-gallon steel drums. We feel the impacts resulting from container disposal should be discussed in the final statement. Land fill of these drums is questioned since the material can be recycled thereby eliminating any potential hazard once and forever.

[4] The other proposed disposal options are not discussed in the type of detail which would allow conclusions to be drawn about their viability.

[5] We note that incinerating Orange Herbicide at the specified temperature, pressure, dwell-time, combined with high efficiency scrubbing, will provide safeguards against the release of highly toxic dioxins. However, the problem of pyrolytic synthesis of dioxins received minor discussion in this revised statement, depending solely on the use of sufficiently high temperatures to complete the destruction. As stated in the draft statement, the formation of dioxins on pyrolysis can occur at lower temperatures; however, the possibility of cold spots in the furnace or its breakdown have been inadequately considered.

[6] We do not dispute the completeness of the Marquardt Company's land-based incinerator study. The analyses of the exhaust gases are adequate and well discussed. However, it is questionable that under actual operational conditions, sustained combustion efficiencies of 99.999% can be maintained consistently, knowing that incinerator design is not a well defined process.

[7] We could not adequately review the shipboard incinerator concept, since the pilot plant or operational data was not presented. Also, the destruction efficiency of 99.9% for this incinerator was not validated by adequate data; therefore, it can only be concluded that this efficiency was an extrapolation from the Marquardt Company study. In an operation of this magnitude with the potentially serious public health considerations, this type of information should be provided.

[8] Unmonitored incineration on-board the ocean vessel as described in the statement does not provide the safety assurances considered necessary for the disposal of Orange herbicide. Lacking are the high-efficient scrubbing devices and monitoring instrumentation necessary to provide adequate health and environmental safeguards. The statement is silent regarding the potential environmental impacts which would occur in the event an accident should occur on the vessel while loaded with Orange herbicide.

[9] There are no complete comparative cost analyses for the two proposed alternatives presented.

[10] It is our opinion that the "worst case" analysis used in defense of minimal environmental impact can be improved. The dispersion model derived in Appendix K is not complete. This should include general mass transfer equations with supporting simplifying assumptions. Also, in a "worst case" analysis, conversions of less than 99.9% should be used especially since this incineration efficiency is not validated by hard data. For example, if 0.1% conversion corresponds to 0.576 Tons of herbicide/day discharge to the atmosphere, for a conversion of only 90%, this would correspond to about 57.6 Tons of herbicide/day discharged to the atmosphere.

[11] The estimated 22-26 days required to incinerate 2.3 million gallons of Orange herbicide using the vessel does not include in the calculations the volume of drum and other wash water which will result from the disposal operation or the time required to load the chemical into the ship in preparation for incineration. Considering these factors, we estimate that the time required to dispose of 2.3 million gallons of Orange herbicide is underestimated.

[12] In conclusion, it is our considered opinion that:

1. Incineration under tightly controlled parameters is an acceptable method of destroying the Orange herbicide;

2. Prior to use of any incinerator, except the one presently certified by actual pilot testing, the same type and quality of pilot tests with gaseous and liquid effluent analyses must be conducted on said incinerator. This will provide the necessary assurances that the selected disposal method protects the public health and safety, reduces to the maximum the potentially serious threat to the environment and is not a contributing factor to contamination of food for man and animal use;

3. Whatever incineration method is selected, adequate and continuous monitoring of the gaseous and liquid effluents therefrom are required;

4. Transfer and transport of the chemical from Gulfport, Mississippi must be provided with proper safeguards and likewise the chemicals on Johnston Island, if they are to be destroyed by shipboard disposal; and

5. Careful consideration must be given the handling, cleaning and ultimate disposal of the contaminated drums.

[13] We feel that the only positive aspect of the on-board incinerator is that it alleviates the problem in a short period of time. The land-based operation will require seven months on a 24-hour/day operation and will require the Air Force to participate. The on-board incinerator appears to transfer the disposal problem and the potential impacts, public health and environmental to another media. The possibility that it may set a precedent for incineration of all hazardous material at sea cannot be dismissed.

[14] Thank you for the opportunity to comment on this statement.

Sincerely,

Charles Custard
Director
Office of Environmental Affairs

RESPONSE TO THE COMMENTS FROM THE DEPARTMENT OF HEALTH, EDUCATION AND WELFARE (23 Aug 74)

1. (Paragraph 2,3,11 HEW Ltr) See Part II.E. for drum cleaning/disposal.

2. (Paragraph 2,3 HEW Ltr) An operations plan will be prepared for all handling, transfer and shipments of Orange which are accomplished in support of the incineration project. This plan will stress personnel and environmental safety and include contingency planning for accidents.

3. (Paragraph 4 HEW Ltr) See Part V, Return to Manufacturers, Fractionation, and Chlorinolysis for information on these alternatives.

4. (Paragraph 5 HEW Ltr) The Vulcanus incinerators utilize a vortex circulation to increase the path of combustibles through the incinerator and to minimize the potential for the creation of cold spots. In addition, temperature is measured at different locations in the incinerator. The Air Force will specify contractually for the minimum temperature within the incinerator. Temperature is very important as regards dioxin destruction and is in fact the reason for the high temperature to be specified in the contract (minimum of 1400$^{o}$C for the Vulcanus). The Orange herbicide combusted in the Marquardt test burn had a high dioxin concentration (~13 mg/kg) compared to the total Orange stock (Part II.F.). No evidence of pyrolytic synthesis was noted in the Marquardt test, see Appendix E.

5. (Paragraph 6,7,8,10 HEW Ltr) The Air Force position is that the environmental impact of the incineration of Orange herbicide can be adequately assessed without further test burns and without monitoring for the proposed action of incineration at sea, see the Air Force response to comments from the EPA, the Marquardt Company, and the Center for Law and Social Policy.

6. (Paragraph 13 HEW Ltr) The Air Force feels that for this project incineration at sea is the more environmentally safe Orange destruction action. Although it is felt that the principal alternative of incineration on Johnston Island can be accomplished in an environmentally safe manner, the potential for damage to the reef and bird communities of the delicate ecosystem of Johnston Atoll warrants concern for any incineration operations on the island. This view is shared in some of the letters of comment to the RDES; see comments from the state of Hawaii and the Center for Law and Social Policy. It is noted that the comments from the State of Hawaii reveal that they are concerned with the negative aspects involved in establishing an incinerator system on Johnston Island; namely, that it could be used for other waste materials in the future.

NOTE: Paragraph 9, HEW Ltr is not within the scope of this environmental statement and paragraph 12 is a restatement of previous paragraphs.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
OFFICE OF THE SECRETARY
WASHINGTON, D.C. 20201

SEP 4 1974

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

This is an addendum to my letter of August 23, 1974 transmitting this Department's comments on the draft Environmental Impact Statement for the "Disposition of Orange Herbicide by Incineration."

We wish to point out the need for clarifying the fact that Orange, as the n-butyl ester (1:1) 2,4-D and 2,4,5-T is not the same chemically as the commercially available herbicide 2,4-D and 2,4,5-T. The environmental impact statement refers to the later and does not indicate the distinction between the physical properties of this chemical and those of Orange. The anticipated toxicity, stability and other characteristics of Orange are somewhat different, the esters are harder to handle and it does not degrade as easy.

Also, we note that the draft statement fails to address the potential for water pollution and the effects of the impact on the marine physical and biological environment from hydrochloric acid and other by-product emissions resulting from the incineration process.

Sincerely,

Charles Custard

Charles Custard
Director
Office of Environmental Affairs

RESPONSE TO COMMENTS FROM THE DEPARTMENT OF HEALTH, EDUCATION AND WELFARE (4 Sep 74)

1. (Paragraph 2, HEW Ltr) Every effort was made to accurately portray the description and characteristics of Orange herbicide, see Part I.A.1. and Part II.F. Part II.F. includes the procurement specifications, the results of analytical analyses for TCDD, and a table citing the general physical/chemical properties of the herbicide. The rather large number of individuals who have had inputs to the statement may have inadvertently contributed to this situation, i.e., lack of distinction between "commercially available herbicide 2,4-D and 2,4,5-T" and Orange herbicide. Any such lack of distinction between Orange herbicide and any other pesticide formulations described/referenced in the statement is certainly unintentional. The statement, "Orange herbicide is not a registered herbicide and cannot be used or sold" appears in Part I.C.3. and Part V.C.1. It is noted that Transvall, Inc., Jacksonville, Arkansas advertises for sale a herbicde called Brush-Rhap® which is registered uder EPA Registration No. 11687-11 and which contains 29.0% butyl ester of 2,4-D, 28.2% butyl ester of 2,4,5-T, and 42.3% inert ingredients. In addition, the Pesticide Handbook Entoma, 24th Edition, College Science Publishers, State College, PA (1972) lists a compound called Woodkill manufactured by the Chemical Co,Division of Techne Corp. St. Joseph Mo, as containing 42.67% butyl ester of 2,4-D and 42.20% butyl ester of 2,4,5-T and registered under EPA #449-28. Another product, Line Rider® 22 (EPA #677-95-AA) manufactured by the Diamond Shamrock Co. contains 28% butyl ester of 2,4-D and 27% butyl ester of 2,4,5-T.

2. (Paragraph 3, HEW Ltr) The environmental impact of hydrogen chloride and other by-product emissions resulting from the incineration process is addressed in Part III.

# United States Department of the Interior

OFFICE OF THE SECRETARY
WASHINGTON, D.C. 20240

In reply Refer To:
FSF/EA
(ER-74/648)

JUL 9 1974

Dear Dr. Welch:

This is in response to your request of May 9, 1974, for review and comments on the proposed Disposition of Orange Herbicide by Incineration, Johnston Island, Pacific Ocean.

Deep well disposal should be avoided. Development of fissures from seismic vibrations could permit migration of the herbicide to ground water.

The plan, as outlined, for the incineration of Orange Herbicide on Johnston Island or at sea in this general area appears to be an acceptable mode of disposal of this material. Maintenance of high performance by the incinerators and constant monitoring of effluents will be required to minimize environmental impacts.

We are concerned also about disposal of the drums. We suggest that the final statement specify the landfill site to be used, if this is to be the method of disposal, and that there be a discussion of potential leaching of herbicide remnants and resulting environmental impacts.

