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SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING AND THEIR ATM--ETC(U)

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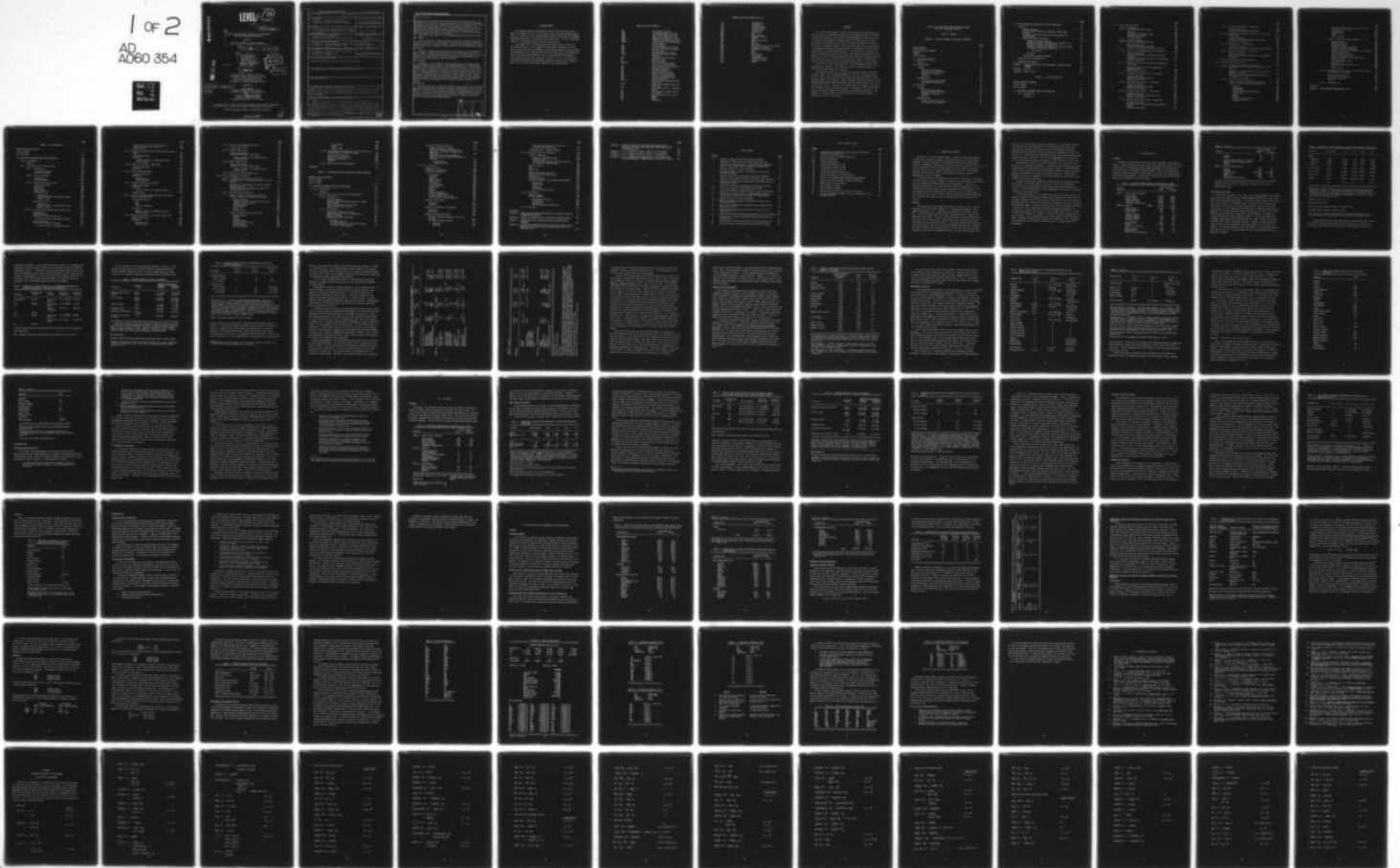
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SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING  
AND THEIR ATMOSPHERIC BEHAVIOR

VOLUME 1.

EXECUTIVE SUMMARY AND GENERAL APPENDICES

9 FINAL REPORT. Jun 76 - Oct 77

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work is directed toward better definition of the specific air pollutants generated from the production of RDX and TNT, together with their attendant raw material manufacture and recovery processes, and the incineration of offgrade and used materials. Plant visits were made to discuss operations and acquire available data. These data, together with survey reports by the USAEHA and technology reports from the arsenals, were used to develop a state-of-knowledge emissions inventory projected to 'mobilization' production rates.		

(Abstract cont'd)

CONT →

Individual emission sources were characterized to the extent possible. The considerable data gaps were identified and flagged for further investigation. A methodology was applied to develop estimates of concentrations of the various compounds that might arise in the air over the plant. The chemical and toxicological characteristics of known emitted compounds were used and their relevant chemical reactivity under photochemical and at ground state was reviewed by literature search. The various possible transformation processes were catalogued. Data gaps were indicated.

Based on this assessment, the following recommendations were developed.

INT PROCESS

Source sampling of a single continuous process line should be conducted in depth to provide data in the identify of pollutants and their relation to process parameters and source controls. These data are prerequisite to further assessment of the air chemistry through dispersion and photochemical modeling.

RDX PROCESS

Further development of currently available process and source emissions data is needed. Source characteristics and process conditions developed herein should be defined and confirmed for use in future assessments. Specific compounds in source emissions need fugitive emissions and emissions from process vents should both be sampled and tested.

RDX CHEMISTRY

Assessment of the potential pollutant reactions in air indicates that known carcinogens may be formed: N-nitrosodimethylamine from dimethylamine emissions and N-nitrosomethylamine from methyamine emissions. Modeling will provide further guidance on the emissions likely to be present in the environment and enable investigators to select test methodology for individual compounds. Sampling should then be employed to define further the emission rates for organic compounds and to quantify each nitrogen oxide species. Further assessment of the potential for formation of toxic levels of these substances using photochemical-diffusion modeling is recommended as the next immediate effort in order to set guidelines for laboratory studies and ambient air testing.

