

M. Pimenton

AMRL-TR-69-116

AD 704176
1-1-70



STUDIES ON ENVIRONMENTAL POLLUTION BY MISSILE PROPELLANTS

FRANK N. DOST, DVM

CHIH H. WANG, Ph.D.

Oregon State University

JANUARY 1970

20060707006

STINFO COPY

This document has been approved for public
release and sale; its distribution is unlimited.

QH
545
M57
D6

AEROSPACE MEDICAL RESEARCH LABORATORY
AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

When US Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Federal Government agencies and their contractors registered with Defense Documentation Center (DDC) should direct requests for copies of this report to:

DDC
Cameron Station
Alexandria, Virginia 22314

Non-DDC users may purchase copies of this report from:

Chief, Storage and Dissemination Section
Clearinghouse for Federal Scientific & Technical Information (CFSTI)
Sills Building
5285 Port Royal Road
Springfield, Virginia 22151

Organizations and individuals receiving announcements or reports via the Aerospace Medical Research Laboratory automatic mailing lists should submit the addressograph plate stamp on the report envelope or refer to the code number when corresponding about change of address or cancellation.

Do not return this copy. Retain or destroy.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Radiation Center Oregon State University Corvallis, Oregon 97331		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE STUDIES ON ENVIRONMENTAL POLLUTION BY MISSILE PROPELLANTS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report 1 July 1967 - 30 June 1969			
5. AUTHOR(S) (First name, middle initial, last name) Frank N. Dost, DVM Chih H. Wang, Ph.D.			
6. REPORT DATE	7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 30	
8a. CONTRACT OR GRANT NO. F 33615-67-C-1750		9a. ORIGINATOR'S REPORT NUMBER(S) AMRL-TR-69-116	
b. PROJECT NO. 6302			
c. Task No. 630204		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Aerospace Medical Research Laboratories Aerospace Medical Division, Air Force Systems Command, Wright-Patterson AFB- Ohio	
13. ABSTRACT The effects of NF_3O on lower organisms have been surveyed. The gas causes minimum damage to plants when exposed for 30 minutes to concentrations as low as 5 ppm. Effects on goldfish maintained in aquaria under 1% NF_3O for 30 minutes were negligible; salmon were moderately sensitive. Microorganisms in soil were only slightly decreased in numbers by one hour of exposure by continuously tumbling soil particles through 1% NF_3O . Potentially useful decontamination reactions were studied. Interhalogens and N_2F_4 can probably be removed from the atmosphere by a mist of aqueous sodium bicarbonate solution. No reagent portable enough and sufficiently effective to remove OF_2 and NF_3O gas from the atmosphere was found. NF_3 is virtually non-reactive.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Trifluoramine oxide (NF_3O)						
AMOX						
Chlorine trifluoride (ClF_3)						
Chlorine pentafluoride (ClF_5)						
Oxygen difluoride (OF_2)						
Decontamination reactions						
Toxicity to microorganisms						
Toxicity to plants						
Toxicity to fish						

SUMMARY

The environmental effects of accidentally released NF_3O have been evaluated by exposing representative species of plants, fish, and microorganisms to the gas under conditions simulating those which might be expected in the field.

Microorganisms (*Agrobacterium radiobacter*, *Arthrobacter globiformis*, *Bacillus subtilis*, and *Pseudomonas fluorescens*) were exposed after inoculation on sterile soil which was then exposed in 100 gram lots to 1% NF_3O for 30 minutes. Only one of the four microorganisms observed showed evidence of decreased viability after exposure, and these effects were moderate.

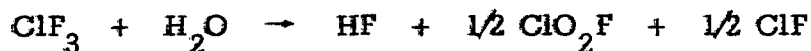
Goldfish (2.5 to 3.0 cm) and Chinook salmon (10 cm) were exposed in groups of ten in 3000 ml of water having a surface area of 635 cm^2 . One percent NF_3O in air was maintained in contact with the surface for 30 minutes; aeration was stopped during this period. Goldfish were not visibly affected by this treatment. Salmon survived 15 minutes of exposure, showing visible distress, but could not survive 30 minutes of contact with 1% NF_3O .

All ten day old plants (beans, corn, squash, peas and sudan grass) exposed to 50 ppm NF_3O for 30 minutes were moderately wilted two days after exposure. Beans were most seriously affected. Most bean leaves existing prior to exposure dropped from the petiole, but leaves emerging after treatment grew normally and total growth appeared not seriously impaired. Concentrations as low as 5 ppm caused detectable wilting of sudan grass 5 days after exposure but squash and corn were not visibly affected by 25 ppm NF_3O . Thirty day old plants suffered similar effects but changes appeared somewhat earlier than in younger plants.

Potentially useful mechanisms for decontamination of spilled inorganic fluorides were investigated. Other than activated charcoal no solid or aqueous reagent was found capable of reacting 1% OF_2 or 1% NF_3O in air except dithionite and the sulfides. Both reactions are slow and the reagents are costly. Activated charcoal reacts rapidly with the gases at these concentrations, but should be expected to induce explosions at higher levels of OF_2 and NF_3O .

The reactions of water with interhalogens were studied in some detail, using ClF_3 as a model compound. In the vapor state one mole of ClF_3 reacted quickly with 1 mole of water, apparently according to the reactions

suggested by Bougon et al, (ref. 9):



ClO_2F formed in this reaction reacted somewhat more slowly in the presence of water and in the absence of ClF_3 , to form ClO_2 and additional HF. Under some conditions either liquid or vapor phase reactions may produce small and varying amounts of ClO_3F . Because of the preferential reaction of ClF_3 with water a ClF_3 cloud should therefore be expected to contain principally ClF_3 and ClO_3F with minimum amounts of ClO_2 until ClF_3 has been exhausted. When ClF_3 contacts great excesses of water, ClO_2F quickly hydrolyzes to various ClO_x^- anions, Cl_2 , ClO_2 and HF.

The biological effects of the various hydrolysis products of ClF_3 , excepting ClO_2F were briefly evaluated. ClO_3F (20 ppm for 2 hours) causes slight leaf curling and uneven pigmentation of bean plants. 2000 ppm for one hour causes severe dehydration, 10,000 ppm caused immediate bronzing of all leaves.

In mammals ClO_3F causes methemoglobin formation. Our estimates of lethality indicated that exposures of 5000 ppm for 15 minutes or 2000 ppm for 40 minutes are 100% lethal. ClO_3F is therefore much less toxic than ClF_3 (ref. 8) and in view of this and the small amount produced from ClF_3 , it probably contributes little to ClF_3 intoxication.

Estimates of ClO_2 toxicity in rats indicate that if ClO_2 is in fact formed in the alveolar space it may contribute significantly to the toxicity of ClF_3 in mammals. In solution it is destructive enough to cause the entire non-acidic toxic effect of ClF_3 upon fish, even though in ClO_2 formation in excess water accounts for only 4% of all introduced chlorine.

The precise extent of the contribution of HF to toxicity of ClF_3 in the rat is not readily assessed because of the limited data available on acute HF toxicity. However, it is clear that HF toxicity is such that it is capable of accounting for much of the toxicity of ClF_3 . These assessments of the concurrent effects of HF and ClO_2 are not incompatible since the acidic and oxidizing components of ClF_3 toxicity to fish were found not to be additive (ref. 6).

The remaining potentially destructive component, Cl_2 , is probably not formed in significant amounts when ClF_3 reacts with water vapor, but it should occur in the decontamination with liquid water or when ClF_3 is dissolved in pools or streams. As such the Cl_2 is also sufficiently lethal to cause the toxicity of ClF_3 to fish.

FOREWORD

This study was initiated by the Biomedical Laboratory of the Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was performed in support of Project 6302, "Toxic Hazards of Propellants and Materials," Task 630204, "Environmental Pollution," under Contract No. F 33615-67-C-1750, with the Science Research Institute, Oregon State University, Corvallis, Oregon. Dr. C. H. Wang was the Principal Investigator for the Oregon State University. Dr. S. A. London, Chief of the Chemical Hazards Branch, Toxic Hazards Division, was the contract monitor for Aerospace Medical Research Laboratories. Research was initiated July 1, 1967 and completed July 31, 1969.

The technical assistance of Thurman Cooper, Vernon Smith and Mrs. Carol Wehr was essential to the conduct of this work.

This technical report has been reviewed and is approved.

C. H. KRATOCHVIL, Colonel, USAF, MC
Commander
Aerospace Medical Research Laboratory

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I Introduction	1
II Methods	4
III Results and Discussion	14
IV Conclusions	33
References	35

SECTION I

INTRODUCTION

Trifluoramine oxide (NF_3O), known also as AMOX, is a prospective oxidizer for spacecraft propulsion. For such an application large quantities must be provided at the launch site, presenting potential local toxic and pollutant hazards in the event of spillage or accidental destruction of a vehicle or test system. Hazards are also associated with production and transport of the agent. In each situation, intoxication of humans and livestock, pollution of various components of the environment, and reduction of crop productivity are possible consequences of accidental release of NF_3O .

The biological effects of NF_3O have so far been the subject of only one study, in which the median lethal concentration (LC_{50}) for rats exposed for 4 hours was found to be 24.2 parts per million (ppm) (ref. 1). The LC_{50} for mice under similar conditions was approximately 18 ppm. For 15 minute exposures of rats the LC_{50} was found to be between 200 and 240 ppm. Estimates made in our own laboratory also suggest toxicity of this magnitude. No studies of other test organisms have been made.

NF_3O was first synthesized by Fox et al (ref. 2). The compound was found to form stable, apparently ionic, complexes with AsF_5 and SbF_5 . Although a strong oxidizing agent in some circumstances, NF_3O was found to resist hydrolysis and attack by oxygen, even at elevated temperatures. Hydrolysis is sometimes accelerated by foreign substances, however (W. B. Fox, personal communication). NF_3O has also been found by Bartlett, et al (ref. 3) to be a secondary product of the reaction of osmium and platinum fluorides with nitric oxide. The same group has also examined the properties of the compound (ref. 4).

The structure of the molecule is tetrahedral, according to nuclear magnetic resonance (NMR) and infrared spectral data (ref. 2). The NMR spectra in the above studies indicate that the fluorine atoms are equivalent and are symmetrically bound to nitrogen. We have made the compound available to Hedberg and his associates at Oregon State University, who have studied it by X-ray diffraction analysis. They also find that the structure is a nearly regular tetrahedron. The N-F bonds have been tentatively assigned a distance of 1.45 Å and the F-N-F bond angle has been found to be 100° . The N = O bond distance is 1.15 Å, which is the length normally expected of a double bond, contrary to that found in trimethylamine oxide (K. W. Hedberg, personal communication). Hedberg has also commented that the molecule is unusual because nitrogen seldom has four-fold coordination in the gas phase.