Sincerely yours,

Stanley R. Scremmes

Deputy Assistant Secretary of the Interior

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
Office of the Assistant Secretary
Department of the Air Force
Washington, D.C. 20330

RESPONSE TO COMMENTS FROM THE DEPARTMENT OF THE INTERIOR LETTER (9 Jul 74)

1. (Paragraph 2 DoI Ltr) Deep well injection is not considered as a viable means of Orange disposal, Part V.D.

2. (Paragraph 3 DoI Ltr) See the Air Force response to the letter of comment from the Center for Law and Social Policy relative to monitoring.

3. (Paragraph 4 DoI Ltr) See Part II.E. for drum dispcsal information.

DEPARTMENT OF TRANSPORTATION
UNITED STATES COAST GUARD

MAILING ADDRESS:
U.S. COAST GUARD (G-WS/73)
400 SEVENTH STREET SW.
WASHINGTON, D.C. 20590
PHONE: (202) 426-2262

JUN 13 1974

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
Office of the Assistant Secretary
Department of the Air Force
Washington, D. C. 20330

Dear Dr. Welch:

This is in response to your letter of 9 May 1974 addressed to the Coast Guard, Office of Marine Environment and Systems, concerning the revised draft environmental impact statement on the Disposition of Orange Herbicide by Incineration.

The Department of Transportation has reviewed the draft statement. The Coast Guard commented as follows:

"The VULCANUS has never demonstrated a 99.9% combustion efficiency for incineration of chlorinated hydrocarbons as indicated on page 16 of subject environmental impact statement. It appears that the agents for the VULCANUS have assumed that the 99.9% combustion efficiency achieved with chlorinated hydrocarbons on another incineration-vessel, the MATHIAS I, also applies to their vessel.

"The Test Facility Schematic on E-7 of subject EIS is not legible even under high magnification.

"It appears safe to conclude that there will be no adverse effect caused by the incineration of Orange Herbicide in a remote area of the Pacific."

The Department of Transportation has no further comments to offer nor do we have any objection to this statement. However, the concern of the Coast Guard should be addressed in the final environmental impact statement.

The opportunity to review this draft statement is appreciated.

Sincerely,

R. I. PRICE
Rear Admiral, U. S. Coast Guard
Chief, Office of Marine Environment
and Systems

0-21

RESPONSE TO COMMENTS FROM THE DEPARTMENT OF TRANSPORTATION (13 Jun 74)

1. (Paragraph 3 DoT Ltr) The comments on the incineration efficiencies of the Vulcanus are correct. However, information on the incineration of chlorinated hydrocarbons aboard the Vulcanus has been received since the revised draft environmental statement was written. This information is summarized under "hydrocarbons" in Part II.B.2. and presented in Appendix N.

2. (Paragraph 4 DoT Ltr) Although the schematic used for the revised draft environmental statement was legible, clarity was lost in the printing process. An effort was made to improve the clarity of the schematic in the final environmental statement.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 11 1974

OFFICE OF THE
ADMINISTRATOR

Dr. Billy E. Welch
Special Assistant for Environmental
Quality
Office of the Assistant Secretary
(Installations and Logistics)
Department of the Air Force
Washington, D.C. 20330

Dear Dr. Welch:

The Environmental Protection Agency has completed its review of the revised draft environmental impact statement (EIS) for the proposed Disposition of Orange Herbicide by Incineration dated April 1974.

The proposed action surfaces major concerns that need to be documented more fully in the environmental statement.

Four important aspects of this proposed action were not discussed in sufficient detail in this draft EIS: incineration, drum disposal, handling safety, and other alternatives. They should be discussed thoroughly in the final EIS. EPA's concerns with these fours aspects of the proposed action are described in the attached comments.

In light of our review of this revised draft statement and in accordance with EPA procedure, we classified the project as "LO" (Lack of Objections) and rated the draft statement as "Category 2" (Insufficient Information). We would be pleased to discuss our classification or comments with you or members of your staff.

Sincerely yours,

Sheldon Meyers

Sheldon Meyers
Director
Office of Federal Activities

Enclosure

Introduction

The Environmental Protection Agency has reviewed the revised draft environmental impact statement prepared by the Department of the Air Force for the disposition of Orange herbicide by incineration. The proposed action is the incineration of approximately 2.3 million gallons of Orange herbicide in a remote area near or on Johnston Island in the Pacific Ocean.

Our comments on this administrative action follow.

Incineration

There is no test data on the Vulcanus incinerator. Extrapolation of the Marquardt data to the Vulcanus incinerator operation is not possible because burner design and destruction concepts differ appreciably from the Marquardt process. For example, the high degree of turbulent mixing which allows short dwell times in the Marquardt process may not be achieved by the Vulcanus incinerator. Theoretically, the Vulcanus incinerator should be able to destruct Orange herbicide and dioxin based on temperatures and reported (but unconfirmed) dwell time. To prove this theory, testing should be conducted to determine concentrations of breadown products, unburned Orange herbicide esters, and dioxin.

Sampling during a very extensive test for particulate was not done isokinetically, thus invalidating the emission data presented (Table D-3) on page E(D-21).

Drum Cleaning (Part II.E.)

U.S. Environmental Protection Agency, "Regulations for Acceptance and Recommended Procedures for Disposal and Storage of Pesticides and Pesticide Containers," (40 CFR Part 165, Federal Register, May 1, 1974) are mandatory to Federal agencies for purposes of

implementing E.O. 11752. Part 165.9(b) specifies triple rinsing or incineration or specially designated land fill for containers which formerly contained organic pesticides. The environmental statement does not contain a firm commitment to this level of treatment. The implication (page 23) that unrinsed containers will be disposed of at sea is in violation of 40 CFR 165.7. The preferred disposal, in our opinion, would be smelting as scrap metal or salvaging for further shipping uses. Disposal by landfill is the least acceptable alternative. If disposal by landfill is the alternative selected, the landfill site should be located such that there is not a chance of runoff into surface or subsurface waterways. The ultimate disposal of container drums should be specified.

Transportation and Handling Safety (Appendix I)

Transfer operations to and from the rail car and to and from the ship are the most hazardous. Consideration might be given to "containerization" or drums with flat car shipment and, perhaps, containerized loading to avoid individual spill opportunities.

The physical movement of 860,000 gallons of orange from its present location at the Naval Construction Battalion Center, Gulfport, Mississippi to Johnston Island is potentially a serious threat to the environment, and the draft statement does not give sufficient information on movement details, such as mode of transportation, off-loading, storage at disposal site, spill containment, decontamination, etc. We recommend the following: (1) careful observance of Department of Transportation safety requirements in the transport of hazardous materials, (2) spelling out of specific modes and routes of transportation so as to plan for any contingency that might occur, (3) separate and individual contingency plans covering such items as immediate field detoxification, health and safety considerations of personnel who might be involved in cleanup, (4) a firm written commitment from the transportation contractor that containment equipment is located and available to the contractor during transportation, and (5) predesignation of the on-scene coordinator prior to any shipment.

Off-loading areas should be equipped with materials and equipment which should be checked thoroughly before

the commencement of each loading or unloading in order to assure safe and dependable operation. Furthermore, responsible persons engaged in off-loading should be given complete instructions in cleanup techniques along with instructions on how to proceed in case of a spill.

While shipment by water is cheaper than land and there has never been a spill during water transport, it might be recognized that material spilled in a waterway would be distributed by the current. A land spill could be much more easily contained. If shipment is made by rail or truck, cleanup teams and equipment should accompany the transport vehicles.

In the matter of storage, whether in bulk or in drums, only those areas especially designed for storage of hazardous materials should be used. Such areas should provide (1) structures to prevent surface water runoff from entering the area, (2) pavement and gutters to collect surface water runoff within the area, (3) drains to channel contaminated runoff to a holding facility, (4) materials and equipment necessary for rapid cleanup of spills, and (5) fencing to control admission to the areas. In addition, storage areas should be located remotely from occupied dwellings.

Alternatives

We must take exception to the statements (page 119) that technology is not currently sufficient to permit the disposal of Orange herbicide by either chlorinolysis or fractionation. Not only are both methods entirely feasible technologically, but they may also offer the most practical means of disposition from the standpoints of economics and resource recovery. These means of disposal deserve much greater consideration than is evident in the EIS.

RESPONSE TO COMMENTS FROM THE ENVIRONMENTAL PROTECTION AGENCY LETTER (11 JULY 1974)

1. INCINERATION: The following is to provide information on the background and purpose of the Marquardt Company test burn of Orange herbicide, see also Part II.C.1. and the Air Force response to the Marquardt Company comments.

a. The Air Force investigated the feasibility of conducting an Orange herbicide test burn at the Rollins Environmental Services industrial waste disposal facilities in New Jersey, Louisiana, and Texas. The Texas site was never considered feasible for a variety of reasons including regulatory agency approval and the potential environmental impact. In addition, the incinerator system was programmed for extensive modification which did not meet the time frame of the disposal project. The Louisiana site, although a candidate for the large scale disposal of Orange, was also programmed for modifications which prohibited it from meeting the test burn schedule. A detailed test burn protocol, including an operational and ecological monitoring program, was prepared for a test burn of Orange herbicide (230 drums) at the New Jersey site. The New Jersey site was undergoing modifications which were acceptable to the test burn schedule. The test burn protocol was presented to representatives of Region II EPA and representatives of the New Jersey Bureau of Air Pollution Control on 4 May 1973. The test burn was tentatively scheduled for Jul 73; however, the following situation developed: comments were not received from the EPA concerning the test burn protocol, the Rollins Environmental Services took longer than anticipated to accomplish the modifications and obtain regulatory agency approval, and the Chairman of the Louisiana Governor's Council on Environmental Quality advised the Air Force that the large scale incineration of Orange in Louisiana would not be welcomed. In addition, an ecological study including aerial infrared photography of the New Jersey site conducted by the Air Force revealed that crops in very close proximity to the incinerator were a species that are very sensitive to chlorophenoxy herbicides; thus, incinerator tests during the growing season involved a possibility for crop damage. The plan for this test burn was, therefore, not concluded and the chance of accomplishing a large scale test burn and subsequent disposal of the entire Orange stock in a conventional commercial incinerator within the U.S. was judged to be very remote. After careful consideration, the Marquardt Company was chosen to conduct a test burn with the SUE® system, see Part II.C.1. for the rationale leading to this selection. The test burn was conducted under Los Angeles Air Pollution Control District Authority to Contract Number A77791. The Marquardt Company test burn was accomplished to obtain data concerning the incineration of Orange under specified incinerator operating conditions to determine contractural specifications to be levied upon any contractor - and not specifically to determine the suitability of the Marquardt system for the large scale disposal of Orange.