INCINERATION

The trend toward air curtain incinerators, instead of the better controlled SITPA II and Rotary Kiln incinerators, presents the possibility that emissions problems will still exist, since such problems persist among municipal incinerators. A strong effort in computer modeling of combustion product generation in the incineration of explosives and propellants is needed to determine the fuel and air feed rates and temperatures required to optimize incinerator operation and minimize pollutant emissions.

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## ABBREVIATIONS AND ACRONYMS

AAP	Army Ammunition Plant
HAAP	Holston Army Ammunition Plant
JAAP	Joliet Army Ammunition Plant
RAAP	Radford Army Ammunition Plant
NAAP	Newport Army Ammunition Plant
VAAP	Volunteer Army Ammunition Plant
USAEHA	United States Army Environmental Hygiene Agency
TNT	Trinitrotoluene
RDX	Cyclotrimethylenetrinitramine
NEDS	National Emissions Data System
TPD	Tons per day
SPS	Source Performance Standards
NAAQS	National Ambient Air Quality Standards
N&P	Nitration and Purification
SA	Spent Acid Tanks
ST	Settling Tanks
NAC/SAC	Nitric Acid Concentration/ Sulfuric Acid Concentration
DSN	Direct Strong Nitric Acid Plant
RWP	Red Water Processing
FB	Finishing Building
AOP	Ammonia Oxidation Plant
NAC	Nitric Acid Concentration
SAC	Sulfuric Acid Concentrator
SAR	Sulfuric Acid Regeneration
TNM	Tetranitromethane
SC/SA	Single Contact/Single Absorption Acid Plant
DC/DA	Double Contact/Double Absorption Acid Plant
CAR	Carcinogenic effects - producing cancer
CNS	Central nervous system effects
EYE	Eye effects
GIT	Gastrointestinal tract effects
ham	hamster
hmn	human
ihl	Inhalation

ABBREVIATIONS AND ACRONYMS (cont'd)

ims	Intramuscular
ipl	Intraplueral
ipr	Intraperitoneal
IRR	Irritant effects
itr	Intratracheal
IVN	Intravenous
MAN	Man
MTH	Mouth effects
MUT	Mutagenic effects
mus	mouse
NEO	Neoplastic effects
orl	Oral
par	Parenteral
PNS	Peripheral nervous system effects
PSY	Psychotropic effects
PUL	Pulmonary system effects
rat	Rat
rbt	Rabbit
SKN	Skin effects
scu	Subcutaneous
TER	Teratogenic effects
unk	Unreported route
wmn	Woman

## FOREWORD

This study by the Research Triangle Institute effects a continuation of effort by the U.S. Army Medical Research and Development Command to delineate the needs for control of the quality of the atmosphere over munitions plants. It focuses on the potential pollutant impact of a mobilized plant, and is essentially an assessment of the status of information needed to develop a sound emissions control program. Three processing operations are considered: the manufacture of TNT by continuous process, the manufacture of RDX, and the incineration of attendant waste materials. Emission source information has been collected and reviewed at the plants; the available information on the air chemistry of identified and suspected pollutants has been collected; data gaps have been identified. Further information needs, relevant to defining and quantifying the potential needs for standards and controls, are described.

The report is bound in four volumes: Executive Summary--Volume 1, RDX/HMX Production--Volume 2, TNT Production--Volume 3, and Open Burning and Incineration of Waste Munitions--Volume 4.

The Executive Summary covers briefly all processes studied, presenting findings, conclusions, and recommendations in turn for the RDX/HMX process, the TNT process, and Burning and Incineration and general appendices showing chemical reactions and toxicity. Those interested in detailed reports of these processes and the air chemistry of their emissions should refer to the other volumes of the report. The study is by nature one of assessment of the status of knowledge of source emissions and their air chemistry. The results have meaning only when presented in the context of the problems addressed. This summary is a little longer than desired, but only because of the need to preserve the content of the study.

SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING  
AND THEIR ATMOSPHERIC BEHAVIOR

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## 1.0 PURPOSE AND APPROACH

The Office of the Army Surgeon General is responsible for development of health and environmental guidelines governing emissions of military-related compounds. The U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) has reported an evaluation of the air pollution potential of seven substances emitted from Army Ammunition Plants (AAP's) for which emissions and air quality standards currently do not exist.<sup>1</sup> The evaluation provides a background for further investigations of possible needs for appropriate air quality standards.

This study provides a continuation of the effort to establish a data base from which either discharge or ambient standards for air pollutants not addressed by the Environmental Protection Agency can be recommended. The study is limited to the production of trinitrotoluene (TNT); the production of cyclo-trimethylenetrinitramine (RDX); and the incineration of waste materials. The investigation required consideration of the nature of the explosives manufacturing processes and the emissions controls applied, the possible emissions, their potential for chemical reaction and photochemical reaction, and their toxicity.

### APPROACH

Visits were made to army ammunition plants at Kingsport, Tenn. - Holston Army Ammunition Plant (HAAP); Radford, Va. - Radford Army Ammunition Plant (RAAP); Chattanooga, Tenn. - Volunteer Army Ammunition Plant (VAAP); Joliet, Ill. - Joliet Army Ammunition Plant (JAAP); and Newport, Ind. - Newport Army Ammunition Plant (NAAP). At each, the processing and operating practices were discussed with plant specialists. Available data were acquired relating to emissions sources and emissions controls. The available data were augmented by survey and test data from the U.S. Army Environmental Hygiene Agency (USAEHA), by relevant reports from Picatinny Arsenal, and from the technical reference facilities of the Defense Documentation Center. The data were assessed where

possible to project emissions source characteristics (stack height, diameter, exit gas flow rate, gas composition) to be expected when the explosives-manufacturing processes were operated at mobilization production rates. Mobilization rates themselves were set based upon information obtained from the plants. In developing the projected emissions, many extensive gaps in the existing data were identified. This led to recommendations for future work to fill the information gaps and provide much needed emissions inventory data.