The present investigation had two objectives. The first was determination of the effects of NF_3O upon plants, microorganisms, and aquatic species under experimental conditions. These observations were intended to provide an estimate of the agricultural and resource damage that might result from release of single large amounts of NF_3O into the atmosphere. Our preliminary findings suggest that NF_3O will have little effect on water-living organisms or microorganisms in soil, but may be expected to cause damage to plant life.

The second objective of this research has been investigation of methods by which the damage caused by inorganic fluoride oxidizing agents may be minimized or prevented. In approaching this problem, several assumptions have been made: (1) These agents probably will not be widely deployed in the near future, but will be used instead at a limited number of launch sites devoted to space exploration and research. (2) Such installations may therefore be located for operational rather than strategic advantage, allowing the establishment of downwind or downrange dilution areas. Economic loss or toxic hazard may then in part be easily avoided by total non-use of the land. (3) In such a situation the over-riding problem is protection of on-site personnel against toxic volatile material at high atmospheric concentration. As an extension of the latter problem, the potential for accidental loss of inorganic fluoride oxidizing agents during transport requires that protection of persons near an accident site also be devised.

This protection might theoretically be achieved by measures ranging from totally self-contained environments for all personnel to very rapid chemical decontamination systems. The latter concept is desirable in some respects but probably cannot be implemented, since any reaction employed must be almost instantaneous while avoiding production of excessive heat and toxic by-products. Such ideal performance is thermodynamically unlikely. A decontamination system must also avoid the risk of inducing uncontrolled reaction of free oxidizer with combustible fuels that may be in the area. The decontaminating reagent used must be in a form which can be transported or projected into the contaminated area by fixed or mobile equipment at a controlled rate and with a specified surface area, to allow control of the reaction rate. The latter requirements can probably be achieved only with an aqueous system.

These considerations place severe restrictions on use of procedures employing most of the potentially applicable decontamination reactions which were studied. For example, we have found that dry activated carbon rapidly adsorbs and/or reacts with both NF_3O and OF_2 , but control of delivery rate, and in turn the rate and temperature of the process would be exceedingly difficult; explosion or fire would be a probable consequence of this treatment. A further danger of solid decontaminants lies in the

adsorption of toxic agents without reaction, to be released later into the environment. Other possible reactions leave products potentially as toxic as the original agent.

Our investigation of NF_3O and OF_2 decontamination emphasized reactions of various reducing compounds in aqueous solution. In qualitative studies, the oxidizing agents were found to react with difficulty in aqueous systems and our present assessment suggests that chemical decontamination of OF_2 and NF_3O in an acceptable period of time may be impossible.

In comparison, the interhalogens present a more hopeful case. Our previous work with fish and microorganisms (ref. 6) suggested that a buffered aqueous solution with reducing capability might destroy interhalogens upon contact. These reactions appear to be suitable, and definition of the products of these reactions has been attempted in order that the biological consequences of decontamination could also be examined. These studies, in which ClF_3 served as the model compound, have produced novel methods for study of vapor phase reactions of interhalogens and water, and have provided an estimate of the nature and amounts of products to be expected in an interhalogen contaminated environment.

SECTION II

METHODS

Biological Effects

The methods used in the study of the biological effects of NF_3O have been adapted directly from those previously described for use with other fluoride-containing oxidizing agents (ref. 5,6). However, since NF_3O is relatively non-reactive, it has not been necessary to maintain the high flow and chamber turnover rates required when working with the interhalogens and N_2F_4 .

NF_3O effects upon plants were examined in Phaseolus vulgaris (beans), Zea mays (corn), Cucurbita sp. (squash), Pisum sativum (peas), and Sorghum vulgare sudanense (sudan grass). These species were exposed for 30 minutes to dynamic atmospheres of 10, 25, and 50 ppm NF_3O , 10 days and 30 days after planting, under preparation and exposure procedures reported previously (ref. 5,6). The younger plants were also subjected to atmospheres of 5 ppm. As in the previous experiments a polyethylene glove bag (Instruments for Research and Industry, Cheltenham, Pennsylvania) was used as an exposure chamber.

Treatment of seeds with NF_3O was carried out under procedures previously described (ref. 5).

Because of its low boiling point and relative insolubility in water, NF_3O was expected to have little effect on fish or soil microorganisms, paralleling the findings with OF_2 and NF_3 (ref. 6). These organisms were therefore studied under simulated field conditions in which a constant dynamic concentration of 1% NF_3O in air was maintained over the surface of the water or soil serving as a medium.

Goldfish (Carassius auratus) 2.5 - 3.0 cm long were obtained from the Santiam aquarium in Brownsville, Oregon and Chinook salmon (Onchorhynchus tshawytscha Walbaum) 10 cm in length were obtained through courtesy of the Oregon Fish Commission. Because of the limited effect on these species no others were examined. The fish were maintained in 3000 ml of water with an exposed surface area of 635 sq. cm.

Methods for preparation of soil, inoculation of organisms and for determining the microbial population of soils have been described previously (ref.6). The species employed were Agrobacterium radiobacter, Arthrobacter globiformis, Bacillus subtilis, and Pseudomonas fluorescens.

Samples of inoculated dry soil (100 gm) were spread evenly in Petri dishes, under a sterile transfer hood. The dishes were covered and moved into a collapsed polyethylene glove bag which served as an exposure chamber. When the chamber was inflated with 1% NF_3O , the Petri covers were removed for 30 minutes, then replaced. Dishes were immediately removed for suspension in sterile water and subsequent plating. The initial experiments were designed to determine whether significant change was caused by NF_3O gas. In the absence of a major lethal effect, more detailed assays were not made.

General Methods for Study of Decontamination Reactions

Two general procedures have been followed, both of which depend upon direct infrared measurement of the toxic agent in the gas phase before and after reaction. Other analyses for study of products of the reactions will be described below. In the first group of procedures, reactions under static conditions in terms of changing concentrations of the parent compound and/or its products were observed directly within the infrared cell. The general methods of observing reactions and concentration changes in the gas phase by use of infrared spectrometry have been described (ref. 7, 8). A Beckman IR-5A Spectrophotometer (Beckman Instruments, Fullerton, California) was used throughout. The gas cell usually employed was machined from Teflon with a 10 cm optical path and was fitted with silver chloride windows (Harshaw Chemical Company, Cleveland, Ohio).

To prepare for the reaction, a known concentration of the gas under study was established in the infrared cell in one of three ways:

1. A small known volume of the agent was injected directly into the cell containing a nitrogen or air atmosphere.
2. A gas mixture was generated according to the measured mass flow rates of the diluent and the toxic agents, and passed through the gas cell.
3. The desired concentrations of gases were approximated in the cell by either method 1 or 2 and then determined more precisely according to predetermined molar absorption data for the agent and the cell employed.

When a gas mixture was prepared by one of these methods, the inlet and outlet valves of the infrared cell were closed until a known amount of the desired reagent was injected as liquid or vapor. When significantly large volumes of gas such as water vapor in air or nitrogen were to be added to the oxidizing agent, the dilution was determined in advance by an identical injection of an inert gas to establish the true zero time con-

centration of the agent. After the reagents were added, the time course of the reaction was followed by monitoring absorption at selected wave lengths. Optical densities observed at the appropriate wave lengths were monitored on a strip chart recorder.

The other general procedure utilized reactions carried out remotely from the infrared measurement cell. Three variations have been used:

1. The reaction mixture was confined in a separate vessel, either to obtain a larger reaction volume or because the reaction demanded special structural features. Small, identical volume samples were then withdrawn periodically after the reaction was started for injection into the gas cell, and changes in concentration were plotted with respect to time. This procedure requires that the initial concentration of the known components in the reaction be quite high in order that the small samples transferred can provide sufficient infrared absorbance. Depending upon the reactivity of the agent in question, transfer to the analytical cell may be by a glass or a polypropylene-neoprene syringe, or by timed transfer with a low volume metering pump.

2. The reaction mixture was continuously recycled through the reaction vessel and the infrared cell. This procedure was especially useful in simulation of field problems, since very large volume systems could be studied. In most cases the reaction vessel was a 61 liter polyethylene tank, and its atmosphere was circulated through the infrared cell and returned by a peristaltic pump with Tygon tubing. Because the configuration of the IR cell precludes proper measurement at flow rates greater than 3 liters per minute, reaction rates cannot be measured precisely in this system. It was especially useful in testing delivery forms of decontaminants, and for observing the diffusion of decontaminant and oxidizing agents.

The delay in observing a change after introduction of a reagent at a known distance from the sampling point is a useful measure of the progress of a decontamination reaction through a toxic atmosphere. If the pumping rate is low, the flow into the reaction vessel does not appreciably perturb the contained atmosphere.

This device was most useful in evaluating solid decontaminants in powder form. Such tests were conducted by first establishing an experimental atmosphere, then injecting the decontaminant into the chamber by pressure from a loosely stoppered tube, or by dropping it from within the chamber from a polyethylene bag opened by a rip wire.

3. The reagents were continuously mixed and passed through the reaction vessel, and the products were then passed through the infrared cell. This procedure has been very effective for judging the effect of

aqueous solutions of decontaminant agents on interhalogens, using equipment described previously (ref. 5) which had been designed for generating solutions of inorganic fluoride oxidizing agents. As an example, an atmosphere containing 1% BrF_5 in nitrogen was passed through the 3.6 liter chamber and through the infrared gas cell at a rate of one liter per minute. When the optical density and therefore the concentration of this mixture reached a steady state, a solution of 1 M sodium bicarbonate was injected into the chamber at a rate of 60 milliliters per minute. These conditions represent 0.45 mmole BrF_5 , 0.60 mmole of sodium bicarbonate and more than three moles of water delivered per minute. The spray configuration was fan-shaped, and droplet size was very small, produced by a fine mist nozzle at a pressure of 40 psi.

This method was also particularly useful in the study of moderately fast reactions with water vapor which can be transported in measurable concentration in nitrogen or other gas. Adjustment of the respective mass flow rates of water-laden gas and the other reactant, usually an interhalogen, regulates their molar ratios to the requirements of the experiment. The reaction vessel may be simply a "T" tube fitting or the infrared cell itself.

Reaction time following mixing can be varied by changing the length of the tubing between the mixing point and the infrared cell, and the time between mixing and observation can be determined as a function of tubing cross section and total flow rate. A major advantage of this procedure is that a measurable steady state condition can be achieved since the rate of introduction of agents is constant. Reactions with a half-time of several seconds can be observed at almost any point in time by changing the length of the transfer plumbing between the mixing chamber and the infrared cell. A further advantage is that once a steady state is reached other treatment may be interposed and its effects on the equilibrium observed directly. A detailed description of the use of this procedure in the study of interhalogens and water vapor follows.