b. The Air Force approach to the destruction of Orange via incineration has been to obtain combustion data and incinerator operating conditions which may be applied to a contractor as contract specifications. In this sense, the extrapolation involves a judgment on combustion efficiency for a given incinerator at prescribed incinerator operating conditions rather than an extrapolation of data in a purely technical nature. It is the Air Force position that sufficient data is available on incineration of Orange so that a judgment can be made on the

efficiency of treatment to be expected under specified incinerator operating conditions. This data includes five studies concerned with the combustion of Orange (Appendix D and E) and the data on incineration by incinerator ships and at the Rocky Mountain Arsenal, see paragraph c. below. It is emphasized that while the relative pyrolysis efficiencies of the Marquardt test burn ranged from 98.98 percent to 99.999 percent, the efficiency of the Vulcanus for environmental impact analyses was selected at 99.9 percent in the RDES. In the final environmental statement, the analyses were also shown for 99.0 percent and 95.0 percent with the conclusion that even these efficiencies may be deemed environmentally acceptable for a 22-26 day period over the open tropical sea (Part III.B.2. and Part III.C.5.). The 95 percent destruction would not be acceptable to the Air Force; however, it is the Air Force position that an efficiency approaching 99.9 percent can be attained, see paragraph c. below.

c. Since the RDES was published, the Air Force has received information concerning the efficiency of incineration of chlorinated hydrocarbons aboard the Mathias and Vulcanus incinerator ships and on the ecological aspects of incineration at sea (North Sea). This information is included in Appendix N and is summarized in Part III.B. and C. This information, while not on Orange herbicide incineration, attests to the high efficiency attained in chlorinated hydrocarbon incineration (99.9 percent) and to the minimal environmental impact of the incinerator emissions. In addition, essentially complete destruction (>99.9 percent) of mustard agent, a material with similar physical/chemical properties as Orange, is accomplished by incineration at Rocky Mountain Arsenal, see Part V.A.2.

d. The stay time for the Vulcanus incinerator has been recalculated due to receipt of more detailed information from Ocean Combustion Service and is reported in Part II.C.2. as approximately 0.6 seconds instead of the original 0.25 seconds.

e. In view of the above, it is the Air Force position that sufficient information is available to adequately assess the environmental impact of the Orange disposal via incineration and that further test programs are not required.

f. The particulate sampling was done according to established procedures for isokinetic sampling. The results showed that isokinetic conditions were not always maintained. This problem is discussed in detail on page E(D-22).

2. DRUM CLEANING

a. See Part II.E. for drum cleaning information.

b. This response below is in reference to the following quote from the EPA letter:

> "U.S. Environmental Protection Agency, 'Regulations for Acceptance and Recommended Procedures for Disposal and Storage of Pesticides and Pesticide Containers,' (40 CFR Part 165, Federal Register, May 1, 1974) are mandatory to Federal agencies for purposes of implementing E.O. 11752." (Emphasis added).

(1) Executive Order 11752, 38 FR 34793, dated 19 December 1973, states that it is the responsibility of heads of Federal agencies to "ensure that applicable standards specified in section 4 of the order are met on a continuing basis" (E.O. at Section 3). Section 4 (a) (7) states that "Heads of Federal Agencies shall insure that their facilities conform to requirements of Federal regulations and guidelines respecting manufacture, transportation, purchase, use, storage and disposal of pesticides promulgated pursuant to the provisions of the Federal Insecticide, Fungicide and Rodenticide Act, as amended by the Federal Environmental Pesticide Control Act of 1972." (FIFRA and FEPCA). EPA issued the above-cited "Regulations and Recommended Procedures" on May 1, 1974. The "Regulations" governing acceptance by EPA of compounds whose registration is cancelled are mandatory and minimize EPA's responsibilities. However, the recommended procedures, Title 40 FR §165 et. seq., are another matter. Note the language employed: "recommended procedures" in Title 40 FR §165.2(c) and §165.8 and "procedures not recommended" in 165.7. Section 165.8 generally states as the standard for agencies to follow, that pesticides ". . . should be disposed of according to the following procedures . . ." (Emphasis added). This language seems to present the procedures for disposal of pesticides as worthy of notice or to attract favorable attention to them. The only "mandatory" reference in the recommended procedures is found at Title 40 FR §165.2(c) which states "These disposal procedures are mandatory only for the Agency in carrying out its pesticide and container disposal operations." (Emphasis added). EPA has, under the Executive Order 11752, authority to establish mandatory guidelines for Federal agencies, but it has chosen not to exercise that authority at this time. The EPA administrator's comments in FR, Vol. 39, No. 85 - Wednesday, May 1, 1974, at page 15237 explains why this choice was made:

> ". . . adequate disposal sites and the necessary facilities are not readily available nationwide, and significant information gaps exist which make it infeasible to write specific criteria for certain disposal methods and procedures. Further, information on the full extent of environmental damages and of the economic impact of such regulations is lacking. Therefore, the Agency has retained the recommended procedures approach. At such time as this information has been obtained and analyzed, consideration will be given to proposing comprehensive regulations relative to storage and disposal."

(2) Since EPA, apparently for sound practical reasons, has not yet chosen to exercise its authority under E.O. 11752, it is our opinion that the recommendatory language of the recommended procedures do not, and were not intended to, establish a Federal regulation or guideline.

(3) Without specific standards binding the agencies, they may use their sound discretion and judgment, within the scope of applicable statutes, in determining the best means of disposing of pesticides.

3. TRANSPORTATION AND HANDLING SAFETY: An Operations Plan will be prepared for handling, transfer, and shipments of Orange which are accomplished in support of the incineration project. This plan will include personnel and environmental safety procedures and describe the monitoring to be accomplished during these operations (see Appendix I. and Part II.E.).

4. ALTERNATIVES: See Part V.I. and V.J. for information on chlorinolysis and fractionation.

JOHN A. BURNS
GOVERNOR

RICHARD E. MARLAND, PH.D.
INTERIM DIRECTOR

TELEPHONE NO.
548-6915

STATE OF HAWAII
OFFICE OF ENVIRONMENTAL QUALITY CONTROL
OFFICE OF THE GOVERNOR
550 HALEKAUWILA ST
ROOM 301
HONOLULU, HAWAII 96813

July 9, 1974

Billy E. Welch, Ph.D
Special Assistant for Environmental Quality
Department of Air Force
Office of the Assistant Secretary
Washington, D.C. 20330

SUBJECT: Disposition of Orange Herbicide by Incineration

Dear Dr. Welch,

[1] As of this date, this Office has received two comments on the subject project. An attached sheet lists the responding agencies. We hope that these comments are helpful to you. We also thank you for giving this Office an opportunity to review the draft environmental statement, particularly in view of the deadline extension you granted.

Although this Office finds the draft environmental statement adequate in most areas, we offer the following comments:

[2] Option I (Incineration at sea)

1. Although burning Orange Herbicide at sea away from civilization and marine life may not have any harmful effect, air pollution still exists as an environmental problem. We should be concerned with limiting the problem of air pollution through the use of a scrubber system with constant monitoring of air emissions throughout the process of incineration instead of an uncontrolled burning operation. Thus, the conclusion in the draft environmental statement that monitoring is unnecessary (p. 64) should be reconsidered. One must not conclude that the environmental impact of air pollution in a populated area is in any way different from the impact in desolate surrounding.

2. A scrubber system in the gas effluent stack would minimize the pollutants in the air. A monitoring system would be able to keep an accurate account of the emissions and any unanticipated high level readings from the stack during the burning of Orange Herbicide.

3. There is little mention of the exhaust from the fuels for the burners. Would the exhaust react with the products emitted from the incineration?

[3] Option II

For incineration at Johnson Island (Option II), there is one area of great concern. One of the waste effluents without the scrubber in the stack is HCl gas (about 18.5 tons daily or 25 ppmv/v). If HCl gas comes in contact with moisture, it converts into hydrochloric acid. Since the relative mean humidity is 75%, the HCl gas could possibly convert to HCl acid. Thus, the off shore waters and the surrounding areas would be contaminated. Marine life may be harmed by the change in pH of the ocean or the acidic aerobic state. Any metal equipment nearby may be damaged by corrosion. Rain is another factor that must be considered since acid-rain may result.

One feasible idea that was briefly mentioned but should be considered in more detail is photodecomposition. Photodecomposition has the advantage of being economical, non-polluting to the air, and recyclable to useful chemicals. Although it is stated on page 84 that 2,3,7,8-tetrachlorodibenzo-p-dioxin is neglible in aqueous suspensions and wet and dry soil, another solvent can be used, like alcohol, where photodecomposition does occur.

The Environmental Center at the University of Hawaii has a major criticism. It is felt that there is insufficient data on the ecology of terrestrial and aquatic biota of Johnson Atoll. Appendix A needs to be expanded to include data describing the species present, their geographical distribution and density, and behavioral characteristics. Although there are detailed data of physical and technological information, the biological aspects are almost ignored. Thus, on that basis the Environmental Center recommends the shipboard alternative for disposition of the Orange Herbicide.

[4] We hope that the final statement will be available for our review, and that it will address the comments presented here.

[5] Thank you very much for the opportunity to review your environmental statement.