Waste materials were, at the time of the plant visits, burned on open ground or in air-curtain incinerators. Enclosed burning techniques were undergoing evaluation and development at the arsenals, however. Visits were made to the Picatinny Arsenal and Tooele Army Depot to obtain additional available data for assessment of emissions from closed incineration. Considerable attention was given to assessment of the methodologies for calculation of the products of controlled combustion.

Although the emissions inventories thus developed are incomplete because of data gaps, and include elements necessarily derived from theoretical principles, one inventory (RDX) provided enough approximate information to justify a limited investigation of likely atmospheric concentrations of emitted substances of plant boundaries.

For both RDX and TNT, the literature was searched to collect data on the chemical properties and potential photochemistry, ground state chemistry, and secondary reactions of both the positively identified emissions and selected suspected emissions. Reaction rate data were compiled to the extent available. The extensive numbers of chemical reactions thus obtained have been interpreted in three ways. First, potentially hazardous compounds are identified by assessing the toxicological properties of the reactants and products. Second, the reactions themselves are screened to provide some focus on expected principal products. Third, methodologies were applied toward estimating concentrations of emitted pollutants at the boundary of a mobilized plant. Additional work on modeling the air chemistry over the plant is needed, however, and recommended.

## 2.0 RDX/HMX STUDY

### FINDINGS

A summary of the emissions and emission rates from HAAP is presented in Table 1. These primary pollutants are classified into three groups. The first classification is comprised of those species designated as air pollutants by the United States Environmental Protection Agency (EPA). The second group consists of organic compounds such as solvents or byproducts released during RDX manufacturing processes. The third and final group includes miscellaneous species not considered in the first group.

TABLE 1. EMISSIONS SUMMARY FROM RDX MANUFACTURING AT HAAP<sup>a</sup>

Compound	Emission Rate	
	lb/day	ton/year
GROUP I. EPA Criteria Pollutants		
Particulates	14,749	2,692
Sulfur Oxides	16,989	3,097
Carbon Monoxide <sup>b</sup>	12,197	2,226
Nitrogen Oxides <sup>b</sup>	64,526	11,776
Nonmethane Hydrocarbons	2,908	531
GROUP II. Organics	TOTAL	( 3,969)
Acetic Acid	12,497	2,281
Acetic Anhydride	230	42
Formic Acid	141	26
Isobutyl Acetate	2	0.4
n-Propyl Acetate	1,134	207
n-Propyl Formate	320	58
Methyl Acetate	733	134
Cyclohexanone	2,278	416
Acetone	2,754	503
Methyl Ethyl Ketone	6	1
Methyl Nitrate	1,558	284
Nitromethane	30	5
Methyl- and Dimethylamine	18	3

TABLE 1. (cont'd)

Compound	Emission Rate	
	lb/day	ton/year
Toluene	52	9
Phenol	0.8	0.1
Trace Organics (Butanol, Propanol, Methanol, Methyl Formate, Formaldehyde)	10	2
GROUP III. Miscellaneous Species		
Methane	1,955	357
Hydrogen	418	76
Carbon Dioxide	2,250,000	410,625
Ammonia	390	71
Nitric Acid	4,409	805
Explosives (Particulates)	2.3	0.4

<sup>a</sup>Assumes full mobilization as defined in Volume 2, Section 6.A.1

<sup>b</sup>Calculated as NO<sub>2</sub>

#### EPA Criteria Pollutants

A qualitative evaluation of the impact of the EPA-designated air pollutants on the local environment can now be made by comparing the emission rates from HAAP with county-wide emission rates. Since only a small fraction of the total area of both counties is covered by HAAP, the munition facility may be considered as a point source or a group of point sources relative to the total county areas. In this comparison using NEDS data, it should be noted that the potential for elevated ambient pollutant concentrations in the vicinity of or downwind from the munition installation is not considered. The plant and counties emission rates are presented in Table 2. From the available data, it appears that the emissions from HAAP make up a small fraction of the total emissions from Sullivan and Hawkins Counties. However, the county emission rates in Table 2 were developed for RDX plant operation at less than full capacity. If HAAP does operate at full mobilization, the county-wide emission rate estimates as well as the percentage of the county-wide emissions due to HAAP would increase.

TABLE 2. COMPARISON OF HAAP EMISSIONS TO COUNTY WIDE EMISSIONS (TONS/YEAR)

Location	Particulates	SO <sub>2</sub>	CO	NO <sub>x</sub>	HC
HAAP <sup>a</sup>					
Area A <sup>a,b</sup>	1,108	2,209	217	1,726	1,782
Area B <sup>a,c</sup>	1,592	2,879	208	3,495	1,038
Total <sup>a</sup>	2,700	5,088	425	5,221	2,820
RTI Estimate <sup>d</sup>	2,692	3,097	2,226	11,776	4,500 <sup>e</sup>
Sullivan Co. <sup>a</sup>	31,024	42,289	71,009	28,965	23,350
Hawkins Co. <sup>a</sup>	19,116	62,541	15,139	38,594	4,469
Total <sup>a</sup>	50,140	104,830	86,148	67,559	27,819
% <sup>f</sup>	5.4	4.9	0.5	7.7	10.1

<sup>a</sup>Data were retrieved from EPA's National Emissions Data System (NEDS); see Reference 2. NEDS is a computerized data bank which holds detailed emissions inventory data for each county in the country. It should be noted that differences in practices of reporting and updating emissions data may prevent comparisons on the same bases.

<sup>b</sup>Located in Sullivan Co.

<sup>c</sup>Located in Hawkins Co.

<sup>d</sup>RTI's emissions estimate assumes full mobilization.