Vapor Phase Reaction of Interhalogens and Water

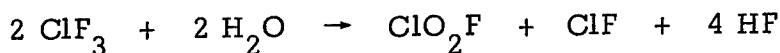
Prepurified nitrogen was saturated with water by bubbling the gas through a fine sparger into triply distilled water. The water content of saturated and nominally dry prepurified nitrogen was established experimentally by passing it through a two-step magnesium perchlorate drying column at a known and constant flow rate, then determining by weight the amount of water accumulated by the drying agent per unit volume of nitrogen. Three determinations of water-saturated nitrogen provided values of 20.4, 19.0 and 20.0 μg water/ml N_2 at one atmosphere and 25° (average 19.8 μg

or 1.1 $\mu\text{mole/ml}$ of N_2). Our sample of prepurified nitrogen as it was delivered from the tank contained 0.48 μg or 0.027 μmoles water per ml under the same conditions.

Since the rate of delivery of water and of interhalogen gas diluted with nitrogen to the reaction mixture could be controlled, the initial molar ratio of the reactants was readily computed. Infrared spectral observation of the parent interhalogen and its products provides the best evaluation with respect to water, under the assumption that water vapor could be admitted in known amounts, and that any amount of water up to an equi-molar concentration would react completely. In the case of ClF_3 , water reacts preferentially with ClF_3 rather than its products, which simplifies the measurement.

Reaction of ClF_3 with Water

The reaction:

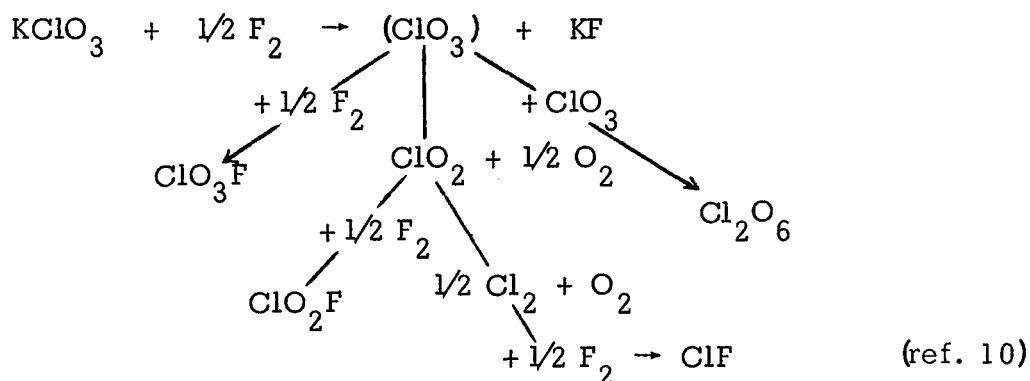


has been presented (ref. 9) as a description of the reaction of ClF_3 with water. Data obtained in our experiments with water vapor indicate that this is essentially a correct suggestion, even when equi-molar amounts of water and ClF_3 are present. When confined in the infrared cell in the absence of water, the ClO_2F formed was shown to remain intact indefinitely. With added water, ClO_2F reacted at a moderate rate, leading to the expectation that this reaction could be observed directly, and at least semi-quantitatively (using the techniques described in the preceding paragraph) by mixing ClF_3 with a known fractional molar excess of water vapor. The feasibility of this simple system depended principally upon the high relative rate of the initial reaction with ClF_3 , and the much slower subsequent reaction of ClO_2F .

Perchloryl Fluoride (ClO_3F) Synthesis

ClO_3F was synthesized after the method suggested by Engelbrecht and Atzwanger (ref. 10) in which potassium chlorate was reacted directly with molecular fluorine. The reaction was carried out in a Teflon column of 3.8 cm (1 1/2") ID and 1.3 cm (1/2") wall thickness, 30.5 cm (12") long. The column was closed with Teflon plugs drilled to permit insertion of thick wall 1/4" Teflon tubing. The column was packed with crystals of KClO_3 and the reaction was initiated at room temperature by passing undiluted fluorine gas through the crystals. The reaction rate was controlled by regulation of fluorine input between 10 and 100 ml per minute. Flow

rates were measured by mass flow meters. The reaction scheme may be represented generally as:



The relative amounts of each product are a function of temperature and the degree of dilution of incoming fluorine. In our use about 40-45% of the mixture was ClO_3F . If the reaction is conducted at lower temperatures, ClO_3F yield will be higher and OF_2 may appear among the reaction products (ref. 11).

The products other than ClO_3F and oxygen were removed by bubbling the gas stream through an alkaline trap containing 10% sodium hydroxide and 5% $\text{Na}_2\text{S}_2\text{O}_3$. The trapping vessel was constructed of polyethylene and filled with polystyrene chips to increase surface contact. The apparatus is illustrated schematically in Figure 1.

The identity of ClO_3F was verified by comparison of infrared absorption spectra at 2-16 microns with spectra established by Engelbrecht and Atzwanger (ref. 10) and by Lide and Mann (ref. 12).

The ClO_3F obtained with this preparation was intended for qualitative study only; for convenience, a modest amount of oxygen was allowed to remain after removal of all other contaminants. Heat capacity data for ClO_3F is not available so the relative mass flow characteristics of both gases could not be used to estimate the dilution more closely. However, by timing passage of the product mixture through the flow meter into a constant head displacement vessel, and assuming heat capacity to be similar to that of ClF_3 , it appeared that dilution was minimal.

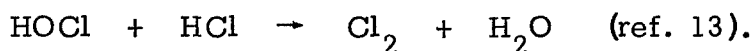
Synthesis of ClO_2

There is a variety of procedures for industrial production of ClO_2 . In most cases, moderate amounts of free chlorine are formed and are acceptable in the intended use of the agent. The ClO_2 synthesis for these experiments was based on a laboratory procedure described by Daniels

and Whitehead (ref. 13) that results in only a small amount of chlorine contamination. The basic reaction is:



The chlorine required for the reaction was produced in the system according to the equilibrium:



The starting material was produced by acidification of NaClO_2 . It has been shown that if HClO_2 is in excess of Cl_2 to the extent of 2 or more to 1, the Cl_2 contamination will be restricted to 0.1% or less (ref. 14).

In the specific procedure we have employed, a stream containing 0.2 M NaClO_2 and 0.05 M $\text{Ca}(\text{OCl})_2$ was mixed at a constant rate with a stream of concentrated HCl . A proportioning pump (Technicon Corp., Tarrytown, New York) delivered HCl at 0.8 ml per minute and the NaClO_2 - $\text{Ca}(\text{OCl})_2$ mixture at 2.84 ml per minute.

The generator unit was constructed from a polyethylene flask with necessary tubing heat-bonded in place (Figure 2).

Under the conditions of our experiments, ClO_2 was produced at 8400 parts per million in a nitrogen flow of 1 liter/min for periods up to 8 hours with no discernible fluctuation in concentration.

The identity of ClO_2 was confirmed by comparison of its infrared and ultraviolet absorption spectra with published infrared (ref. 15) and ultraviolet (ref. 16) spectra.

Measurement of Oxidizing Species in Aqueous ClF_3 Solution

The nature and quantity of the products of ClF_3 hydrolysis in great excesses of water were determined by the procedures outlined by White (ref. 17). In essence these are:

(1) The species responsible for the total oxidizing capacity of the solution (Cl_2 , ClO_2 , ClO^- , ClO_2^- , ClO_3^-) were reacted with KI , and the iodine liberated was titrated with 0.1 N sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$).

(2) Hypochlorite (ClO^-) was measured after degassing the solution of Cl_2 and ClO_2 at neutral pH with nitrogen gas. A known amount of 0.1 N sodium arsenite was added in slight excess of the remaining oxidants, and the excess titrated with 0.1 N iodine solution.