Sincerely,

Richard E. Marland
Interim Director

Attachment

LIST OF RESPONDING AGENCIES

State

1. Department of Planning & Economical Development (June 19, 1974)
2. Environmental Center (July 3, 1974)

DEPARTMENT OF PLANNING
AND ECONOMIC DEVELOPMENT

JOHN A. BURNS
Governor

SHELLEY M. MARK
Director

EDWARD J. GREANEY, JR.
Deputy Director

250 South King St. / Honolulu, Hawaii 96813 / P. O. Box 2359 / Honolulu, Hawaii 96804

June 19, 1974

Ref. No. 1057

MEMORANDUM

TO: Dr. Richard E. Marland, Interim Director
Office of Environmental Quality Control

FROM: Shelley M. Mark, Director

SUBJECT: Review of Revised Draft Environmental Statement for Disposition of Orange Herbicide by Incineration

We have reviewed the above subject draft. It appears to be a very detailed and conscientious appraisal of the environmental impacts which may be expected. However, since the subject matter is of a very scientific nature and may be of direct concern to the State of Hawaii due to our geographical position, it is recommended that detailed comments be sought from other State agencies that have the necessary expertise to adequately evaluate this proposal.

# University of Hawaii at Manoa

**Environmental Center**
Maile Bldg. 10 • 2540 Maile Way
Honolulu, Hawaii 96822
Telephone (808) 948-7361

Office of the Director


July 3, 1974

MEMORANDUM

TO: Richard Marland

FROM: Jerry M. Johnson, Acting Director

SUBJECT: Revised Draft Environmental Impact Statement for Disposition of Orange Herbicide by Incineration, April 1974

[1] I have reviewed the subject EIS and have the following comments to offer.

[2] I find the statement to be adequate in most aspects. In fact I believe the Department of the Air Force, except for the one major exception delineated below, should be commended for the overall quality of the document.

[3] My only major criticism is that insufficient data are provided on the ecology of terrestrial and aquatic biota of Johnston Atoll. Appendix A is a very brief and unsatisfactory summarization of what appears to be a comprehensive baseline ecological survey of the biota of concern. Without data describing the species present, their geographical distribution and density and their major behavioral characteristics, the reviewer is able to neither assess the significance of the individual species and their communities nor the possible impact on them of the on-land incineration alternatives. I can understand the reluctance of the U.S. Department of the Air Force to reproduce the entire document summarized in Appendix A for each copy of the final draft EIS. However, it is impossible for the reviewer to obtain a copy of the document from the Department of the Air Force, if at all, within the time constraints placed on the review process. I believe the originating agency could have

done a much better job of summarizing. The Department went to great detail and cost in presenting other aspects (Appendices D, E and K). Thus I find the almost complete lack of biological data somewhat of an enigma. This lack appears to be a cavalier disregard for the biological aspects and a somewhat enthusiastic and overriding concern for the physical and technological considerations.

[4] On the basis of the data provided in the Final Draft, I can only recommend the shipboard alternative as a reasonable mode for orange herbicide disposal. I foresee the deleterious consequences of this alternative as being minimal. Furthermore, the ship could possibly be used for future disposal of chemicals as well. If a permanent incineration structure were placed on the Island, a tremendous economic pressure would be created for disposal thereon of future military wastes and mistakes. It is not only the incinerator effluents that would be of concern on land. The stresses created on the biota by the logistical aspects alone could be serious.

Jerry M. Johnson

JOHN A. BURNS
GOVERNOR

RICHARD E. MARLAND, PH.D.
INTERIM DIRECTOR

TELEPHONE NO.
548-6915

STATE OF HAWAII
OFFICE OF ENVIRONMENTAL QUALITY CONTROL
OFFICE OF THE GOVERNOR
550 HALEKAUWILA ST
ROOM 301
HONOLULU, HAWAII 96813

July 11, 1974

Billy E. Welch, Ph.D.
Special Assistant for Environmental Quality
Department of the Air Force SAG/ILE
Office of the Assistant Secretary
Washington, D.C. 20330

SUBJECT: Draft Environmental Statement on Disposition of Orange Herbicide By Incineration

Dear Dr. Welch,

This Office had received an additional comment from Dr. John L. T. Waugh, Chemistry Department at the University of Hawaii on the subject above. We are forwarding the comment to you in order for it to be reviewed. Please append it to our correspondence dated July 9, 1974.

We hope that this has not been a great inconvenience to you. Thank you for your cooperation in this matter.

Sincerely,

Richard E. Marland
Interim Director

Attachment

1st July, 1974.

To: Dr. Jerry M. Johnson,
Environmental Center.

From: John L.T. Waugh,
Chemistry Department.

## Air Force Proposal on ORANGE Herbicide Disposal

This is a lengthy and annoying report, which illustrates in many places, the ridiculous wastefulness, the enormous expense, the uncontrolled planning, the limited thinking, and the casual disregard for areas remote from Washington, associated with Defense Department operations. It is pointed out on the inside of the cover of this several-hundred-page report that it is economically printed on recycled paper, although the subject matter involves the single-minded topic of destroying an accumulation of 2.3 million gallons of herbicide, on which apparently millions of dollars have already been spent on shipping it back and forth around the world, storing and re-drumming, apart from the initial manufacturing cost. It is most difficult to believe that one or more of the seven manufacturers of this material could not devise a method of converting the ORANGE herbicide into useful industrial chemicals such as carbon tetrachloride, carbonyl chloride, hydrogen chloride, and chlorine, for a fraction of the cost already involved for shipping and storage, and in a fraction of the 3-year period which has now elapsed since the Department of Defense stopped using this material in Vietnam. Why should one or more of the original manufacturers not put some research effort into developing the necessary technology at whatever capital expense is necessary, rather than compounding the problem by erecting facilities simply for the destruction of this massive amount of material, at a site which is only 717 miles southwest of Hawaii?

The above question is based on the assumption that the sea-going incineration plan, even aboard a special ship such as the VULCANUS, will hopefully be abandoned; the lack of abilty of any person, technical department, or governmental agency of any country, to accurately forecast ocean and climatic conditions during the period of injecting many thousands of tons of hydrogen chloride, carbon monoxide and dioxide, particulate carbon, into the environment during the incineration of such large amounts of material, especially under conditions where access to technical advice, control, monitoring, is remote, would appear to make this mode of destruction a very risky and ill-advised venture. At least, in a land-based operation, a reasonable degree of control can be excercised and the number of possibly indeterminate hazards greatly reduced. Since the herbicide is apparently all contained in 55-gallon drums, the emptying, decontamination, and disposal of these 40,000-odd drums alone is a maj - problem. Incidentally, the MARQUARDT COMPANY report, appears to be the only part of this whole document which gives some detailed consideration to this aspect of the overall disposal problem.

It would seem reasonably sensible to suggest that instead of shipping the 0.86 million gallons of herbicide from Gulfport, Mississippi, to Johnson Island, at the estimated cost of $450,000, constructing incineration facilities there, remote from the technical and manufacturing centres in the country, that Dow, Hercules, or one of the other 5 original manufactures of the ORANGE herbicide, should be contracted to utilize, further develop if necessary, their present technolgy, with a view to recovering the chlorine content of these 2,300,000 gallons of material in some industrially useful form.

RICHARD E. MARLAND, PH.D.
INTERIM DIRECTOR

TELEPHONE NO.
548-6915

STATE OF HAWAII
OFFICE OF ENVIRONMENTAL QUALITY CONTROL
OFFICE OF THE GOVERNOR
550 HALEKAUWILA ST.
ROOM 301
HONOLULU, HAWAII 96813

July 15, 1974

Dr. Billy E. Welch
Special Assistant for Environmental Quality
Department of Air Force SAG/ILE
Office of the Assistant Secretary
Washington, D.C. 20330

SUBJECT: Draft Environmental Statement on Disposition of Orange Herbicide by Incineration

Dear Dr. Welch,

This Office has received an additional late comment from the Department of Agriculture (State of Hawaii) dated July 10, 1974 on the above subject. We are forwarding the comment in hopes that it may be reviewed even at this late date. Please append it to our correspondence dated July 9, 1974.

We apologize for the inconvenience created by this comment. We look forward to the final environmental statement.

Thank you for your cooperation in this matter.

Sincerely,

Richard E. Marland
Interim Director

Attachment

JOHN A. BURNS
GOVERNOR

FREDERICK C. ERSKINE
CHAIRMAN, BOARD OF AGRICULTURE

WILLIAM E. FERNANDES
DEPUTY TO THE CHAIRMAN

STATE OF HAWAII
DEPARTMENT OF AGRICULTURE
1428 SO. KING STREET
HONOLULU, HAWAII 96814

July 10, 1974

MEMORANDUM

TO: Dr. Richard E. Marland, Interim Director
Office of Environmental Quality Control

SUBJECT: Draft Environmental Impact Statement
Incineration of Orange Herbicide
Department of the Air Force - Johnston Island

This draft environmental impact statement addresses concerns relating to disposal of Orange herbicide. Orange herbicide contains approximately equal parts by volume of the normal butyl ester of 2,4-dichlorophenoxyacetic (2,4-D) and the normal butylester of 2,4,5-trichlorophenoxyacetic (2,4,5-T) acid. A small quantity, known as Orange II, contains the isooctyl ester of 2,4,5-T instead of the normal butylester. No direct agricultural impact is anticipated.

Herbicidal formulations containing 2,4-D or 2,4,5-T are used for control of plant pests in agricultural operations in Hawaii. In 1968 197,227 pounds of 2,4-D and 6,128 pounds of 2,4,5-T were used in sugar cane plant pest management. Other operations used about 1,400 pounds 2,4-D and 14,000 pounds 2,4,5-T. Control of plant pests in pastures depends upon the continued use of 2,4,5-T although this use is declining as better control is achieved.

An impurity, 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD), in some lots of Orange herbicide is teratogenic (malformed fetuses and living offspring) in experimental animals. For this reason military and certain other uses of 2,4,5-T ceased in 1970. There are approximately 860,000 gallons and 1,400,000 gallons in storage at Gulf Port, Mississippi and Johnston Island, Pacific Ocean, respectively.

Controlled incineration at high temperature is recommended for disposal. Two alternative controlled incineration methods described are for either units mounted on a vessel designed specifically for disposal of toxic combustible wastes or located at a leeward site on Johnston Island. Regardless of the choice of system, Johnston Island will be the site for storage and handling as part of the disposal system.