<sup>e</sup>Includes 3969 tons/year of organic solvents.

<sup>f</sup>This value is the percent contribution of the army installation to county wide emissions for the two-county area, with HAAP not at mobilization.

EPA regulations include source performance standards (SPS) which specify the maximum permissible emissions rates for several types of industries. Currently, these regulations have not been established for the explosives

manufacturing industry. To set HAAP emission rates (Table 1) into perspective, capacities of sources subject to EPA SPS with emissions equivalent to HAAP are presented in Table 3. It has been found that the nitrogen oxide emissions from HAAP are equivalent to those from a coal-fired boiler in a power plant having a capacity of 360 megawatts or a nitric acid plant which produces 21,509 TPD. On this basis, the nitrogen oxide emissions appear to be significant and are expected to have a noticeable impact on the local environment.

TABLE 3. CAPACITIES OF SOURCES SUBJECT TO EPA PERFORMANCE STANDARDS WITH EMISSIONS EQUIVALENT TO THE HAAP RDX INSTALLATION

Pollutant	Emission Rate lb/day	Source Category	Emission Regulation <sup>a</sup>	Equivalent Capacity
Particulate	14,749	Coal-fired boiler	0.1 lb/10 <sup>6</sup> BTU	576 MW <sup>b</sup>
SO <sub>2</sub>	16,969	Coal-fired boiler	1.2 lb/10 <sup>6</sup> BTU	55 MW
		Sulfuric Acid Plant	4 lb/ton	4242 TPD
CO	12,197			
NO <sub>x</sub>	64,526	Coal-fired boiler	0.7 lb/10 <sup>6</sup> BTU	360 MW
		Nitric Acid Plant	3.0 lb/ton	21,509 TPD
HC	24,654			

<sup>a</sup>See Reference 3.

<sup>b</sup>MW = megawatt; conversion assumes power plant efficiency of 32 percent.

A major issue for EPA criteria pollutants (GROUP I in Table 1) is the question of compliance with air quality standards. National Ambient Air Quality Standards (NAAQS) are given in Table 4, nondegradation guidelines in Table 5. An estimate of ground level concentrations can be made for the

TABLE 4. NATIONAL AMBIENT AIR QUALITY STANDARDS<sup>a</sup>

Pollutant	Averaging Time	Maximum Concentration	
		Primary Standard <sup>b</sup>	Secondary Standard <sup>c</sup>
Suspended particulate matter	Annual	75 $\mu\text{g}/\text{m}^3$	60 $\mu\text{g}/\text{m}^3$
	24 hr	260 $\mu\text{g}/\text{m}^3$	150 $\mu\text{g}/\text{m}^3$
Sulfur oxides	Annual	0.03 ppm	0.02 ppm
	24 hr	0.14 ppm	0.10 ppm
	3 hr		0.5 ppm
Carbon monoxide	8 hr	9 ppm	9 ppm
	1 hr	35 ppm	35 ppm
Nitrogen oxides	Annual	0.05 ppm	0.05 ppm
Nonmethane hydrocarbons	3 hr (6-9 am)	0.24 ppm	0.24 ppm
Photochemical oxidants as ozone	1 hr	0.08 ppm	0.08 ppm

Additional standards have been proposed for asbestos, beryllium, mercury, and lead; they are being prepared for fluorides, polycyclic organic compounds, odors (including hydrogen sulfide), chlorine, hydrogen chloride, arsenic, cadmium, copper, manganese, nickel, vanadium, zinc, barium, boron, chromium, selenium, pesticides, radioactive substances, and aeroallergens.

<sup>a</sup>See Reference 4.

<sup>b</sup>Primary standards have been established to protect public or human health.

<sup>c</sup>Secondary standards have been established to protect soil, water, vegetation, materials, and animals as well as to maintain personal comfort, weather, and visibility.

TABLE 5. MAXIMUM ALLOWABLE INCREASE IN CONCENTRATION FOR SO<sub>2</sub> AND PARTICULATE MATTER<sup>a</sup>

Pollutant	Class I ( $\mu\text{g}/\text{m}^3$ )	Class II ( $\mu\text{g}/\text{m}^3$ )	Class III ( $\mu\text{g}/\text{m}^3$ )
Particulate matter			
Annual average	5	10	10
24 hr maximum	10	30	150
Sulfur dioxide			
Annual average	2	15	(0.02 ppm)
24 hr maximum	5	100	(0.10 ppm)
3 hr maximum	25	700	(0.5 ppm)

<sup>a</sup>See Reference 5. The recently promulgated nondegradation regulations affect only new sources, in contrast to NAAQS which affect both existing and new sources. These regulations require weighing the incremental deterioration against social and economic considerations and limiting increases in sulfur dioxide and particulate matter concentrations within each of three classification areas. The nondegradation guidelines will not allow industrial development in areas designated Class I, will permit a modest increase in industrial development in Class II areas, and will allow industrial development in Class III areas as long as NAAQS are met.

<sup>b</sup>Federal Secondary Ambient Air Quality Standard.

primary pollutants by employing well established meteorological dispersion models.\* For secondary pollutants (pollutants that are formed in atmospheric reactions), models coupling both chemistry and meteorology are required. Because of the inherent inaccuracies of dispersion modeling and the many assumptions that are made (e.g., assumptions involving the plant location, the plant characteristics, and the emission source characteristics), the accuracy of

\*Meteorological dispersion models can be applied to primary pollutants only if these pollutants are assumed to be nonreacting.

ambient air concentration estimates from such meteorological models is limited to  $\pm$  200-300 percent. The dispersion analysis does, however, give a general feeling for the effect that an industry has on air quality, and these analyses are often used to assess the environmental impact of new industries by comparison of predicted air quality with applicable standards.