(3) Chlorite (ClO_2^-) determination also requires removal of Cl_2

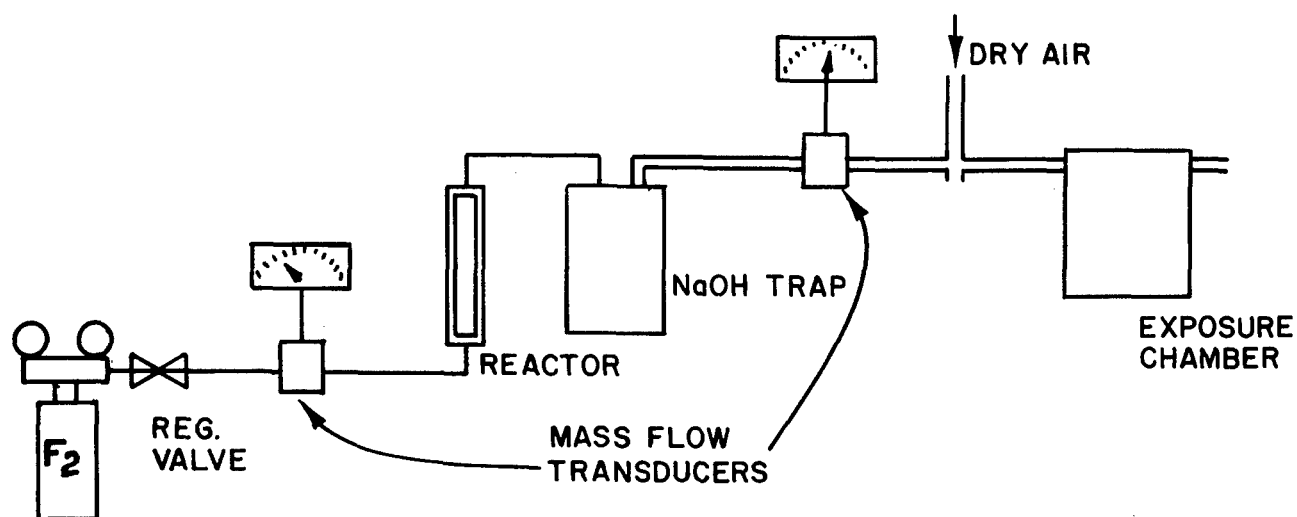


Figure 1 Apparatus for synthesis of ClO_3F

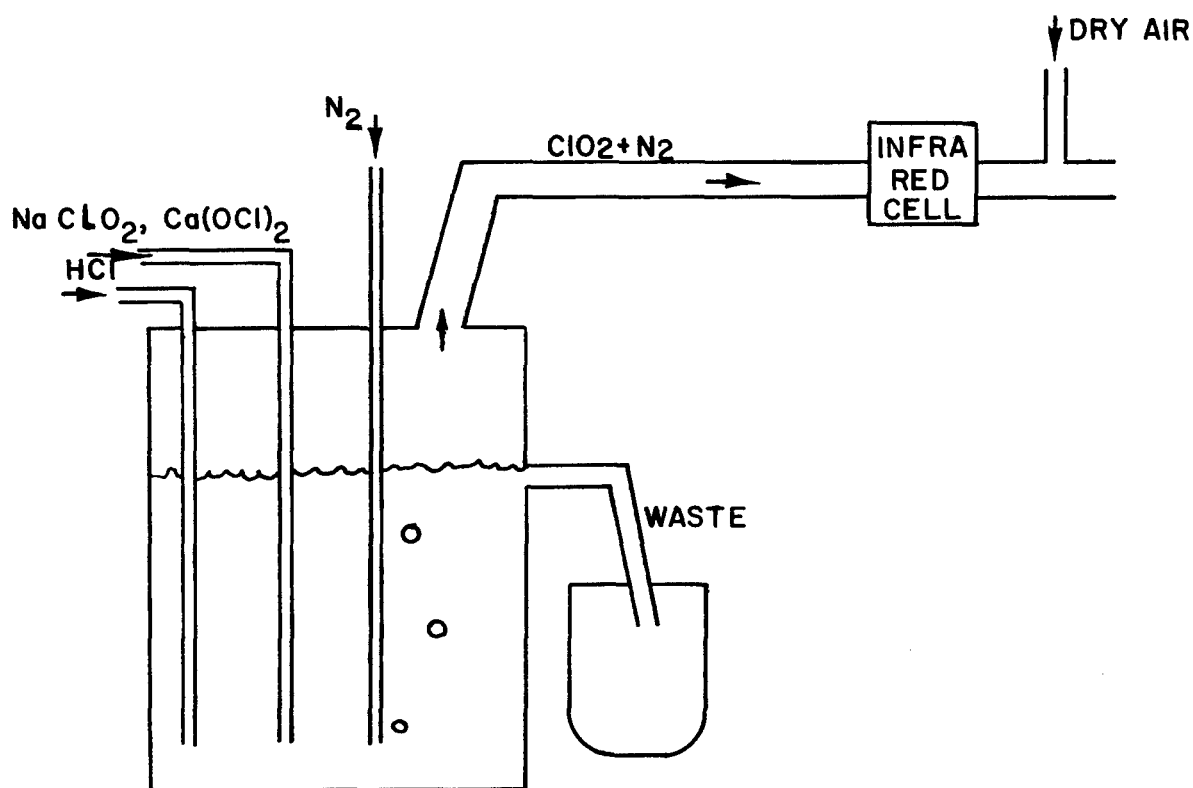


Figure 2 Apparatus for synthesis of ClO_2

and ClO_2 , then acidification to pH 3. Excess KI was added and liberated iodine titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

(4) Chlorine dioxide (ClO_2) and chlorine (Cl_2) were measured by repeating step 3 without removal of Cl_2 and ClO_2 by gas flushing. Cl_2 and ClO_2 were equal to the total less the sum of ClO_2^- and ClO^- . This step excluded ClO_3^- by lowering pH; ClO_3^- was calculated by subtracting step 4 step 1.

(5) Chlorine was measured by buffering the sample to pH 7, adding KI to slight excess, and titrating the liberated I_2 with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. This total included Cl_2 plus 20% of the ClO_2 present. Steps 4 and 5 provided the necessary information to calculate net Cl_2 and ClO_2 . The inclusion of 20% of the ClO_2 present in the Cl_2 determination was based upon an empirical finding by White (ref. 17) and by Kerenyi (ref. 18).

ClO_4^- has been reported to be a negligible product of ClO_2F degradation (ref. 19) and should arise from no other ClF_3 degradation product. It is therefore ignored for the purposes of these experiments. In addition, we have evaluated its toxicity and found that it does not exert appreciable effects upon fish. The amount of chloride present was not pertinent to the proportional inventory of oxidizing species. We have assayed chloride ion in other experiments and found that only limited amounts of the chlorine of ClF_3 emerge as chloride in solution.

Reaction of NF_3O and OF_2 with Solid Potential Decontaminants

The effects of solid reagents upon NF_3O and OF_2 were studied with the infrared cell located downstream of the reaction. One to five grams of activated carbon or molecular sieve (Linde 5-A or 13-A) of graded particle size was settled in a 10 millimeter polycarbonate column by gentle tapping. The diluted oxidant gas under study was then passed without treatment through the IR gas cell to measure the initial optical density. The stream was then switched through the reagent column prior to the gas cell and the difference measured. If the reaction or absorption by the column was slow relative to the rate of passage, the optical density decreased to a level corresponding to the concentration of contaminant remaining in the stream. When the reactive capability of the column was exhausted, the optical density slowly returned to the level observed prior to the experiment. If the column was highly effective, the active material was totally removed from the gas stream until the reactive or retention capacity of the column was reached.

Reactions of OF_2 and NF_3O with solids were often found to produce heat and may be temperature dependent. To permit measurement of thermal characteristics, a thermometer was incorporated into the column which was then heavily insulated. Heat production of reactions with solid decontamin-

ants was estimated by comparison of reaction temperatures with those induced by a standard heat source incorporated into an identical column. The standard figures were established during various rates of flushing by nitrogen. This information in turn allowed estimation of the heat liberated during passage of a reactive gas through the column. An ideal system would provide for feedback regulation and recording of flow rate to maintain constant temperature. However, our demands were qualitative and this refinement was not provided.

Activated charcoal (Matheson, Coleman & Bell, E. Rutherford, New Jersey) was prepared by sieving to 3 size grades of greater than 20 mesh, 20-34 mesh, and 34-60 mesh. Charcoal of powder consistency was used only by release into a static NF_3O atmosphere in the large reaction chamber.

Various molecular sieves were used as received in the form of extruded pellets, or were ground to coarse powder. Unrefined mineral faujasite was ground prior to use. These materials were also treated by soaking in 10% potassium iodide solution followed by drying, and by introducing increased calcium into the molecular sieves in exchange for sodium. These changes were undertaken in attempts to increase the activity of the materials.

SECTION III

RESULTS AND DISCUSSION

The Chemical Character of NF_3O as It May Relate to Biological Effect.

When undiluted NF_3O was confined for 48 hours over water or sodium hydroxide solutions, very small amounts of fluoride appeared in solution. It is presumed that this fluoride ion was derived from impurities since increased pH failed to cause appreciable change in the accumulation of fluoride in solution. NF_3O reactions in aqueous systems are possible if a reducing agent is present, however. Acidified solutions of potassium iodide react with NF_3O , but at a low rate. In a typical case, 15 mmoles KI was injected into a 4 L vessel containing 2% NF_3O gas, providing a molar ratio of $\text{NF}_3\text{O}/\text{KI} = 3.6/15$. The half-time of NF_3O disappearance, as observed by the decreasing infrared absorption of gas samples, was about one hour. Ultimately, the reaction was completed with the entire fluorine content of the NF_3O atmosphere accountable as fluoride ions in the solution. This modest reaction capability should not be ignored completely in exposures of aquatic organisms despite our evidence (below) that substantial exposure to the agent does not injure warm water fish and is only moderately toxic to salmon. If NF_3O were resistant to biological transport because of its insolubility, the systemic effects in mammals reported by Lee (ref. 1) could not easily take place.

Biological Effects of NF_3O

Of the variety of potential biological targets of NF_3O , plants seem to be the most suitable test organisms because of their clearly graded responses to differences in atmospheric concentration of intoxicants. During the first two days after exposure of 10 day old plants to 5 ppm NF_3O in air, there was no evidence of effects upon any of the plant species. By five days, minor wilting of sudan grass occurred, but other species remained unaffected. No further observable damage developed in 14 days.

The effects of 10 ppm NF_3O were also first seen in sudan grass two days after exposure. Tips were wilted and there was some degree of desiccation. By the fifth day a few white spots appeared on the early leaves of peas and bean plants, and the wilting of sudan grass persisted. Corn and squash were apparently unaffected. Little further change appeared in these plants.

Bean and pea plants and sudan grass that were exposed to an atmosphere of 25 ppm NF_3O were desiccated slightly at the end of exposure, but

there was no visible effect upon corn or squash. Five days after this exposure all plants exhibited a few discrete bleached areas. Some bean leaves dropped off leaving the petiole intact on the stem. Sudan grass was moderately wilted, and the tips of the corn leaves were slightly lighter in color than normal leaves.

All of the plants exposed to 50 ppm NF_3O were somewhat wilted two days after exposure. Beans were most seriously affected followed in order by peas, sudan grass, squash, and corn. By the fifth post-exposure day, most bean leaves that had emerged prior to the time of exposure dropped off the petiole, and the wilting and bleaching effects were markedly greater than seen at 25 ppm.

There was very little further change in the various species by the 7th day after exposure. In all cases leaves which emerged after exposure appeared normal in growth rate and morphology, and even in plants such as beans, which suffered severe leaf loss at 50 ppm, total growth was not drastically affected. It appears that beans especially should serve as an effective indicator of the degree of area exposure, because the effects were graded according to increased contact with the toxic agent.

Exposures of plants to 100 and 200 ppm NF_3O caused more extreme damage. The petioles of bean plants dropped from the stem along with the leaves at these levels of exposure. After two weeks, while control bean plants came into bloom and later formed pods, none of the bean plants exposed to 100 and 200 ppm NF_3O was capable of flowering. Other species exposed to 100 and 200 ppm NF_3O suffered similar damage to that caused at 50 ppm. While some growth retardation resulted at these levels, none of the species apparently suffered lethal damage and the new growth emerging after exposure appeared normal.

More mature plants (30 days old) were affected in almost the same pattern as younger plants. Generally, beans appeared somewhat more sensitive than other species, and 10 ppm NF_3O , the lowest concentration used in this series, caused minor curling of bean leaves. This effect appeared somewhat sooner after exposure in older plants. Although immature sudan grass was the most sensitive of the young plants to very low concentrations of NF_3O , effects on 30 day sudan grass were equivocal.

Effect of NF_3O upon Seed Germination

One hour of exposure to undiluted NF_3O markedly inhibits germination of all species tested except peas, but the survival of any seeds after such massive treatment indicates the limited effect of the gas. Exposures to 50% and 10% NF_3O had only minor effects. The samples of squash seeds used for exposures to 100% NF_3O were sterile and no conclusions could be

TABLE I
EFFECTS OF 60 MINUTE EXPOSURES OF SEEDS TO NF₃O
AT VARIOUS HIGH CONCENTRATIONS

	Control Seed Germination			Treated Seed Germination			<u>Treated %+</u> <u>Control %+</u>
	+	-	%+	+	-	%+	
100% NF ₃ O							
BEANS	225	175	56	70	330	18	0.33
CORN	370	30	93	75	325	19	0.20
PEAS	385	15	96	390	10	98	1.02
SUDAN GR	373	27	93	12	388	3	0.03
50% NF ₃ O							
BEANS	99	1	99	91	9	91	0.92
CORN	100	0	100	94	6	94	0.94
PEAS	98	2	98	94	6	94	0.96
SQUASH*	31	69	31	0	100	0	--
SUDAN GR	87	13	87	86	14	86	0.99
10% NF ₃ O							
BEANS	99	1	99	99	1	99	1.0
CORN	100	0	100	91	9	91	0.91
PEAS	98	2	98	96	4	96	0.98
SQUASH*	31	69	31	56	44	56	1.8
SUDAN GR	87	13	87	85	15	85	0.98

+ Number of seeds germinating

- Number failing to germinate

%+ Percent germinating

* Available seed populations defective. These results must be considered to be qualitative only.

made. A second supply of squash seeds used at lower exposures was also defective, although some limited qualitative information was gained (Table I).