The environmental impact statement provides an adequate assessment of the technology of Orange herbicide incineration. Option 1, incineration at sea is

preferred. No significant detrimental environmental effects can be expected from this method of disposal.

Analysis of risks from adoption of Option 2, incineration on Johnston Island, are less well defined. Use of coral rock or sea water scrubbers would create disposal problems. Direct atmospheric discharge of combustion products with due consideration of wind directions and velocities would be preferred.

Biological monitoring was described. There are some concerns for the adequacy of the monitoring protocol. Baseline sampling was limited to a few days in October 1973. The choice of top predatory animals and the dominant plant (coral) species would appear to be adequate for monitoring. However, frequency of sampling, number of sample per site and species were inadequately described for evaluation. A detailed sampling protocol keyed to operational schedules is lacking. It is recommended that such a protocol be provided for review prior to any Johnston Island operations. Such a sampling protocol should be developed showing relation to shoreside handling and storage operations even though incineration at sea is practiced.

Thank you for the opportunity to review this document as it relates to our concerns.

for FREDERICK C. ERSKINE
Chairman, Board of Agriculture

RESPONSE TO COMMENTS FROM THE STATE OF HAWAII LETTERS (9,11 and 15 Jul 74)

1. (Paragraph 2-1 S of Hawaii 9 Jul 74 Ltr) Installation of an acidic gas scrubber on the incinerator ship is not practical. Such a system would require considerable energy for operation. And unless a caustic scrubber was used (requires cargo space for alkaline chemical), the liquid discharge from the scrubber would result in localized water pollution. The stack discharge of combustion gases into the atmosphere actually provides for dispersion of the material into the atmosphere rather than concentrating possible impurities into liquid scrubber discharges. The bulk of the incinerator discharges is non-persistent and non-reactive, or subject to photodecomposition and/or hydrolysis. The discharge of such material into a desolate ecosystem for a short period of time should result in a negligible impact. The position that "air pollution" may occur during this period is appreciated; however, it is deemed acceptable since it has minimal impact on the ecosystem.

2. (Paragraph 2-3 S of Hawaii 9 Jul 74 Ltr) No auxiliary fuel is used for the "burners" during the incineration of Orange herbicide. However, auxiliary fuel is used to bring the incinerator to operating temperature prior to injecting the herbicide which is capable of sustaining the necessary incineration temperature.

3. (Paragraph 2-2 S of Hawaii 9 Jul 74 Ltr) See the response to the letter of comment from the Center for Law and Social Policy relative to monitoring.

4. (Paragraph 3-1 S of Hawaii 9 Jul 74 Ltr) The Air Force does not presently plan to incinerate the Orange herbicide at Johnston Island. However, if the principal alternative of incineration on Johnston Island is initiated, the environmental impact upon the ocean adjacent to Johnston Island associated with the discharge of hydrogen chloride from an incinerator stack on Johnston Island is discussed in Part III.C.5.c., Reef Area. A "worst case" analyses revealed that any damage to the reef on an acute basis would be minimal and that the long term chronic effects can not be predicted. Meterological constraints and ambient air monitoring would be utilized to insure that hydrogen chloride would not adversely affect personnel, structures, or the environment. Information or the reaction of hydrogen chloride in air and effects on structures is included in Part III B.2.c.

5. (Paragraph 3-2 S of Hawaii 9 Jul 74 Ltr) Sufficient data is not available to appraise the removal of TCDD from Orange via photodecomposition.

6. (Paragraph 3-3 S of Hawaii 9 Jul 74 Ltr) As stated on the initial page of Appendix A, the document "Ecological Baseline Survey of Johnston Atoll Central Pacific Ocean" was not included for the sake of space conservation but was availabe by request from the USAF EHL, Kelly AFB, TX. It is interesting to note that only one request for Appendix A was received, and they were provided a copy.

7. (Paragraph 4 U of Hawaii, Manoa 3 Jul 74 Ltr) There are no present interests for establishment of a permanent incinerator on Johnston Island. In fact, the Air Force intends to incinerate at sea.

8. (Paragraph 1 & 3, Atch to S of Hawaii, 11 Jul 74) Efforts to return the Orange herbicide to manufacturers for reprocessing have been explored and they are described in Part V.

9. (Paragraph 2, Atch to S of Hawaii, 11 Jul 74) "Worst Case" analyses are presented for decomposition compounds resulting from incineration at sea and at Johnston Island (Part II.B. and II.C.). The distruction of Orange herbicide in "land based" incinerators was also considered, but they were not viable alternatives for reasons presented in Part II.A., II.B. and V.A.

10. (Paragraph 2, Atch to S of Hawaii, 11 Jul 74) The section on drum cleaning and disposal in the Marquardt Co. report was written by Air Force personnel. However, a new section on the disposal of drums has been included in the final environmental statement (Part II.E.).

11. (Paragraph 7 D of Agriculture, Hawaii 10 Jul 74 Ltr) The comments on biological sampling and concern for the adequacy of sampling protocol are appreciated. It is realized that the data from samples collected in Oct 1973 is somewhat meager. This data has been updated and is presented in Part III. C.1. A detailed protocol of sampling, including biological sampling, would be implemented if any Orange herbicide is incinerated on Johnston Island.

STATE OF MISSISSIPPI

OFFICE OF THE GOVERNOR

WILLIAM L. WALLER
GOVERNOR

WM. M. HEADRICK
COORDINATOR OF FEDERAL-STATE PROGRAMS

# STATE CLEARINGHOUSE FOR FEDERAL PROGRAMS

TO: Dr. Billy E. Welch, Special Assistant for Environmental Quality
Office of the Assistant Secretary
Department of the Air Force
Washington, D. C. 20330

State Clearinghouse Number
74051501

Date: May 15, 1974

PROJECT DESCRIPTION: Draft Environmental Statement -- Disposition of Orange Herbicide by Incineration -- Revision of January 1972 Statement.

( x ) 1. The State Clearinghouse has received notification of intent to apply for Federal assistance as described above.

( x ) 2. The State Clearinghouse has reviewed the application(s) for Federal assistance described above.

( --) 3. After proper notification, no State agency has expressed an interest in conferring with the applicant(s) or commenting on the proposed project.

( --) 4. The proposed project is: ( ) consistent ( ) inconsistent with an applicable State plan for Mississippi.

( --) 5. Although there is no applicable State plan for Mississippi, the proposed project appears to be: ( ) consistent ( ) inconsistent with present State goals and policies.

COMMENTS: The attached comments represent the review of this project when disposition by incineration within the Continental United States was proposed. By conferring with all participants, these comments are validated for this statement. Each item in the summary letter of the Air and Water Pollution Control Commission applies whether incineration takes place on this Continent or at sea. The urgency of moving this to a safer storage place is increased due to the passage of more than two years.

This notice constitutes FINAL STATE CLEARINGHOUSE REVIEW AND COMMENT. The requirements of Office of Management and Budget Circular No. A-95 have been met at the State level.

Edward A. May, Jr.
Assistant to the Coordinator

SUITE 400, WATKINS BLDG. • 510 GEORGE STREET • JACKSON 39201 • (601) 354-7570

STATE OF MISSISSIPPI
EXECUTIVE CHAMBER
JACKSON

WILLIAM LOWE WALLER
GOVERNOR

February 11, 1972

Honorable Aaron J. Racusin
Acting Assistant Secretary of the Air Force
Installation and Logistics
Office of the Secretary
Department of the Air Force
Washington, D. C. 20330

Re: Draft Environmental Statement-Disposition of Orange Herbicide by Incineration - January 1972--AF-ES-72-2D

Dear Mr. Racusin:

In compliance with applicable regulations, the above captioned environmental statement has been reviewed by appropriate State agencies concerned with various aspects of the disposition. Comments from State agencies are summarized in the latter prepared by the Air and Water Pollution Control Commission, and are enclosed herewith.

It is my opinion that the attached environmental statement is satisfactory.

I recommend that full consideration be given to the comments of our agencies in the final review.

Sincerely,

Bill Waller

BILL WALLER
GOVERNOR

STATE CLEARINGHOUSE FOR FEDERAL PROGRAMS

Federal-State Programs
Office of the Governor
510 Lamar Life Bldg.
Jackson, Mississippi 39201
Telephone 354-7570

State Clearinghouse No.

72020901

Date: February 9, 1972

TO: Aaron J. Racusin
Acting Assistant Secretary of the Air Force
Installation and Logistics
Office of the Secretary
Department of the Air Force
Washington, D. C. 20330

PROJECT DESCRIPTION: Department of the Air Force Draft Environmental Statement -- Disposition of Orange Herbicide by Incineration - January 1972 AF-ES-72-2D

( x ) 1. The State Clearinghouse has received notification of intent to apply for Federal assistance as described above.

( -- ) 2. The State Clearinghouse has reviewed the application(s) for Federal assistance described above.

( -- ) 3. After proper notification, no State agency has expressed an interest in conferring with the applicant(s) or commenting on the proposed project.

( -- ) 4. The proposed project is ( ) consistent ( ) inconsistent with an applicable State Plan for Mississippi.

( -- ) 5. Although there is no applicable State Plan for Mississippi, the proposed project appears to be ( ) consistent ( ) inconsistent with present State goals and policies.

COMMENTS: The summary of comments from all State agencies concerned is included in the attached letter from the Air and Water Pollution Control Commission. This completes the review.

This notice constitutes FINAL STATE CLEARINGHOUSE REVIEW AND COMMENT. The requirements of U.S. Office of Management and Budget Circular No. A-95 have been met at the State level.

David R. Bowen
Coordinator of Federal State Programs

# Air & Water Pollution Control Commission

STATE OF MISSISSIPPI

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Glen Wood, Jr.
EXECUTIVE DIRECTOR
POST OFFICE BOX 927 TELEPHONE 354-6783
SIXTH FLOOR ROBERT E. LEE BUILDING
JACKSON, MISSISSIPPI 39205

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ASSOCIATE MEMBERS
STATE PARK SYSTEM
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A & I BOARD
PAUL BURT
GEOLOGICAL SURVEY
W. H. MOORE

February 8, 1972

RECEIVED
FEB 9 - 1972

Mr. Edward A. May, Jr.
Assistant to the Coordinator
Federal-State Programs
Office of the Governor
510 Lamar Life Building
Jackson, Mississippi

Dear Mr. May:

This letter is in reference to yours of January 26, concerning the draft environmental impact statement entitled "Disposition of Orange Herbicide by Incineration". A meeting was held in our office with concerned agencies of the State on February 3, to conduct a technical review of this statement and to coordinate the state's position in this matter. Copies of the impact statement had previously been forwarded to these agencies.