In this study, a meteorological model for non-reactive emissions was employed to estimate pollutant concentrations at various distances downwind of their sources.<sup>6</sup>

HAAP presents a problem in modeling because of its two separate areas. To simplify matters, the bend in the Holston River was ignored and Area A was assumed to be directly upstream from Area B. A particular stable set of meteorological conditions was also assumed. Using these assumptions, the ground level concentrations (specifically, at 1.5 meters height) at various locations along the downwind boundary of Area B were calculated. These maximum plant boundary concentrations ( $\mu\text{g}/\text{m}^3$  and ppm) for the emissions from Areas A and B are presented in Table 6.

Of the EPA criteria pollutants, the concentrations of particulates, sulfur dioxide, carbon monoxide and nonmethane hydrocarbons fall within the permissible concentration levels established by EPA in the NAAQS (see Table 4). However, the ambient concentration of nitrogen dioxide at the boundary of HAAP exceeds this permissible level by a factor of approximately 55. At full mobilization, it appears that the nitrogen dioxide emissions from HAAP will have a significant impact on the environment of the surrounding area. If any new RDX facility is to be built, it would have to be built in a Class III area, since the ambient particulate concentration is greater than that established for areas designated as Class I and II (see the nondegradation guidelines in Table 5). This assumes the projections of the model are valid. With a factor of 55 for the concentration excess, the assumption seems reasonable.

Once in the atmosphere, the ultimate fate of these EPA criteria pollutants is fairly straightforward. The particulate material will be deposited on the earth's surface. The sulfur dioxide will be oxidized to sulfates and sulfuric acid which will form aerosols. The fate of these aerosols will then include rainout or dry deposition. The carbon monoxide in the atmosphere will be oxidized to carbon dioxide. The fate of the nitrogen oxides (nitric oxide and

TABLE 6. MAXIMUM "GROUND LEVEL" CONCENTRATIONS NOTED AT BOUNDARY<sup>a,b</sup>

Compound	Area A $\mu\text{g}/\text{m}^3$	Area B $\mu\text{g}/\text{m}^3$	Total $\mu\text{g}/\text{m}^3$	Total ppm
<b>Group I. EPA Criteria Pollutants</b>				
Particulates	141.5	9.93	151.4	$6.4 \times 10^{-2}$
Sulfur Oxides	134.4	33.4	167.8	$3.52 \times 10^{-1}$
Carbon Monoxide	403.3	---	403.3	<b>2.72</b>
Nitrogen Dioxide	220.8	<b>4872</b>	<b>5093</b>	$3.42 \times 10^{-3}$
Nonmethane Hydrocarbons	5.32	17.0	22.3	
<b>GROUP II. Organics</b>				
	Total (136.5)	Total (1984)	2120	<b>1.94<sup>c</sup></b>
Acetic Acid	1.71	1807	1809	$5.76 \times 10^{-1}$
Acetic Anhydride	---	87.7	87.7 <sup>d</sup>	$2.10 \times 10^{-2}$
Formic Acid	---	13.4	13.4	$7.14 \times 10^{-3}$
Isobutyl Acetate	---	$1.48 \times 10^{-1}$	$1.48 \times 10^{-1}$	$3.12 \times 10^{-5}$
n-Propyl Acetate	40.1	---	40.1	$9.63 \times 10^{-3}$
n-Propyl Formate	2.20	---	2.20	$6.13 \times 10^{-4}$
Methyl Acetate	2.47	6.90	9.37	$3.10 \times 10^{-3}$
Cyclohexanone	---	153	153	$3.32 \times 10^{-2}$
Acetone	---	187	187	$7.90 \times 10^{-2}$
Methyl ethyl Ketone	---	$4.22 \times 10^{-1}$	$4.22 \times 10^{-1}$	$1.67 \times 10^{-4}$
Methyl Nitrate	1.10	119.1	120.2	$3.32 \times 10^{-2}$
Nitromethane	$2.09 \times 10^{-1}$	$8.92 \times 10^{-1}$	1.10	$4.43 \times 10^{-4}$
Methyl & Dimethylamine	---	<sup>2</sup>	<sup>2</sup>	---

TABLE 6. (cont'd)

Compound	Area A $\mu\text{g}/\text{m}^3$	Area B $\mu\text{g}/\text{m}^3$	Total $\mu\text{g}/\text{m}^3$	Total ppm
Toluene	---	3.05	3.05	$8.11 \times 10^{-4}$
Phenol	$2.65 \times 10^{-2}$	---	$2.65 \times 10^{-2}$	$6.91 \times 10^{-6}$
Trace Organics (Butanol, Propanol, Methanol, Methyl Formate, Formalde- hyde)	88.64	$6.11 \times 10^{-1}, \text{d}$	89.25	$1.36 \times 10^{-1}, \text{e}$
Group III. Miscellaneous Species				
Methane	64.0	---	64.0	$9.86 \times 10^{-2}$
Hydrogen	13.8	---	13.8	$1.69 \times 10^{-1}$
Carbon Dioxide	47,760	15,050	62,810	35.0
Ammonia	---	38.8	38.8	$5.60 \times 10^{-2}$
Nitric Acid	---	550.3	550.3	$2.14 \times 10^{-1}$
Explosives (Particulates)	---	$1.65 \times 10^{-1}, \text{f}$	$1.65 \times 10^{-1}$	---

<sup>a</sup>"Ground Level" = 1.5 m

<sup>b</sup>Assumes full mobilization

<sup>c</sup>ppm carbon

<sup>d</sup>The ambient concentrations ( $\mu\text{g}/\text{m}^3$ ) for a particular compound should be consistent with the emission rate given in Table 3 varying somewhat with source height, velocity, and temperature. The value of the ratio between the emission rate (tons/year) and ambient concentration ranges from 2 to 7 for all the emitted compounds except acetic anhydride and trace organics. For acetic anhydride and trace organic emissions, this ratio has values of 0.5 and 0.02, respectively. It is believed that the calculated ambient concentration of these compounds is higher than it actually would be.

<sup>e</sup>Calculated using the molecular weight of methane.