NF_3O produces minimal effects upon goldfish and microorganisms. A concentration of 1% (10,000 ppm) NF_3O maintained over water for 30 minutes under the aquarium conditions specified had no readily apparent toxic effect on goldfish. The gas has measurable though limited toxicity to salmon during the period of gas-water contact. Exposure for 30 minutes to 1% NF_3O was 100% lethal to salmon; all died within 15 minutes of the end of the exposure. Contact for 15 minutes caused visible distress, but all affected fish survived. The fish were quiet during the first few minutes of exposure, then began breaking water in an attempt to leave the medium. Some sloughing of mucus occurred, but was minor compared to the amounts seen during ClF_3 or HF intoxication.

It must be remembered that aeration was stopped during exposure to maximize the effects of the gas. This procedure has more serious consequences for salmon than for warm water fish, and probably contributed to the toxicity of NF_3O to salmon. Even with the observed damage to salmon, we do not consider NF_3O a serious threat to fish. A concentration of 1% or above should not persist for extended periods; at worst, organisms in the immediate area of an accident may be affected. With diminishing concentration, any dissolved gas is lost to the atmosphere, and the water loses its toxicity. We find that water exposed to lethal concentrations of NF_3O is non-toxic to fish 30 minutes following contact. It seems doubtful, therefore, that NF_3O liberated into the atmosphere would significantly influence aquatic species.

Microorganisms in sterile soil were also not seriously affected by exposure to 1% NF_3O . A minor decrease in population of A. radiobacter as a result of NF_3O exposure may be inferred from our experiments (Table II), but the decrease could not be considered sufficient to cause more than transient interruption of soil microbial activity.

Decontamination of NF_3O and OF_2 ; Reaction with Activated Charcoal

NF_3O in air reacted very readily when passed through a column containing 1 gm activated charcoal (approximately 83 mmole carbon). At the highest concentration (4%) tested, NF_3O was removed completely during a period of 40 minutes when passed through the column at 800 ml per min. The observable concentration downstream from the reaction then rose slowly for an additional 15 minutes. Ignoring the latter period, this means that each mmole of carbon reacted with about 0.67 mmole NF_3O . The degree of adsorption without reaction was not established, but it was clear that extensive destruction of the agent took place, since the effluent gases from

TABLE II Effect of 1% (10,000 ppm) NF₃O in Air on Microorganisms Inoculated on Sterile Soil. Exposure Time--30 Minutes.

Series A

Organism	Dilution Level			
	10 ²	10 ³	10 ⁴	10 ⁵
	Percent Survival after Treatment			
Agrobacterium radiobacter	*	*	*	83
Bacillus subtilis	*	*	*	92
Pseudomonas fluorescens	*	*	*	100

Series B

Organism	Dilution Level			
	10 ⁴	10 ⁵	10 ⁶	10 ⁷
	Percent Survival after Treatment			
Agrobacterium radiobacter	*	70	46	
Arthrobacter globiformis	*	100	100	
Bacillus subtilis	*	*	*	54
Pseudomonas fluorescens	*	*	91	100

*Control and treated organisms too numerous to count

the column contained substantial amounts of NO_2 and CO_2 . NOF was detected as well, but we do not know whether this was split off intact in the degradation of NF_3O , or whether NF_3O decomposed with formation of the NF_2 radical, which was subsequently oxidized. In each of such experiments substantial heat was generated; the relative contribution of reaction by charcoal and thermally induced reaction or decomposition with or without carbon as a participant is not known.

NF_3O in larger static volumes was reacted rapidly with carbon particles projected as a cloud. When 50 gms (4.2 moles) of finely particulate activated charcoal were blown into the 6l liter reaction chamber containing 1% NF_3O , the atmosphere was completely altered in about 1 minute. The reaction with 10 grams of charcoal was slightly slower. No estimation of product distribution was attempted. In these experiments the molar ratio of carbon to NF_3O was very high, 420 to 2.7, and was probably responsible for the relatively rapid disappearance of NF_3O . It is possible that such a decontamination measure might be employed on the periphery of a contaminated area, but we believe that if activated carbon were placed in contact with higher concentrations of NF_3O , a severe reaction or explosion between the oxidizer and carbon might be propagated.

No further studies of reaction between NF_3O and carbon have been made because of the apparent unsuitability of the reaction for decontamination. Despite this opinion, if NF_3O is considered sufficiently useful as a propellant to justify major use, further chemical and engineering studies of the potential of carbon as a decontaminant should be made. The reactions of NF_3O and carbon appear to be intrinsically interesting, and if studied further may provide some insight into the behavior of the N-F linkage as it exists in NF_3 or N_2F_4 .

A similar series of experiments has been conducted with OF_2 , except that concentrations higher than 1% were not evaluated for reasons of safety. Activated charcoal reacts readily with OF_2 in the large volume chamber, or where the gas is passed through a charcoal column. The reaction generates substantial amounts of heat, but we have not established whether this originates in chemical reactions or adsorptive activity. A significant portion of the OF_2 treated in this manner can be recovered by elution from the charcoal column with nitrogen or air.

The use of activated carbon in response to area contamination with OF_2 is therefore even less suitable than when used for NF_3O decontamination. While carbon may ultimately be adaptable for immediate removal of OF_2 , the problem of subsequent continuous release of the intact gas into the atmosphere appears forbidding.

Decontamination of NF_3O and OF_2 ; Reaction with Reducing Agents in Aqueous Solution

Several reagents in aqueous solution have been evaluated as decontaminants of 1% NF_3O in the atmosphere:

Reagent		Concentration	Medium
Hypophosphite	$(\text{H}_2\text{PO}_2^-)$	1 M	2 N NaOH
Dithionite	$(\text{S}_2\text{O}_4^{2-})$	1 M	2 N NaOH
Sulfite	(SO_3^{2-})	1 M	2 N NaOH
Bisulfite	(HSO_3^-)	1 M	2 N NaOH
Hydroxylamine	(NH_2OH)	1 M	2 N NaOH
Sulfide	(S^{2-})	1 M	pH 4.5
Hydrogen Sulfide	(HS)	1 M	pH 4.5
Potassium Iodide	(KI)	1 M	pH 4.5
Potassium Iodide	(KI)	1 M	pH 3.0

Of this group, the sulfides and dithionite reacted most effectively, although neither was efficient. The former compounds are also quite toxic and therefore not suitable for decontamination. Dithionite is almost as reactive as the sulfides, and apparently produces no by-products of significant toxicity. Unfortunately, both reactions are quite slow.

Reactions of 1% OF_2 in air with a comparable group of prospective decontaminants have been studied in a similar manner:

Reagent		Concentration	Medium
Dithionite	$(\text{S}_2\text{O}_4^{2-})$	1 M	2 N NaOH
Sulfite	(SO_3^{2-})	1 M	2 N NaOH
Sulfide	(S^{2-})	1 M	pH 7
Sulfide	(S^{2-})	1 M	pH 4
Hydrogen Sulfide	(HS)	1 M	50% ethanol
Nitrite	(NO_2^-)	1 N	1N NaOH
Potassium Iodide	(KI)	1 N	pH 7
Sodium borohydride	(NaBH_4)	1.5 M	pH 8

003053

Again, dithionite was the only one of these reagents to show even limited promise, but the time required for reaction was quite long; preliminary study indicates that the half-time of the reaction of an excess of dithionite with 1% OF_2 exceeds 15 minutes.

It is recognized that the laboratory conditions under which these agents were experimentally used were in many cases prohibitive to field employment. In each case the conditions were deliberately adjusted to provide maximum potential for reaction under laboratory conditions, with the intent that promising reactions might be explored under conditions more nearly resembling those expected in the field. Such adjustments included the use of very fine sprays to maximize surface area, extension of reaction time, and recycling of the atmosphere through the solution.

These experiments suggest that a rapid chemical decontamination procedure for NF_3O and OF_2 is not feasible. There are other concepts that might be applied,³ but the engineering demanded may be formidable. As an example, high volume negative pressure ducting away from the facility may deserve consideration. Associated with such a system, a combustion reaction with fuel could be controlled in the same manner as are exhaust products of propellant test facilities. Even if this type of engineering were successfully applied at launch sites, application of the methods to spills arising in transport would probably be very difficult.

Regardless of the methodology employed in removing such materials as NF_3O and OF_2 , continuous personnel protection systems must be supplied. It is our belief that the acute tolerance for OF_2 is zero; at the concentration that may exist in the moments after an accident, a few seconds of exposure perhaps one inspiration, may be lethal.

Reactions Applicable to Decontamination of N_2F_4

We have demonstrated (ref. 7) that N_2F_4 reacts with water in the gas phase if oxygen is present, producing nitrogen dioxide and hydrogen fluoride. Discrete intermediates in the reaction sequence include nitrosyl fluoride and nitric oxide. The same study showed that the reaction would not proceed in the presence of oxygen or water alone. We have stored pure N_2F_4 over water in polyethylene vessels for several weeks and found no spectral evidence of reaction. Further, when N_2F_4 in nitrogen alone was passed through a fine spray of water to maximize surface contact, the gas did not react detectably.

In the overall reaction of N_2F_4 with water and oxygen, four moles of hydrogen fluoride will probably be formed per mole of N_2F_4 , and if the reaction is employed in decontamination this acid must be neutralized. The most suitable agent for this purpose is the bicarbonate ion, which is stable in storage and is useful in the decontamination of interhalogens as well.

While reactions that should be useful in the decontamination of N_2F_4 are readily accomplished in aqueous systems, the reaction of the gas with carbon was explored briefly. The reaction proceeds readily, with NOF , NO_2 and CO_2 appearing among the products. No attempts were made to quantitate this reaction system.

Decontamination of NF_3

The decontamination of accidentally released NF_3 was not considered a major problem because of its relatively low toxicity. Nevertheless, the effects of activated charcoal and several reducing agents in aqueous solution on gaseous NF_3 were observed, and none produced a detectable reaction.