The consensus of this meeting is enumerated below:

1. Department of the Air Force should explore further possibilities for use of the material under adequate control measures, preferably by the federal government, as in national and state forests or by returning to commercial use through some acceptable channel. Apparently the alternative of giving this material away was not explored. It is felt that destruction of the material would be a needless waste and would create further expense. It is recognized that such action as suggested might require some emergency authority from Environmental Protection Agency but this should pose no great difficulty since a similar material is in everyday use.

2. In the event incineration is taken as the alternative, it is requested that the federal government assume the responsibility for all transportion of the material to the point of incineration and provide all necessary safety measures, such as, but not limited to, shipping materials in small quantities and providing the necessary absorbents at the convenient locations if shipped by rail.

3. It is requested that the material be removed from its present location at Keesler Air Force Base beginning immediately and without regard to the final disposition of the material. It is felt this is absolutely essential because of the proximity of the material to recreational and shellfish waters, as well as large densely populated areas, and further because of the history of hurricanes and tornadoes in that particular section of the country. It is our feeling there are many other areas in the continental United States which would provide a much safer depository for this material.

4. The Mississippi Air and Water Pollution Control Commission should be notified in advance of any proposed movement of the material, of the routes to be taken, and of the safety precautions.

Copies of this statement are being forwarded to all of the involved agencies, as noted on the attached sheet.

Yours very truly,

Glen Wood, Jr.
Executive Director

GWjr:js

Copies furnished:

Mr. Billy Joe Cross, Director
Mississippi Game & Fish Commission
Post Office Box 451
Jackson, Mississippi

Mr. Joe D. Brown, Director
Division of Sanitary Engineering
State Board of Health
Post Office Box 1700
Jackson, Mississippi 39205

Mr. William J. Demoran
Marine Biologist
Gulf Coast Research Lab
Post Office Box AG
Ocean Springs, Miss. 39654

Mr. Bobby R. Tramel
Bureau of Sport Fisheries
and Wildlife
Post Office Drawer FW
State College, Miss. 39762

Mr. Jack W. Pepper, Water Engineer
Mississippi Board of Water Commissioners
416 North State Street
Jackson, Mississippi 39201

Dr. R. A. McLemore, Director
Mississippi Department of Archives and History
Post Office Box 571
Jackson, Mississippi 39205

Attention: Mr. Elbert Hilliard

Colonel Wendell D. Lack, State Forester
Mississippi Forestry Commission
1106 Woolfolk State Office Building
Jackson, Mississippi 39205

Mr. O. T. Guice, Jr., Director
Division of Plant Industry
P. O. Box 5207
State College, Mississippi 39762

Mr. William H. Moore
Director and State Geologist
Mississippi Geological Survey
Post Office Box 4915
Jackson, Mississippi 39216

Mr. Spencer E. Medlin, Comptroller
Mississippi Park System
717 Robert E. Lee Building
Jackson, Mississippi

RESPONSE TO COMMENTS FROM THE STATE OF MISSISSIPPI LETTER (15 May 74)

1. See Part I for Air Force action toward EPA registration of Orange herbicide.

2. The Mississippi Air and Water Pollution Control Commission will be notified of any proposed large scale movement of the herbicide in Mississippi. In addition, the Commission will be apprised of plans for dedrumming and transfer of the herbicide from the NCBC, Gulfport to the incineration ship.

THE AMERICAN EAGLE FOUNDATION
SUITE 300 1729 H STREET, N.W. WASHINGTON, D.C. 20006 · A/C 202-298-6105

DONALD D. CARRUTH
PRESIDENT

WILLIAM G. ALLEN
VICE PRESIDENT

June 25, 1974

Dr. Billy E. Welch
Special Assistant For Environmental Quality (SAFILE)
Office of the Secretary
U.S. Department of the Air Force
Room 4D873, The Pentagon
Washington, D.C. 20330

Dear Dr. Welch:

[1] This office has reviewed with great interest the "Revised Draft Environmental Statement -- Disposition of Orange Herbicide by Incineration, April 1974, AF-ES-2D(1)".

[2] The February and March 1972 responses to the January 1972 draft environmental statement made available to the Council on Environmental Quality and the public gives strong support to not allowing residual stocks of Orange Herbicide to be disposed of in any of the fifty states of the United States. Further research on the disposition of this herbicide by government, private and educational organizations,at the request of the Air Force, gives additional support to the need for destroying this chemical waste by high-temperature incineration through the use of the M/V Vulcanus -- a specially equipped and designed vessel which has been used in North Sea waters for destroying hazardous/toxic chemical wastes for the past 22 months.

[3] Since the European generated industrial chemical waste is not of the same chemical-mix as that of Orange Herbicide, and since the February 15, 1974 letter of transmittal by the President, National Academy of Sciences to the President of the Senate, Speaker of the House of Representatives, and the Secretary of Defense, of the report: "The Effects of Herbicides in South Vietnam, Part A -- Summary and Conclusions", we feel that the national as well as the international interests surrounding the actual destruction of residual stores of Orange Herbicide would be best served by a monitoring of the vessel's incineration process.

[4] The monitoring project should include the taking of necessary samples of stack emissions and the product being incinerated, under varying burner and firing conditions, fluid

feed and air flow rates and combustion temperatures; and determine by methods to be prescribed, the parameters of fallout patterns and rates of salt water assimulation of such fallout to a depth of at least two meters below the water surface.

[5] We appreciate your consideration in making available to our national environmental organization copies of the Air Force's revised draft EIS of April 1974.

Sincerely yours,

Donald D. Carruth

Donald D. Carruth
President

RESPONSE TO COMMENTS FROM THE AMERICAN EAGLE FOUNDATION LETTER (25 Jun 74)

1. (Paragraph 2 AEF Ltr) The Final Environmental Statement proposes the destruction of Orange herbicide by incineration under a proposed action of incineration at sea on a specially equipped vessel or as the principal alternative of incineration on Johnston Island. In addition, it is also felt that the herbicide could be incinerated in an environmentally safe manner at the U.S. Army Rocky Mountain Arsenal (RMA), CO, see Part V.A.2.

2. (Paragraph 3,4, AEF Ltr) The monitoring project described in the American Eagle letter as regards incineration on board a vessel at sea is very comprehensive and represents quite a formidable task. The disposal of Orange seems to become a vehicle by which extensive data would be obtained on the incineration process. The fact that the Vulcanus has been "used in North Sea waters for destroying harardous/toxic chemical waste for the past 22 months" seems to refute the need for extensive monitoring of a one time (26 day) incineration of Orange in the Pacific Ocean. The environmental assessment of the proposed action of incineration at sea (Part III) and the information available on the efficiency of incineration of chlorinated hydrocarbons at sea and their associated environmental impact (see Parts III.B.2. and III.C.5.) also minimize the need for stack and ecological monitoring. The Air Force position is that operational monitoring of the Vulcanus incinerators (temperature, fuel/air flow, pressure, etc.) is adequate for the proposed action of incineration at sea and that stack sampling and analyses is not required. See also the Air Force response to the comments from the Center for Law and Social Policy and the EPA.

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CENTER
FOR
LAW
AND
SOCIAL
POLICY

1751 N STREET, N.W. WASHINGTON, D.C. 20036 202 872 0670

Ruby I Compton
Roger S Foster
Richard A Frank
Paul R Friedman
Paul D Gewirtz
Eldon V C Greenberg
Marcia D Greenberger
Robert M Hallman
Charles R Halpern
Benjamin W Heineman, Jr
Joseph N Onek
Lois J Schiffer
Lawrence H Schwartz
Edward P Scott
Attorneys at Law

June 26, 1974

Dr. Billy E. Welch
Special Assistant for
Environmental Quality
The Pentagon
Room 4 D 873
Washington, D.C. 20330

Dear Dr. Welch:

Revised Draft Environmental Statement on Disposition of Orange Herbicide by Incineration

[1] On May 13, 1974, the Department of the Air Force published a notice (39 Fed. Reg. 17120) soliciting comments on the Department's Revised Draft Environmental Impact Statement on Disposition of Orange Herbicide by Incineration [AF-ES-72-2D(1)]. The following comments on that impact statement are submitted on behalf of the Friends of the Earth and the National Audubon Society (hereafter "the environmental organizations"), two environmental organizations with a worldwide membership of more than 350,000 persons and an established history of concern about pollution of the marine environment. The environmental organizations have undertaken numerous efforts to improve the quality of the marine and coastal environment by means of testimony, policy analysis, educational programs and litigation.

[2] The issue addressed in the impact statement is the disposition of 2.3 million gallons of Orange herbicide presently stored at Johnston Island and in Gulfport, Mississippi. The herbicide is highly toxic as are some of its components, e.g., dioxin. The impact statement thoroughly examines several alternative means of disposing of the Orange herbicide, including the possibility of returning the herbicide to the manufacturers, deep

(injection) well disposal, burial in underground nuclear test cavities, sludge burial, microbial reduction, chlorinolysis, soil biodegradation, and incineration. The impact statement proposes the incineration method, rejecting the others as being either inadequate to destroy the dioxin, otherwise environmentally unsound, or only in the developmental stage and thus unavailable for present use. The impact statement recommends that incineration take place either on board a specially designed vessel in the open tropical ocean west of Johnston Island or in a facility constructed on Johnston Island.

[3] The environmental organizations concur that the only reasonable method of disposal is incineration. We strongly urge the adoption of incineration at sea. Incineration at sea, as the impact statement clearly reveals, is the most environmentally sound of the two methods for the following reasons.