<sup>f</sup>Consists of  $6.6 \times 10^{-2} \mu\text{g}/\text{m}^3$  RDX and  $9.86 \times 10^{-2} \mu\text{g}/\text{m}^3$  TNT.

nitrogen dioxide) will involve conversion to nitric acid and nitrates with subsequent removal by rainout and dry deposition. The hydrocarbons will be oxidized into carbon dioxide, water, and aerosols.

In addition, the hydrocarbons and nitrogen oxides are also precursors of the secondary pollutant and photochemical oxidant, ozone. Ozone is generated and accumulates in the cyclic process illustrated under the Section Known or Potential Secondary Reactions (see Volume 2 of this report). In the cycle, free radicals (R) are generated from organic compounds by processes following the photolysis of nitrogen dioxide. These free radicals combine with atmospheric oxygen to form peroxy radicals ( $RO_2$ ) which are capable of oxidizing nitric oxide to nitrogen dioxide. For each molecule of nitric oxide oxidized to nitrogen dioxide by a non-ozone species, a molecule of ozone accumulates in the atmosphere. At high hydrocarbon and nitrogen oxide concentrations representative of urban atmospheres, the concentration of hydrocarbons is more influential than that of nitrogen oxides in dictating the resulting ozone concentration. At lower hydrocarbon and nitrogen oxide concentrations representative of nonurban atmospheres, the ozone concentration is thought to be influenced more strongly by the nitrogen oxide concentration. Thus, injection of nitrogen oxides into nonurban air may enhance the ozone generative potential of the air mass. It should be noted, however, that under conditions where the concentration of nitrogen oxides is in substantial excess of the concentration of hydrocarbons, oxidant formation is inhibited and any ozone that may enter such an atmosphere is quickly destroyed by its reaction with the nitrogen oxides.

Since explosives plants are sources of both organic and nitrogen-containing compounds, the setting of the facility as well as the magnitude of the emissions relative to the local emissions will determine the impact on both the local and downwind oxidant levels. The data in Table 1 show that the emission rate of nitrogen oxides is at least four times that of any other EPA criteria pollutant and that the mass ratio of the emission rates of nitrogen oxides to nonmethane hydrocarbons is approximately 22. The dominant impact of this ratio in the immediate vicinity of the RDX facility will be to destroy any ozone which may enter the plume and inhibit its formation until atmospheric

processes facilitate attainment of a more favorable nitrogen oxide-hydrocarbon ratio. Thus, the concentration of ozone in the plume should be less than that in the surrounding air parcels. In the atmosphere downwind from HAAP, the ratio may be more favorable to ozone production. However, it is difficult to ascertain the contribution of a single source to rural oxidant levels at long distances downwind because the ozone precursors may be emitted by many sources within the region.

#### Non-EPA Criteria Pollutants

Other emissions associated with the manufacture of RDX include such compounds as methane, toluene, alcohols (methanol, propanol, and butanol), phenol, aldehydes (formaldehyde and acetaldehyde), ketones (acetone, methyl ethyl ketone, and cyclohexanone), organic acids (formic and acetic acids), esters (methyl formate, methyl acetate, propyl formate, propyl acetate, and isobutyl acetate), acetic anhydride, ammonia, amines (methyl- and dimethyl-amine), nitric acid, nitromethane, and methyl nitrate. Emission rates for some of these compounds can be found in Table 1. A discussion of their potential atmospheric chemistry is in Volume 2 of the report. The maximum ground level concentration at the boundary of HAAP can be found in Table 6. The total ambient concentration of organics was found to be 1.90 ppm (carbon).

As previously mentioned, hydrocarbons (organic compounds) and nitrogen oxides are ozone precursors.<sup>7</sup> The organic non-EPA criteria pollutants will also generate ozone in the atmosphere (see Known or Potential Secondary Reactions). However, among these pollutants, differences exist in structure and reactivity. To assess their reactivity in the atmosphere, the rate of nitrogen dioxide formation (ppm/min), the maximum concentration of ozone produced (ppm), and the total amount of ozone produced within a given time period (ppm/min) have been measured from experiments conducted in smog chambers. The reactivities of selected organic compounds were obtained from several studies, and their reactivities relative to toluene are summarized in Table 7.<sup>8,9</sup>

TABLE 7. SUMMARY OF SMOG CHAMBER RESULTS FOR SELECTED ORGANIC SOLVENTS  
(RELATIVE TO TOLUENE)

Compound	Relative Reaction Rate with NO <sub>2</sub> ppm/min	O <sub>3</sub> Max ppm	O <sub>3</sub> Dosage ppm/min
Toluene	1.00	1.00	1.00
Ethyl alcohol	0.50 <sup>a</sup>	1.00	---
<u>I</u> sopropyl alcohol	0.45 <sup>a</sup> 0.61 <sup>b</sup>	0.65 0.20	--- 0.15
<u>n</u> -butyl alcohol	1.00 <sup>a</sup>	1.40	---
Formaldehyde	1.58 <sup>c</sup>	0.42	0.34
Acetaldehyde	2.66 <sup>c</sup>	1.98	1.97
Acrolein	1.70 <sup>c</sup>	1.70	1.58
Benzaldehyde	0.30 <sup>c</sup>	0.08	0.05
Acetone	0.30 <sup>a</sup> 0.24 <sup>b</sup>	0.07 0.0	--- 0.0
Methyl ethyl ketone	0.55 <sup>a</sup> 0.90 <sup>b</sup>	0.90 0.64	--- 0.54
Cyclohexanone	0.80 <sup>a</sup> 0.82 <sup>b</sup>	0.60 0.23	--- 0.36
Ethyl acetate	0.5 <sup>a</sup>	0.80	---
<u>n</u> -butyl acetate	0.70 <sup>a</sup>	0.85	---
<u>I</u> sobutyl acetate	0.90 <sup>a</sup> 0.58 <sup>b</sup>	1.00 0.18	--- 0.07

<sup>a</sup>See Reference 40. Initial conditions: 1.5 ppm (by volume) organic solvent, 0.6 ppm NO<sub>x</sub> (0.57 ppm NO and 0.03 ppm NO<sub>2</sub>), relative humidity 20%, temperature 22°C to 32°C, and irradiation time 5 hrs. No actual data are reported for Toluene.