Decontamination of Interhalogens

The known reactions of interhalogens with water suggest that simple spraying of large volumes of water in the form of a mist into an interhalogen laden atmosphere should effectively remove the compounds. The same treatment should effectively react with these chemicals if pooled in the liquid state. In fact, all published discussions on handling procedures for interhalogens emphasize the precaution of using water as a mist to slowly react and cool the spilled material. Washing of spilled interhalogens with bulk water may be expected to result in explosions. In view of the known acidity of interhalogen solutions (ref. 6), a buffering agent, most suitably bicarbonate, should also be included with the aqueous decontaminant. Since it is known that oxidizing components derived from the interhalogen are reduced on contact with soil (ref. 6), decontaminant solutions presumably need not include reducing agents. This is fortunate because the storage life of many reducing compounds is limited, whereas sodium bicarbonate can be maintained in solution indefinitely.

Experiments in which dynamic atmospheres of 1% ClF_3 (or BrF_5) were treated with a spray of sodium bicarbonate at rates providing a molar ratio of $\text{NaHCO}_3/\text{ClF}_3 = 60/45$ show that these interhalogens disappeared in 5 to 7 seconds after the spray was started. Because this rate of disappearance is less than can be accurately resolved by our observation system, an exact rate was not determined.

The reaction with ClF_5 was much slower. Only after raising the delivery rate of bicarbonate solution five-fold was it possible to completely destroy ClF_5 during the residence time of the gas in the reaction vessel. In terms of the relative time of disappearance of the absorption spectrum of ClF_5 , the reaction required at least 30 seconds for completion. Nonetheless, it is believed that this general method of decontamination is probably suitable for all interhalogens.

The injection of water alone as a spray into a static atmosphere of 1% ClF_3 or ClF_5 produced similar disappearance of the interhalogens, leaving residual water with a significant content of HF. ClF_3 was found to disappear within one minute after injection of a fine spray of 10 ml water or bicarbonate solution into the 6l L chamber, and ClF_5 disappeared in 7 minutes. When a solution of 2N KI was injected similarly, ClF_5 disappeared in about 2 minutes, although on a molar basis there was less KI than ClF_5 in the atmosphere. The molar excess of water to interhalogen in these experiments was about 20 fold.

Products of Interhalogen Reaction with Water and Their Biological Effect.

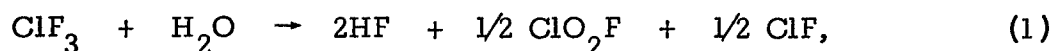
The products of any decontamination reaction must be considered potentially dangerous, and there was good reason to expect biological effect from degradation products, interhalogens. Previous studies of the effects of interhalogens on fish showed that the oxidizing degradation products in ClF_3 solutions were as lethal as the effect attributable to the acidity of the solution, and that some components of the solutions which were associated with lethality apparently disappeared when left open to the environment (ref. 6). A variety of postulated products of ClF_3 hydrolysis, principally chlorine-oxygen anions, were evaluated for toxicity during those studies, but none appeared to be associated with biological effect. ✓

In contrast with solutions of ClF_3 , the oxidizing products of ClF_5 hydrolysis were found to have a lower degree of lethality. BrF_5 solutions, which contained substantial oxidation potential, were found to be lethal only because of their acidity.

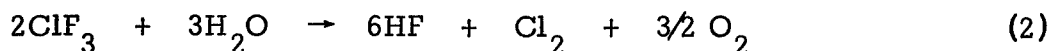
Because of these observations it was expected that decontamination of interhalogens, especially ClF_3 , with water would result in formation of volatile or dissolved products that might be toxic to personnel in the contact area. In uncontrolled exposure, these products should also be expected to form in the water-saturated respiratory gases of mammals and in the micro-climate of leafy plants. This potential danger has stimulated further investigation into the nature of interhalogen hydrolysis products and the biological consequences of their formation. In proceeding with these investigations ClF_3 was used as the model interhalogen for liquid and vapor phase reactions because of the greater toxicity of its oxidizing components in solution (ref. 6).

Reactions of ClF_3 with Water

The reaction of ClF_3 with water has been studied by Bougon et al (ref. 9), and while the reaction conditions were not precisely specified, these workers found that excess ClF_3 in the presence of water would react according to the following:



with subsequent formation of Cl_2 , O_2 and ClO_3F as well. If water was in excess, they observed a reaction which was suggested to be:



Small amounts of ClO_3F were also observed.

Our early observations of the products of ClF_3 dissolved directly in great excesses of water showed clearly, however, that large amounts of oxidizing species other than those specified in reaction 2 were present (ref. 6). In addition, a portion of this activity was found to volatilize from solution, leaving the solution with very little biological effect attributable to oxidizing species. It later became evident that a variety of ClO_2^x anions were represented in the species remaining in solution, and that none was toxic or volatile.

The description by Bougon et al (ref. 9) of reactions between ClF_3 and water to form ClO_2F and subsequently ClO_2 suggested that ClO_2 was the volatile toxic component of ClF_3 solutions. At that time, however, we did not succeed in identifying ClO_2 , primarily because our efforts were concentrated on determining general biological effects of ClF_3 solutions. We

did attempt to make a solution containing ClO_2 to test its general toxicity. Our preparation was not appreciably toxic, and the contribution of ClO_2 to the observed biological effect of ClF_3 solutions was discounted at that time. We have found only recently that the conditions then employed for ClO_2 synthesis may have been controlled incorrectly, resulting in little information of ClO_2 .

In seeking a suitable identity for the volatile toxic component of ClF_3 reaction with excess water, we obtained published infrared spectra of the various expected products, other than Cl_2 and HF . Some studies of ultra-violet absorption spectra were also obtained, and in this a source of confusion arose which required several months to resolve. We found that under some conditions the volatile products of ClF_3 hydrolysis included a compound with an infrared absorption spectrum characteristic of ClO_2 . When the products of the reaction were extracted with carbon tetrachloride either directly from aqueous solution, or from neutral gas passed through the solution, the ultraviolet absorption spectrum in no way matched the single published ultraviolet spectrum we had found (ref. 20). A good deal of effort was expended in establishing the nature of the discrepancy because of the supposed toxic potential of the product. Only recently we found in the German literature a paper published in 1936 (ref. 16) presenting ultraviolet spectral data on ClO_2 which precisely matched our data, resolving the issue. The source of the misleading spectrum (ref. 20) has not been defined; spectra of other compounds described in that paper match those seen in our work or in that of other investigators.

These various experiments and references provided an identification of at least ClO_2F and ClO_2 as expected chlorine-bearing products of ClF_3 hydrolysis. At this point, however, the scheme appeared applicable only in great excesses of water; because of potential reactions with atmospheric and respiratory water a more complete description was attempted.

Our first step in defining the system was to test equation 1 by reacting limited amounts of water vapor as it was mixed continuously with excess ClF_3 gas. In each experiment one mole of ClF_3 was found to react with one mole water (Table III) to yield a mixture of ClF_3 , ClO_2F and HF , with minor amounts of other products. ClO_2F was identified by its infrared absorption spectrum as compared with that published by Smith *et al* (ref. 21) and by Arvin and Aymonino (ref. 22). The initial reaction was very rapid; the gases were mixed as they entered the infrared cell at a combined flow rate of 315 ml per minute, and sufficient ClF_3 disappeared immediately to account for the entire available water supply. Excess ClF_3 and all products were found to persist at unchanged concentration when the interval between gas mixing and observation was increased or gas flow was stopped for prolonged observation of the static gas mixture. If equi-molar amounts of ClF_3 and water vapor were reacted, both components were

utilized completely. The stoichiometry of the reaction is such that concentrations of up to 2.5% ClF_3 (slightly more than 1 mmole/L) should be expected to react completely with saturated water vapor at 25°. If this is the case, no intact ClF_3 should be expected to reach the pulmonary surfaces unless a truly massive exposure is encountered.

TABLE III
Vapor Phase Reaction of Water with Excess ClF_3

Experiment	mMole ClF_3 excess	mMole ClF_3 reacted	mMole H_2O available
3	0.044	0.28	0.3
4	0.044	0.28	0.3
5	0.318	0.29	0.3
6	0.308	0.30	0.3
7	0.630	0.29	0.3
8	0.622	0.29	0.3

When water vapor was introduced faster than ClF_3 , the excess reacted with the ClO_2F formed initially in the apparent ratio of approximately 2 moles of ClO_2F to 1 mole water (Table IV). This ratio is based on the assumption that 1/2 mole of ClO_2F is available per mole of initially reacted ClF_3 according to reaction 1. The products detected in the infrared cell were ClO_2 and small amounts of ClO_3F . This reaction proceeds more slowly than that between water and ClF_3 , and it is possible that small amounts of other compounds present, such as ClF and ClF_3 , remove sufficient water to give ratios slightly lower than 2.

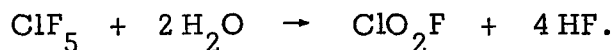
TABLE IV
Vapor Phase Reaction of Excess ClO_2F with Water

Experiment	A mMole ClO_2F reacted	B mMole Water available	A/B
9	0.158	0.085	1.86
10	0.104	0.059	1.76

The remaining significant primary product of ClF_3 vapor phase hydrolysis is HF. As ClF_3 gas contact water, 2 moles of HF should be formed per mole of water. Since the reaction is rapid, exposures to large amounts of ClF_3 will result in formation of somewhat more than 2 mmoles of HF per liter of respiratory ventilation, if maximum water saturation of respiratory gases may be assumed and if the reaction with tissue and surface water are ignored. Below 2.5% ClF_3 in air, the amount of HF formed will depend upon ClF_3 concentration.

Reactions of ClF_5 with Water Vapor

In what was apparently the first published description of ClF_5 reactions, Smith (ref. 23) found the compound to be relatively non-reactive with water, but Pilipovich et al (ref. 24) found more recently that ClF_5 was violently reactive with water in any form, forming ClO_2F according to the reaction:



The detailed procedures for observing these reactions were not presented in either paper.

When we mixed gaseous ClF_5 and water vapor under dynamic conditions, no reaction was detected even when the reaction period was extended for as long as 30 seconds. To further prolong the reactions, the infrared cell was used as a static reaction vessel, in which water vapor was mixed with 1.5% ClF_5 . The molar ratio of ClF_5 removed to water initially present was approximately 0.5, and was reproducible. We were unable to observe formation of the expected ClO_2F because the overall reaction proceeded very slowly to form silicon tetrafluoride (SiF_4) as a terminal product. The source of the silicon contaminant is unknown. No other infrared visible products appeared to provide clues as to whether SiF_4 originated as a reaction product of ClO_2F , HF or of the parent compound. The observed consumption ratio of approximately one mole ClF_5 to two moles water indicates, however, that the reaction did form ClO_2F and HF as suggested by Pilipovich (ref. 24).