[4] The most toxic and environmentally hazardous byproduct of incineration is hydrogen chloride. The best means of minimizing the potential hazards of hydrogen chloride is to disperse the gas over the widest possible surface area. To achieve this end, incineration aboard a moving vessel is clearly preferable to incineration on Johnston Island. If the incineration occurs on Johnston Island, the hydrogen chloride will drain off the land and will collect in the waters adjacent to the Island. Since the hydrogen chloride would disperse over a smaller surface area, concentration levels could be significantly higher and the environmental impact more severe.

[5] Incineration at sea, west of Johnston Island is far preferable. These waters are generally poor in nutrients, and marine life is scarce when compared to that found in coastal areas or near island dwellings. Furthermore, if incineration occurs on Johnston Island, the human inhabitants and flora and fauna might be adversely affected by the combustion gases, as might the ecologically important bird community located on nearby Sand Island. By incinerating at sea, the Orange herbicide can be disposed of at a down-wind location sufficiently distant from both Johnston and Sand Islands.

[6] Our support for incineration is based on several assumptions. First, the combustion temperatures must remain at least 1400°C throughout the entire operation. This requirement must be met to destroy all of the toxic components of the herbicide. Second, the impact statement mentions that incineration operations are subject to mechanical malfunctions and outlines failsafe measures required to protect the environment and provide safety of personnel. These recommended safeguards range from procedures to preclude and contain any spillage of Orange herbicide during transportation to the incineration site to installation of mechanized devices which prevent the feeding of herbicide into the incinerator's burners if combustion chamber temperatures fall below 1400°C. We assume that these suggested failsafe procedures will be utilized. As an added precautionary measure, we recommend that stack samples be collected periodically and held for analysis, in order to demonstrate, if necessary, that the toxic components of the Orange herbicide were, in fact, destroyed.

[7] Finally, the impact statement does not indicate whether the 45,000 storage drums would be cleaned before disposal, nor does it propose a method of drum disposal. We suggest the drums be cleaned with a light petroleum in order to remove as much herbicide as possible. The cleaning fluid should then be incinerated in the same manner as the Orange herbicide. Although the impact statement finds this process to be expensive, it appears to be the only means of destroying substantially all of the Orange herbicide. After cleaning, the drums should be smelted.

[8] A major omission of the impact statement is its failure to relate the disposition to the Marine Protection, Research and Sanctuaries Act of 1972 (33 U.S.C. §1401), and the Convention on Marine Pollution by Dumping of Wastes and Other Matter (London, 1972). The Marine Protection, Research, and Sanctuaries Act prohibits "transporting from the United States...except as authorized by permit...any...material for dumping...into ocean waters" (33 U.S.C. §1411(a)).

[9] The act defines dumping as the "disposition of matter of any kind or description" (33 U.S.C. §1422(c),(f)). While incineration is not a normal form of dumping, it does come under the purview of the Act and the safeguards of the Act should be applied.

[10] The Convention on Marine Pollution by Dumping of Wastes and Other Matter prohibits, "any deliberate disposal at sea of wastes and other matter from vessels" without obtaining a dumping permit (Articles III, IV). Although this Convention is not yet in force, the United States has deposited its instrument of ratification, as have others. Because of this and since the Convention may be in force at the time the Orange herbicide is incinerated, the U.S. should comply with at least the objectives and spirits of the Convention. Article VI of the Convention requires that records of the nature and quantities of all matter permitted to be dumped, the location, time, and method of dumping be reported to the new international organization which will be created under the Convention. We suggest that the United States report the required information to all countries who have ratified the Convention. The U.S. would satisfy the permit requirement by complying with the Marine Protection, Research and Sanctuaries Act.

[11] If you have any questions concerning the above, we would be happy to amplify our comments or provide additional information.

Sincerely,

Richard A. Frank

Richard A. Frank

RAF:cl

RESPONSE TO COMMENTS FROM THE CENTER FOR LAW AND SOCIAL POLICY LETTER (26 Jun 74)

1. (Paragraph 4 CL & SP Ltr) The environmental impact upon the ocean associated with the discharge of hydrogen chloride from an incinerator as a result of incineration of Orange on Johnston Island is discussed under "Reef Area," Part III.C.5.a. A worst case analyses reveals that any damage to the reef on an acute basis would be minimal and that any long term chronic effects on the reef could not be predicted. A monitoring plan would be in operation should any Orange be incinerated on Johnston Island. Monitoring stations would be selected to include evaluation of water in the plume fall-out area and around the reef. However, the Air Force does not presently plan to install a facility for the incineration of Orange at Johnston Island.

2. (Paragraph 5 CL & SP Ltr) If Orange herbicide is incinerated on Johnston Island meteorological constraints and an ambient air monitoring program will be in operation to insure that personnel, the bird community on Sand Island, and flora and fauna are not affected.

3. (Paragraph 6 CL & SP Ltr) The final contract for any incineration of Orange will include specifications on temperature requirements, operational monitoring and recording (temperature, fuel flow, air flow, operating pressures, etc.) and failsafe procedures.

4. (Paragraph 6 CL & SP Ltr) The desirability of collecting stack samples for subsequent analysis upon completion of the incineration phase of the project (non-real time monitoring) is appreciated. The feasibility and necessity of such action has been studied by the Air Force. The Air Force's position is that neither real time nor non-real time monitoring is required for this disposal project. This position is based on the evaluation of the environmental impact which would result from incineration of Orange at sea. The analysis based on an anticipated Orange destruction of 99.9% reveals that insignificant impact would occur. For perspective, the worst case analyses was also accomplished for Orange destruction efficiencies of 99.0 and 95.0% with the results indicating what is deemed as a minimal and acceptable environmental impact (see Parts III.B.2. and III.C.5.). Information received on incineration of chlorinated hydrocarbons at sea shows that the incinerators utilized by the vessels tested were capable of essentially complete destruction of the hydrocarbons with negligible environment impact. This information is contained in Appendix N and summarized in Part III.B. and III.C. The incineration of mustard agent at Rocky Mountain Arsenal is accomplished by incineration with essentially total destruction of the agent (see Part V.A.2.). In view of the above, it is the Air Force's position that the operational monitoring (temperature, fuel flow, etc.) will be sufficient for this relatively short project and that neither real time nor non-real time monitoring is required.

5. (Paragraph 7 CL & SP Ltr) See Part II.E. for drum disposal information.

THE Marquardt COMPANY
CCI Corporation 16555 SATICOY STREET • VAN NUYS, CALIFORNIA 91409 • TELEPHONE (213) 781 2121 • TWX 910 495 1710 • CABLE MARQCOR

June 21, 1974
Ref: 2000/115

Department of the Air Force
Office of the Assistant Secretary
Billy E. Welch, Ph.D.
Special Assistant for Environmental Quality
Washington, DC 20330

Dear Dr. Welch:

The following comments are provided in response to the USAF Revised Draft Environmental Impact Statement for the Disposition of Orange Herbicide by Incineration, April 1974, AF-ES-72-2D(1).

We are pleased that our unique SUdden Expansion (SUE®) burner was selected as the incinerator used to perform the only two full-scale test burns of Herbicide Orange and that a copy of our Final Draft Report on the Destruction of Orange Herbicide, February 1974, was included as Appendix E of the Revised Impact Statement. This report documents the 99.998% destruction efficiency of the SUE® incineration system.

1. The SUE incinerator (a commercial incinerator) system tested by the USAF in no way resembles the definition of a "conventional" liquid waste incinerator as defined in Part V.A.1.a. Appendix E of the Revised Draft Impact Statement contains a detailed description of the SUE incinerator system, pages E (B-1) through E (B-10). The combustion efficiency of 99.998% demonstrated in the test program is extremely high for an incineration process, and we know of no other commercial incinerator with documented efficiency approaching 99%.

   Part II C.2.(c)(1) states that the incineration systems installed on the ship Vulcanus are conventional incinerators.

2. Part II C.2.(c)(3) and (4) states that information from Ocean Combustion Service B.V., Rotterdam, The Netherlands, indicated that 99.9% of chlorinated hydrocarbons feed is destroyed. No information, data, test reports, or references are provided to support this claim. Further, no mention of tests or data substantiating the ability to destroy the dioxin (TCDD) is made.



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3. Part II C.2.(c)(3) states that data presented in Appendices D and E indicate that incineration of Herbicide Orange can be successfully accomplished on board the Vulcanus. All referenced test data representative of full-scale incineration of Herbicide Orange was obtained from the SUE® burner incinerator system. As recognized combustion experts, with 29 years of corporate combustion experience, we disagree with this statement for two reasons:

   (a) Data from one type of combustion system cannot be assumed to apply to a different type or size combustion system without extensive testing to validate the assumption. It is only conjecture that the incinerator on the ship Vulcanus would destroy Herbicide Orange at an efficiency of 99.9% since no tests have been run on the ship incinerator. Los Angeles County, for instance, requires afterburners on solid and liquid waste incinerators as a result of testing units with a single chamber like the incinerator on the Vulcanus. Combustion efficiency is closely related to the efficiency of fuel and air mixing in a unit, combustion frequency, combustion stability and stay time. Large-diameter combustion chambers often present mixing problems, combustion frequency problems, and combustion stability problems that result in low combustion efficiency and products of partial combustion. Partial incineration results in destructive distillation and often produces more undesirable products than dumping the raw product into the atmosphere.

   (b) Experience has proven that mixing, burning rates, and efficiencies determined from one size burner cannot be applied to a different size burner of the same type (let alone a different type of burner). One incinerator chamber (three burners of unknown size) on the Vulcanus would incinerate Orange at a rate of 6-2/3 pounds per second (pps) versus .14 pps for a 12-inch-diameter SUE® burner. Scaling is avoided in the Marquardt system by adding additional 12-inch-diameter SUE® burner modules to increase system capacity without changing combustion efficiency.

Mixing of fuel (herbicide) and air is the single most critical parameter in the incineration process. This fact was proven by tests conducted at Marquardt (Appendi. E) establishing that the poppet nozzle could not be used above 2/3 of the stoichiometric herbicide/air ratio, whereas the standard SUE slot nozzle injectors could be used with very high overall burning efficiencies. In fact, the poppet nozzle/SUE burner combination somewhat resembles the mixing process in most commercial incinerators. Thus, if an incinerator with burners other than the slot nozzle-equipped SUE type is used to destroy the herbicide, it cannot be assumed that it will operate in the same fashion and with the same efficiency as the SUE system without thorough testing and data analysis. Viscosity of the fuel (Orange Herbicide) directly affects the efficiency of any nozzle. The herbicide had to be heated to a minimum of 90°F (best results at 180°F) to reach efficient destruction. Heating 20 to 24 tons per hour to 90°F+ may present a major problem on board the Vulcanus.