<sup>b</sup>See Reference 8. Initial conditions: 4 ppm organic solvent, 2 ppm NO, and irradiation time 6 hrs. Toluene data: NO<sub>2</sub> rate 10.4 ppb/min, O<sub>3</sub> Max 0.44 ppm, and O<sub>3</sub> Dosage 67 ppm-min.

<sup>c</sup>See Reference 9. Initial conditions: 1 ppm organic solvent and 0.5 ppm NO<sub>x</sub>. Toluene data: NO<sub>2</sub> rate 4.4 ppb/min, O<sub>3</sub> Max 0.355 ppm, and O<sub>3</sub> Dosage 72<sup>x</sup> ppm-min.

If the data from these studies are comparable, then the reactivities of these selected organic compounds can be assessed. From the data in Table 7, it appears that acetaldehyde and acrolein have the greatest reactivity with nitric oxide and produce the greatest concentration of ozone. At the other extreme, benzaldehyde and acetone appear to be the least reactive and produce the smallest concentration of ozone.

### Atmospheric Chemistry

In the atmosphere, the lifetime of an air contaminant is largely determined by the propensity of the compound to photodissociate and by its reactivity with species such as ozone and hydroxyl radicals. A compilation of half-lives ( $t_{1/2}$ ) has been assembled in Table 8 for selected air contaminants associated with RDX installations. These half-lives consider each pathway to be independent of the others and do not consider secondary or competitive pathways. The photolytic half-life assumes a first order reaction with the light intensity equivalent to that with the sun at a zenith angle of  $40^\circ$  ( $z = 40^\circ$ ).<sup>10,11</sup> The half-life in the presence of ozone assumes a constant ozone concentration equal to the NAAQS,  $[O_3] = 0.08$  ppm (see Table 4). A range of half-lives is presented for the compound in the presence of hydroxyl radicals, because the mean ambient hydroxyl radical concentration currently is not well established. Since it is believed to lie between  $0.5$  and  $5.0 \times 10^{-7}$  ppm ( $0.5 \times 10^{-7} < [OH] < 5 \times 10^{-7}$  ppm),<sup>9</sup> these two values were chosen to bound the disappearance rate due to hydroxyl radical attack.

Nitric oxide and nitrogen dioxide are the most reactive species in this atmosphere. Half of the nitric oxide may react within minutes with ozone to form nitrogen dioxide and within hours with hydroxyl radicals to form nitrous acid. In the atmosphere, half of the nitrogen dioxide may photodissociate into nitric oxide and atomic oxygen within one minute. The nitrogen dioxide may also react with ozone or hydroxyl radicals within hours. In contrast, nitrous oxide is one of the least reactive species; the half-life of its reaction with hydroxyl radicals is great ( $t_{1/2} = 1.72 - 17.2 \times 10^4$  days).

Both nitrous acid, a secondary pollutant, and nitromethane rapidly photolyze. Within minutes, the atmospheric concentrations of these compounds

TABLE 8. HALF-LIVES OF SELECTED AIR CONTAMINANTS ASSOCIATED WITH THE MANUFACTURE OF RDX<sup>a,b</sup>

Compound (A)	A + h $\nu$ $\rightarrow$ $t_{1/2}$	A + O <sub>3</sub> $\rightarrow$ $t_{1/2}$	A + OH $\rightarrow$ $t_{1/2}$
Methane	---	9.4 x 10 <sup>5</sup> days	87-870 days
Toluene	---	330 days	2.1-21 hr
Carbon Monoxide	---	1.0 x 10 <sup>7</sup> days	4.6-46 days
Methanol	---	?	16.5-165 hr
<u>n</u> -propanol	---	?	4.1-41 hr
<u>n</u> -butanol	---	6.3 x 10 <sup>3</sup> days	2.3-23 hr
Phenol	?	?	-29.5-295 min <sup>c</sup>
Formaldehyde	99 min	1.9 x 10 <sup>6</sup> days	1.1-11 hr
Acetaldehyde	12 hr <sup>d</sup>	120 days	46.2-462 min
Acetone	14 hr	?	-12-120 hr <sup>e</sup>
Methyl Ethyl Ketone	14 hr	2.2 x 10 <sup>6</sup> days	4.7-47 hr
Cyclohexanone	?	4.3 x 10 <sup>5</sup> days	2.5-25 hr
Formic Acid	---	?	2.8-28 days
Acetic Acid	---	2.4 x 10 <sup>4</sup> days	20.5-205 days
Methyl Formate	---	?	?
Methyl Acetate	---	?	?
<u>n</u> -propyl formate	---	?	?
<u>n</u> -propyl acetate	---	?	?
Isobutyl Acetate	---	?	?
Acetic Anhydride <sup>f</sup>	---	?	?
Ammonia	---	?	4.0-40 days
Methylamine	---	?	42.6-426 min
Dimethylamine	---	?	<42-420 min
Nitric Oxide	---	0.33 min	2.8-28 hr
Nitrogen Dioxide	1.1 min	3.0 hr	3.5-35 hr

TABLE 8. (cont'd)

Compound (A)	A + hv → $t_{1/2}$	A + O <sub>3</sub> → $t_{1/2}$	A + OH → $t_{1/2}$
Nitrous Oxide	---	---	(1.72-17.2) x 10 <sup>4</sup> days
Nitrous Acid	5.8 min	---	7.0-70 hr
Nitric Acid	55 hr	---	6.9-69 days
Nitromethane	4.3 hr	?	16.5-165 hr
Methyl Nitrate	92 hr	---	?
Sulfur Dioxide	120 hr	6 x 10 <sup>4</sup> days	26-260 hr

<sup>a</sup>The half-life of a reaction is defined by the equation,  $t_{1/2} = 0.693/k$ . Except for the photolyses of nitrous acid and sulfur dioxide, the rate constants are those reported in the preceding sections. The rate constant for the photolysis of nitrous acid is from Reference 10 and that for the photolysis of sulfur dioxide from Reference 11.