Reactions of ClF_3 in the same system did not produce SiF_4 .

We have observed that when 1 - 2% ClF_5 was confined in polyethylene, it decreased in concentration with no corresponding increase in other infrared visible products. Pilipovich (ref. 24) found that ClF_5 would dissolve in Kel-F and Teflon, and we assume that a similar effect has occurred in polyethylene.

Because of the relatively limited immediate importance of the problem of ClF_5 hydrolysis, and the amount of preparation needed for a detailed analysis, no further study was made.

Biological Effects of ClF_3 Vapor-phase Hydrolysis Products: ClO_2F

All of the immediate and secondary products of vapor-phase ClF_3 hydrolysis (ClO_3F , ClO_2F , ClO_2 and HF) as well as the $\text{ClO}_2^\times$ anions which appear in reactions of ClF_3 in liquid water, must be considered as potential contributors to the toxicity of ClF_3 even though some occur in very small quantities. Of these, ClO_2F was arbitrarily considered to act as ClO_2 even though we have shown that its reaction with water vapor is slow enough that some ClO_2F originating with high ClF_3 exposures will probably reach the pulmonary surface. We assume that the water content of the membrane will quickly convert ClO_2F to ClO_2 , HF and $\text{ClO}_2^\times$ anions, since we have found that in great excesses of liquid water ClO_2F may not survive long enough to be detected. It is unfortunate that we were unable to proceed with a comparison of the effects of ClF_3 and ClO_2F . It may be speculated that exclusive of the influence of HF , ClO_2F may serve as a dessicant, diminishing pulmonary water. The consequent interference with membrane function may then result in failure of transport for both respiratory gases and water, and ultimately allowing raw ClF_3 gas into the lung. It is questionable whether a victim could survive long enough for this effect to occur.

Biological Effects of ClF_3 Vapor-phase Hydrolysis Products: ClO_3F

ClO_3F has been a compound of almost entirely academic interest, although there has been some consideration of its use as a propellant oxidizer (ref. 5), and its toxicity has apparently never been evaluated. The only allusion to the toxicity of ClO_3F that we have found appeared in a footnote to a discussion of its chemistry; when the reference given was examined, it did not mention ClO_3F . ClO_3F is quite stable (ref. 10). Our experiments suggest that it is soluble in water and that some will remain in aqueous solution even under reduced vapor pressure. The stability of ClO_3F suggests that it should be no more than moderately toxic, but in view of the toxicity of such relatively stable agents as OF_2 , it was necessary to determine whether even the small amounts to be found after ClF_3 hydrolysis might be biologically active.

Since the bean has proved to be an effective indicator of general plant toxicity, it was the only species used in this evaluation. The first plant exposures to ClO_3F were made at the very high concentration of 10,000 ppm (1%). The result was an immediate and complete bronzing of all leafy portions of the plant. We assume this effect to be an oxiditive reaction on chlorophyll. ClO_3F also exerts measurable toxic effects upon plants during less severe exposures:

ClO_3F in Air ppm	Exposure Period	Effect
2,000	1 hour	Leaves curled at edges, apparent severe dehydration
1,000	1 hour	Similar, less severe
200	2 hours	Some curling of leaves, uneven pigmentation
20	2 hours	Slight curling, limited but discernable areas of uneven pigmentation

As a comparison, ClF_3 has been shown to affect bean plants in exposures as low as 10 ppm for 15 minutes (ref. 6). On the basis of a time x concentration (ct) calculation, this level is several times lower than the lowest observed effective exposure to ClO_3F , and since ClO_3F concentration is low in a ClF_3 -water system, its effect almost certainly does not contribute appreciably to ClF_3 environmental toxicity. It is of interest, nonetheless, that as inert as ClO_3F is, it does attack plants, in contrast to NF_3 which, at a concentration of 1%, caused no detectable damage to plants during one hour exposures (ref. 6).

Toxicity of ClO_3F to fish was not evaluated.

ClO_3F is an active methemoglobin former in mammals, as is NF_3 , but it may have a more complex action. As the toxic concentration of NF_3 was lowered, the concentration-time factor required for lethal exposures was moderately increased, probably because of reduction of methemoglobin during exposure. Among other evidence, this suggests that the primary damage by NF_3 was limited to formation of methemoglobin. Rats intoxicated with ClO_3F , on the other hand, showed no evidence of an extended concentration-time index in the limited trials conducted. In contrast to NF_3 , which is lethal after 60 minutes of exposure to 10,000 ppm, animals exposed to 5,000 ppm ClO_3F died in 15 minutes ($5,000 \times 15 = 75,000$), those exposed to 2,000 ppm died in 40 minutes ($2,000 \times 40 = 80,000$). Animals exposed to 2,000 ppm for 25 minutes and 1,000 ppm for 60 minutes survived indefinitely. In previous work (ref. 8), we have examined ClF_3 intoxicated animals for MHb formation and in no case was an increase over normal levels found. This suggests that ClO_3F does not participate actively in mammalian intoxication by ClF_3 , a conclusion further supported by the fact that the lethal dose of ClF_3 , 800 ppm/15 minutes, is several times less than that of ClO_3F .

Biological Effects of ClF_3 Vapor-phase Hydrolysis Products: ClO_2

ClO_2 is volatile and disappears from aqueous solution readily if the vessel is left open to the atmosphere. It is active enough as an oxidant that it is widely used in industry, especially in paper production, as a bleaching and decolorizing agent. In spite of this industrial use of ClO_2 , its toxicology has only been explored to a limited extent. Dalhamn (ref. 26) found that a group of rats exposed for three minutes at three weekly intervals to respective concentrations of 3400, 1000, and 800 ppm ClO_2 exhibited decreased weight gain and moderate renal pathology. Exposures to 260 ppm ClO_2 for two hours caused nasal and conjunctival discharge and bleeding, and pulmonary edema. No estimate of lethality at this concentration was made. Gloemme and Lundgren (ref. 27) reported on a series of clinical exposures of humans, but could not document exposure duration, ClO_2 concentration, or the amount of chlorine in the atmosphere. Other reports which appear principally in industrially oriented literature fail to differentiate between the results of primary experiments and quoted work. Some of the latter has apparently been drawn from internal reports of industrial concerns and cannot be verified.

We have conducted range-finding experiments to estimate the lethality of ClO_2 to rats and fish. These studies show that ClO_2 may contribute significantly to the toxicity of ClF_3 in rats and that it is destructive enough to be responsible for the entire non-acidic toxic effect of ClF_3 upon fish (ref. 6).

It should be remembered that the proportion of ClF_3 converted to ClO_2 is greatly different in the vapor and liquid states. If ClF_3 is at low concentration in air, it may be expected to react with water vapor in such a way that much or all available chlorine is incorporated in ClO_2F , which then is converted to ClO_2 . The relative amounts of ClF_3 and available water vapor in the environment, including the respiratory gases or the microclimate of the leaves, will generally dictate the progress of the reaction. For example, a high concentration of ClF_3 will desiccate the atmosphere until all ClF_3 is gone. Our experiments have suggested that with ClO_2F and ClF_3 present concurrently, ClF_3 will preferentially react with water vapor, leaving ClO_2F intact. ClO_2F may or may not decompose before contact with respiratory water; we have pointed out above that even if ClO_2F derived from moderate concentrations of ClF_3 reaches the pulmonary membrane, it should degrade to ClO_2 before or during absorption.

A comparison of the toxicity of HF , ClF_3 , and ClO_2 is enlightening. Machle *et al* (ref. 28) found that 1500 mg HF/m^3 (approximately 1800 ppm by volume) was lethal to rats after 5 minutes exposure, but 1000 mg HF/m^3 (1200 ppm) was tolerated for 30 minutes and survived without lethality, although tissue pathological changes occurred. Rozenholtz

et al (ref. 29) conducted similar experiments, finding the LC_{50} for HF vapor to be 4970 ppm after 5 minutes of exposure, 2689 ppm after 15 minutes and 2042 ppm after exposures of 30 minutes. We have found that 800 ppm ClF_3 (which could be converted to 2400 ppm HF, if hydrolysis proceeds to the extent expected) is lethal to rats in exposures of 15 minutes or more (ref. 8). This limited information is not sufficient to suggest however that HF is or is not responsible for a major portion of ClF_3 toxicity. Among other considerations ClF_3 causes much more contact damage, such as corneal necrosis, nasopharyngeal and skin burns (ref. 8) than does HF (ref. 29). If differences do exist, they may be a function of the degree of hydrolysis of ClF_3 since there may be such extensive removal of water from the respiratory tract that the reactivity or absorption of NF at the membrane could be altered.

The toxicity of ClO_2 is about the same as ClF_3 on the basis of the number of equivalents of chlorine involved. At a concentration of 500 ppm ClO_2 , two of five exposed rats died after 30 minutes of inhalation and none died in a group exposed for 15 minutes. All exposed animals succumbed after 30 minutes exposure to 1000 ppm ClO_2 . This information appears to suggest that the toxicity of ClF_3 to rats has two major components which are somewhat independent. A similar relationship has previously been shown in intoxication of fish by ClF_3 (ref. 6), in which the lethality of solutions was similar after neutralization of acidity or after reduction of the oxidizing species.

Fish appear much more sensitive to ClO_2 than mammals. In the limited time available, we were able to obtain only Chinook salmon and we did not expose a warm-water species. The salmon were lethally affected after 2 hours of exposure to a concentration of about 10^{-6} M ClO_2 compared with a lethal concentration of 2.5×10^{-4} M ClF_3 at pH 6.5 for an exposure of similar duration. In other words, pure ClO_2 in solution is as much as 250 times more toxic than the oxidizing component of a ClF_3 solutions on a mole/mole basis.

The observations of the respective toxicities of ClO_2 and ClF_3 are explained in terms of the differences in the reaction of ClF_3 with deficient and excess water. We have already described the almost complete conversion of ClF_3 to ClO_2 and then ClO_2 in the presence of limited amounts of water. In a great excess of water, the respective concentration of the products resulting from ClF_3 reaction with water will vary with the rate at which the reagents are brought together. Our previous experience (ref. 6) suggested moderate differences in biological effect among solutions prepared by different procedures, or among solutions in which ClF_3 was introduced at markedly different rates into water.

A systematic study of the proportional distribution of ClF_3 hydrolysis products as a function of mixing rate may be of value in evaluating biological

effects of such solutions, but because of time limitations we have analyzed a single preparation only. This has provided an estimate of the expected relative amounts of chlorine-bearing products with oxidation potential to be found in ClF_3 solutions. A total of 500 ml ClF_3 gas was injected into 3000 ml water over a 20 minute period, and the product concentrations in the solution examined were: ClO_3^- , 0.0236M; ClO_2^- , 0.0026 M; ClO_2 , 0.0022 M; ClO^- , 0.0146 M; and Cl_2 , 0.0072 M. ClO_4^- production from ClO_2F , from which each of the ClO_x products arises, is negligible. ClO_2 represents about 4% of all chlorine^x in the system and Cl_2 about 13%.