A further complication arises in very large-diameter incinerators because of the potential for stratifying of zones of burning gases which have different fuel/air ratios. It is impossible to detect this improper mixing by measuring the temperature of the gases at various points because the same temperature can be reached by lean (excess air) burning or by overstoichiometric (insufficient air) burning. The combustion products in the two cases are vastly different and in the case of the overstoichiometric mode probably will contain large quantities of raw or partially decomposed herbicide.

Stay time is no cure or substitute for adequate mixing. The combustion process (more properly defined as oxidation) proceeds very slowly after the initial flame front and requires extremely highlevels of turbulence with very short mixing paths. None of these characteristics have been shown to exist in the Vulcanus units. Therefore, it is our opinion that if the mixing in the burners does not approach 100% efficiency, 99.9% destruction efficiency cannot be achieved.

4. The comparison of incineration times of the two proposed systems (22 - 26 days for the Vulcanus vs. 200 days for the land-sited system on Johnston Island) is technically accurate, but misleading from a total-time-required aspect. In order to realistically compare the two options for a time-and-facility cost, the following considerations must be incorporated into the analysis:

   (a) The land-based system can be fabricated at the contractor's plant and shipped in easily assembled modules. Fabrication and installation time of a SUE liquid incineration system on Johnston Island would be equivalent to availability of the Vulcanus.

   (b) A SUE burner system consisting of 10 burner cans equivalent to the land-based Option 2 system would require a small portable 2500-gallon feed tank which would be continuously charged by the drum-emptying facility (1 drum/5 minutes = 12 drums/hour X 55 gallons = 600 gallons/hour). Such a 10-can SUE® burner system would consume the Orange Herbicide at a rate of 600 gallons/hour. System capacity can be increased by adding additional 12-inch-diameter SUE burner modules which incinerate the herbicide at a rate of 60 gallons/hour each.

   (c) Appendix I 4.a. and Part II E. indicate that all drum emptying will be conducted on Johnston Island. Drums would be shipped from Gulfport to Johnston Island via rail and ship. This implies that the Vulcanus would steam to Johnston Island, berth, load 925,493 gallons of Orange Herbicide, and then steam to the burn area for incineration at sea. No time estimate for this operation is included.

   (d) No POL storage tanks approaching 1,000,000-gallons capacity are shown on Johnston Island. In order to obtain efficient utilization of the Vulcanus incineration capacity, 950,000 gallons of Orange Herbicide would have to be available for loading when the ship berthed. At the rate of 12 drums/hour (660 gallons) it would take 60 working days (24 hours per day) to fill the 1,000,000-gallon tank to the required 950,000 gallons.

At the stated rate, the Vulcanus can incinerate its complete capacity of 925,493 gallons in 8.6 days. Allowing 3 days from its berth at Johnston Island to the incineration area and the same time to return to berth, the total voyage would take 15 days. Thus, the ship would either sit idle for 45 days or cycle to an alternate assignment.

(e) The cost, time, and environmental impact of building a 1,000,000-gallon tank on Johnston Island has not been addressed.

(f) If the drum-emptying operation is to be performed in Mississippi, a separate impact statement should be prepared or the subject impact statement expanded to include this additional operation.

(g) Use of a portion of the existing POL storage tanks on Johnston Island would provide a tank capacity of approximately 50,000 gallons (the assumption is made that two 25,000-gallon diesel tanks would be made available; the remaining tanks would be required for normal operations). Therefore, the Vulcanus would have to stay in port 55 days to take on a complete load. Allowing 1/2 day to load each 50,000 gallons (9 X 1/2 = 4.5 days), the total cycle time per voyage would be 74 days (4.5 + 3 + 3 + 8.6 + 55).

(925,493 gallons - 50,000 gallons available at start = 875,493 gallons

$$\frac{875{,}493 \text{ gallons}}{50{,}000 \text{ gallons/tank}} = 17.5 \text{ tanks}$$

$$\frac{50{,}000 \text{ gallons/tank}}{15{,}840 \text{ gallons/day}} = 3.16 \text{ days/tank}$$

3.16 days/tank X 17.5 tanks = 55 working days @ 24 hours/day)

In view of the above-mentioned facts, it appears that the time required for Option I and Option II is similar. If a 1,000,000-gallon tank were constructed, Option I would be approximately 180 days plus tank construction time plus tank flushing and flush fluid incineration time plus tank dismantling and removal. If an existing 50,000-gallon storage tank capacity is assumed, Option I becomes 220 days.

5. Part II D.1.C states that the cargo (Orange) can be discharged directly into the sea in the event that the safety of the Vulcanus and her crew is threatened. Discharge of 925,000 gallons of Herbicide Orange into the Johnston Island area, open tropical ocean, or long-range effects on the Hawaiian Islands is not considered or included in the "worst case" evaluations.

We appreciate the opportunity to review and comment on this Draft Environmental Impact Statement. We respectfully request copies of other comments when received and a copy of the final Impact Statement when it is released.

Very truly yours,

THE MARQUARDT COMPANY

R. J. Haas, General Manager
Environmental Systems Division

RESPONSE TO COMMENTS FROM THE MARQUARDT COMPANY LETTER (21 Jun 74)

1. (Paragraph 1 TMC Ltr) The revised draft environmental statement did not state that the SUE® incinerator is a conventional incinerator. The flame and fuel/air characteristics of the SUE® system are felt to be very important in the acquisition of data on Orange combustion from which judgments can be made concerning overall requirements for efficient combustion. Undoubtedly such a judgment can be made with better validity than had another specialized incinerator system such as molten salt, fluidized bed, or a system which utilizes pure oxygen as the oxidizer been selected for the test incineration. It is noted the Air Force initially intended to perform a test burn in a conventional incinerator but opted for the SUE® when plans for the conventional incinerator could not be concluded (see Part II C.1.).

2. (Paragraph 2 TMC Ltr) Neither the Vulcanus nor any other incinerator vessel has been used for the destruction of Orange and its TCDD contents. Some information on the incineration of chlorinated hydrocarbons on incinerator ships has been submitted to the Air Force (see Appendix N). This information reports incinerator efficiencies greater than 99.9% and attest to the negligible short term environmental impact associated with incineration at sea. Information from Rocky Mountain Arsenal also reports a high efficiency of destruction of mustard agent, 99.9% (see Part V.A.2.).

3. (Paragraph 3 TMC Ltr) The Marquardt Company has taken exception to the following statement on page 15 of the revised draft environmental statement: "A comparison of incineration characteristics of the 'Vulcanus' versus those known to be acceptable based on the data presented in Appendices D and E indicated that Orange herbicide can be successfully incinerated on board the 'Vulcanus'." The company's position is stated in the following quote from paragraph 3 of their letter: "Data from one type of combustion system cannot be assumed to apply to a different type or size combustion system without extensive testing to validate the assumption." There is no basic disagreement with this statement as regards the direct extrapolation of data. The question is --- can a judgment be made on the probable destruction of Orange herbicide via incineration with the data that is presently available? Such data includes five studies concerned with the combustion of Orange and the data on the incinerator ships and Rocky Mountain Arsenal. The Air Force's position is that such a judgment can be made in fact, this position was the underlying reason for the course of action which resulted in the test burn at the Marquardt Company. That is, the Marquardt test burn was designed to obtain data on overall incinerator operation/efficiency which could be used for contractural purposes (see Part II.C.1.).

4. (Paragraph 3 TMC Ltr) The following comments are concerned with the need for an efficient injection system and mixing in the incinerator. The Marquardt system was proven to be extremely efficient for both the poppet nozzle and the slot nozzle and for all fuel feed temperatures(viscosity). Table I-6, page E(I-13) and Table 2, page E-35 show that the relative pyrolysis efficiency is 99.99 percent for both Run I (poppet nozzle, Orange feed temperature 66-63°F, $W_f/W_a$ 0.086) and Run III (poppet Nozzle,

Orange feed temperature 92-90°F, $W_f/W_a$ 0.106). Run II was conducted under the same conditions as Run I except that the feed temperature was 98/96°F and had a relative pyrolysis efficiency of 99.98 percent. The shift to the slot nozzle allowed a higher fuel flow rate and higher efficiencies of 99.998-99.999 percent were attained. The flow rate increase is attributed to the hydraulic characteristics of the nozzle; the higher combustion efficiency is attributed to the greater efficiency of the slot nozzle as an injection system. The Marquardt system was extremely efficient for all test runs and the slot injection system was responsible for the highest destruction rate and efficiency. It is emphasized that the effiencies with the poppet nozzle were quite high and that as the Marquardt Company letter states "...the poppet nozzle/SUE® burner combination somewhat resembles the mixing process in most commercial incinerators." It is the Air Force's position that a properly engineered incinerator system which can operate under specified overall combustion conditions, and is equipped with a well designed injection system and a turbulent combustion space would be an acceptable incineration system.

5. (Paragraph 4 TMC Ltr) Both incineration at sea and on Johnston Island have been programmed to PERT Charts and the project times are not similar. The present plan for incineration at sea does not include the construction and use of large volume storage tanks. When the incinerator ship is loaded at Gulfport, railroad cars will be utilized to transfer the Orange (dedrummed) from NCBC to the dock. On Johnston Island aircraft refuelers will be utilized to transfer the Orange from a dedrumming facility to the ship. A dedrumming/loading rate of 1,000 drums per day is planned. These transfer systems are readily attainable for scheduling purposes, easily managed and controlled, and very satisfactory from an environmental impact standpoint. The activities conducted at both Mississippi and Johnston Island will be well planned and include complete environmental and industrial hygiene considerations.

6. (Paragraph 5 TMC Ltr) Information on possible environmental impact resulting from the jettisoning of the Orange cargo or sinkage of the incinerator ship has been included in Part III.C.5.a.

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