The significance of this breakdown may be appreciated in comparing the biological effect of such solutions with the effect of pure ClO_2 as determined in our own studies and the effect of Cl_2 as reported by the Water Pollution Research Board of Great Britain and quoted by Doudoroff and Katz (ref. 30). A ClF_3 solution containing 15 μg fluoride/ml, which is lethal to salmon in about 20 minutes, contains about 0.75 mmole fluoride and 0.25 mmole chlorine per liter. Of the chlorine present, 4% is assumed to be ClO_2 which is equivalent to approximately 10^{-5} M. It must be recognized that this system will probably change immediately when fish are admitted, but the starting conditions may be expected to approximate the described situation. Our experiments with salmon show that 10^{-6} M ClO_2 is lethal in about the same time required for the above ClF_3 solution. Although these numbers differ by an order of magnitude, they may be considered comparable nonetheless, illustrating the sensitivity of fish to ClO_2 , and the presence of sufficient ClO_2 in aqueous ClF_3 solutions to cause major toxic effects.

In the toxic ClF_3 solution containing 15 μg fluoride/ml, Cl_2 is expected to exist at a concentration of 3.2×10^{-5} M, according to the above analysis. It has been reported that 0.3 ppm Cl_2 is very toxic to trout (ref. 30). On a weight/weight basis this is about 10^{-5} M, which is on the order of the concentration expected in our experiments. The implication from these findings is that HF, ClO_2 or Cl_2 are each sufficiently lethal and may be present in sufficient quantity to cause the toxicity of ClF_3 to fish.

SECTION IV

CONCLUSIONS

The studies of biological effects of NF_3O which have been conducted thus far in our laboratories constitute only a survey. This general view has provided enough information, however, to indicate that a single loss of NF_3O into the environment should cause only moderate damage to lower organisms. Toxicity to mammals in the immediate vicinity of release of the compound may be significant, on the basis of work by other investigators (ref. 1), and should be examined further.

The removal of any type of inorganic fluoride oxidizing agent that has been accidentally released in a given area presents major problems. Probably in no case is there a procedure which can protect life at the immediate site of spillage unless individual protective systems are in operation prior to release. It is doubtful that OF_2 or NF_3O can be removed from the atmosphere by any practical method other than eventual dispersal by dilution. In the case of OF_2 , which is lethal at concentrations of 10 ppm after 10-15 minutes of exposure, the problem of personnel protection is especially significant.

N_2F_4 is somewhat less destructive than the other compounds of interest in this study, but its volatile hydrolysis products (NO , NO_2) (ref. 7) are less likely to be effectively trapped in aqueous decontamination media than the products of interhalogen hydrolysis. In event of a massive spill these gases may accumulate in dangerous concentrations requiring secondary decontamination efforts.

With sufficient amounts of a water solution of sodium bicarbonate or other neutralizing agent the interhalogens and their toxic hydrolysis products can probably be destroyed in a relatively short period after release. The danger of severe local reactions during decontamination is such that a controlled total reaction of large amounts of interhalogen may not be feasible, however.

An additional aspect of interhalogen toxicity, especially that of ClF_3 must also be considered. Limited amounts of ClF_3 in humid air react to form ClO_2F . Because ClF_3 reacts with water vapor in preference to ClO_2F only small amounts of ClO_2 will be formed. Advancing front of a ClF_3 cloud should then consist of ClF_3 and ClO_2F almost exclusively, and should begin to form ClO_2 only when most of the ClF_3 has been reacted. The nature of this process in respiratory gases can only be guessed at, but at concentrations that are not greatly above the maximum survivable

level at a given exposure period enough pulmonary moisture should be available to react with ClO_2F forming ClO_2 and HF .

If decontamination with large volumes of aqueous solution is attempted, a variety of relatively innocuous ClO_x^- anions, HF , Chlorine (Cl_2) and some ClO_3F and ClO_2 will form. If these products can be kept in solution until they can be carried to the ground they will be reduced and neutralized on contact, and the products should be no more toxic in run-off water than fluoride salts (ref. 6). In practice a mixture of the reactions expected with no decontamination and with ideal decontamination should be anticipated. Furthermore, we have found that the circumstances under which ClO_3F was produced are not entirely predictable, and if this agent occurs in quantity a problem similar to nitrogen trifluoride contamination may arise.

REFERENCES

1. Lee, C.C. and W.B. Jacobs, 1968, "The Absorption, Distribution, Excretion and Toxicity of Trifluoramine Oxide," Toxicol. Appl. Pharm., Vol. 131, pp. 76-88.
2. Fox, W.B., J.S. MacKenzie, N. Vanderkodi, B. Sukornick, C.A. Wamser, J.R. Holms, R.E. Eibeck, B.B. Stewart, "Trifluoramine Oxide," 1966, Jour. Am. Chem. Soc., Vol. 36, p. 2604.
3. Bartlett, N., S. Beaton and N. Jha, 1966, "Oxidizing Trends in the Third Transition Series Hexafluorides," Chem. Commun. p. 108.
4. Bartlett, N., J. Passmore and E.J. Wells, 1966, "Nitrogen Oxide Trifluoride," Chem. Commun., Vol. 1966, pp. 213-214.
5. Reed, D.J., F.N. Dost and C.H. Wang, 1967, Inorganic Propellant Oxidizers. I. Their Effects Upon Seed Germination and Plant Growth. AMRL-TR-66-187, Vol. I, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
6. Dost, F.N., D.J. Reed and C.H. Wang, 1968, Inorganic Fluoride Propellant Oxidizers. II. Effects Upon Microorganisms, Fish and Plants. AMRL-TR-66-187, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
7. Dost, F.N., A. Finch, D.J. Reed and C.H. Wang, 1969, "The Decomposition of Tetrafluorohydrazine in the Presence of Oxygen and Water," Jour. Inorg. Nucl. Chem. in press.
8. Dost, F.N., D.J. Reed, A. Finch and C.H. Wang, 1968, Metabolism and Pharmacology of Inorganic and Fluorine Containing Compounds, AMRL-TR-67-224, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
9. Bougon, R., M. Carles and J. Aubert, 1967, "Reaction du trifluorine du chlore avec l'eau," Comptes Rendes Acad. Sci. Paris, Vol. 265, pp. 179-182.
10. Engelbrecht, A. and H. Atzwanger, 1956, "Perchloryl Fluoride, ClO_3F . Preparation and Some Physical and Chemical Properties," Jour. Inorg. Nucl. Chem., Vol. 2, pp. 348-357.

11. Sicre, J. and H. Schumacher, 1957, "Herstellung von reinem Perchloryl fluorid," Angew. Chemie., Vol. 69:266.
12. Lide, D. and D. Mann, 1956, "Infrared Spectrum and Structure of Perchloryl Fluoride," Jour. Chem. Physics, Vol. 25, pp. 1128-1129.
13. Daniels, D. and J. Whitehead, 1957, "Laboratory Preparation of Chlorine Dioxide," Chem. and Indust., p. 1214.
14. Rapson, W., 1956, "The Mechanism of Formation of Chlorine Dioxide From Sodium Chlorate," Tappi, Vol. 29, pp. 554-556.
15. Nielson, A. and P. Woltz, 1952, "The Infrared Spectra of ClO_2 ," Jour. Chem. Physics, Vol. 20, pp. 1878-1883.
16. Luther, R. and R. Hoffman, 1936, "Das Verhalten von Chlordioxyd, gelöst in Tetrachlorkohlenstoff, im Dunkeln und im Licht," Zeit. Phys. Chem., Vol. 177, pp. 17-28.
17. White, J., 1942, "Determination of Available Chlorine in Solutions Containing Textone," American Dyestuff Reporter, pp. 484-487.
18. Kerenyi, P., 1963, "Determination of ClO_2 , Cl_2 and NaClO_2 in Treated Water," Vodni Hospodarstvi, Vol. 13, pp. 21-23. As abstracted in Chem. Abstracts, Vol. 59, No. 3646 h.
19. Sicre, J. and H. Schumacher, 1956, "Über die Herstellung und einige Eigenschaften des Chlorylfluorids (ClO_2F)," Zeit. anorg. u. allgem. Chem., Vol. 286, pp. 232-236.
20. Spurny, Z., 1962, "The Ultraviolet Spectra of Chlorine and Its Oxides in Carbon Tetrachloride," Talanta, Vol. 9, pp. 885-889.
21. Smith, D., G. Begun and W. Fletcher, 1964, "Infrared and Raman Vibrational Spectra of ClO_2 ," Spectrochim. Acta, Vol. 20, pp. 1763-1770.
22. Arvin, A. and D. Aymonino, 1963, "IR Spectrum of ClO_2F ," Spectrochim. Acta, Vol. 19, pp. 1449-1456.
23. Smith, D. 1963. "Chlorine Pentafluoride," Science, Vol. 141, pp. 1039-1040.
24. Pilipovich, D., W. Maya, E.A. Lawton, H.F. Bauer, D.F. Sheehan, N.N. Ogimachi, R.D. Wilson, F.C. Gunderloy, Jr. and V.E. Bedwell, 1967, "Chlorine Pentafluoride. Preparation and Properties," Inorg. Chem., Vol. 6, pp. 1918-1919.

25. Holzmann, R., 1966, "The Nature of an Advanced Propellant," in: Advanced Propellant Chemistry, American Chemical Society Advances in Chemistry Series, Washington D.C.
26. Dalhamn, T., 1957, "Chlorine Dioxide, Toxicity in Animal Experiments and Industrial Risks," A.M.A. Arch. Ind. Health, Vol. 15, pp. 101-107.
27. Gloemme, J. and K-D Lundgren, 1957, "Health Hazards from Chlorine Dioxide," A.M.A. Arch. Ind. Health, Vol. 16, pp. 169-176.
28. Machle, W., A. Thaman, K. Kitzmiller and J. Cholak, 1934, "The Effects of Inhalation of Hydrogen Fluoride. I. The Response Following Exposure to High Concentrations," Jour. Ind. Hyg., Vol. 16, pp. 129-145.
29. Rozenholtz, M., T. Carson, M. Weeks, F. Wilinski, D. Ford and F. Oberst, 1963. "A Toxi-pathologic Study in Animals After Brief Single Exposures to Hydrogen Fluoride," Am. Ind. Health. Assoc. Jour. Vol. 24, pp. 254-261.
30. Doudoroff, P., and M. Katz, 1950. "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. I. Alkalies, Acids, and Inorganic Gases," Sewage and Industrial Wastes, Vol. 22, pp. 1432-1458.