<sup>b</sup>A blank space (---) designates that the reaction between a particular species and light, ozone, or hydroxyl radical is unimportant in the atmosphere. A question mark (?) indicates that the rate constant for the reaction between a species and light, ozone, or hydroxyl radical was unavailable.

<sup>c</sup>The half-life of the addition reaction between o-cresol and hydroxyl radical.

<sup>d</sup>The rate constant used to determine this half-life is the rate constant for the photolysis of acetaldehyde at a solar zenith angle of 0° ( $z = 0^\circ$ ).

<sup>e</sup>The rate constant between acetone and hydroxyl radicals was estimated, see Reference 41.

<sup>f</sup>The half-life for the hydrolysis of acetic anhydride is 4.3 min.

are cut by half. Nitric acid, on the other hand, photodissociates at a negligible rate relative to nitrous acid and nitromethane; it has a half-life of fifty-five hours. Like its analogue nitric acid, methyl nitrate also photodissociates slowly ( $t_{1/2} = 92$  hr).

None of the organic compounds emitted from HAAP react with ozone at an appreciable rate; all reactions with ozone have half-lives of days. However,

the alcohols, aromatics, aldehydes, ketones, and amines are oxidized by hydroxyl radicals within hours. The higher molecular weight alcohols, aldehydes, and ketones react faster than those of lower molecular weight (i.e., butanol reacts faster than methanol, acetaldehyde faster than formaldehyde, and methyl ethyl ketone faster than acetone). The reaction between dimethylamine and hydroxyl radical is believed to be more rapid than that between methylamine and hydroxyl radical.<sup>12</sup>

In addition to their reactions with hydroxyl radicals, the aldehydes and ketones may photodissociate. Formaldehyde, acetaldehyde, acetone, and methyl ethyl ketone are known to photolyze within hours. It is believed that cyclohexanone also will photolyze approximately within the same amount of time.

To determine the total effect of the emissions from HAAP on the atmosphere, the secondary pollutants must also be considered. Two of the chief secondary pollutants in this atmosphere are ozone and nitrous acid. The formation and chemistry of ozone and the potential effects of explosives emissions on its formation and destruction were both discussed earlier. Nitrous acid, a secondary pollutant, is formed in an equilibrium reaction involving nitric oxide, nitrogen dioxide, and water and also in the reaction between nitric oxide and hydroxyl radicals. Nitrous acid in the presence of secondary amines can lead to the formation of carcinogenic nitrosamines either in ambient air or in the work place. Since the secondary amine, dimethylamine, is emitted from HAAP, nitrosamine formation is anticipated. No data or estimates of the quantity of this carcinogenic substance were obtained. Limited chemical modeling of the reactivity of dimethylamine is recommended to provide such estimates.

#### Toxicity (See Appendix 2 for further detail)

Most of the compounds emitted from HAAP are known to irritate the eyes and/or mucous membranes of the upper respiratory tract. Besides being irritants, methanol, acetaldehyde, acetone, methyl ethyl ketone, propyl formate, methyl acetate, propyl acetate, and methyl nitrate are also narcotics. In addition, formaldehyde is a suspected carcinogen of the lung and dimethylamine is known to react with nitrous acid in the atmosphere to form N-nitroso dimethylamine, a known carcinogen.<sup>13</sup> Permissible threshold level values for the compounds emitted from HAAP are presented in Table 9.

TABLE 9. PERMISSIBLE THRESHOLD LEVEL VALUES OF EMISSIONS  
FROM HAAP<sup>13</sup>

Compound	TLV <sup>a</sup>
Methane	---
Ethane	---
Toluene	100
Carbon Monoxide	50
Methanol <sup>b</sup>	200
<u>n</u> -propanol <sup>b</sup>	200
<u>n</u> -butanol	---
Phenol <sup>b</sup>	5
Formaldehyde	2
Acetaldehyde	100
Acetone	1,000
Methyl Ethyl Ketone	200
Cyclohexanone	50
Ketene	0.5
Diketene <sup>c</sup>	---
Formic Acid	5
Acetic Acid	10
Methyl Formate	100
<u>n</u> -propyl formate	---
Methyl Acetate	200
<u>n</u> -propyl acetate	200
<u>Isobutyi</u> Acetate	150
Acetic Anhydride	5
Ammonia	25
Methylamine	10
Dimethylamine	10

TABLE 9. (cont'd)

Compound	TLV <sup>a</sup>
Hexamine	---
Nitric Oxide	25
Nitrogen Dioxide	5
Nitrous Oxide	---
Nitromethane	100
Nitric Acid	2
Methyl Nitrate	---
Cyclonite	---
Sulfur Dioxide	1 mg/m <sup>3</sup>

<sup>a</sup>Unless otherwise stated, the units of the threshold level values are ppm.

<sup>b</sup>Threshold level values for this compound refers to the recommended upper limit in concentration which should contact the skin.

<sup>c</sup>Less toxic than ketene, see Reference 14.

## RECOMMENDATIONS

### Process and Source Emissions

The emissions from the production of RDX-Composition B at HAAP at mobilization rates have been estimated using currently available process and source emissions data. While this inventory appears to be suitable for a first assessment of the air chemistry, it needs further development:

1. All source characteristics should be reviewed on location to confirm source heights, diameters, exit gas temperatures and flow rates.

2. The emissions from process vents showing any significant flow rate should be further identified by sampling and testing, using a chemical identification scheme in which the sample is fractionated into characteristic groups of compounds with gas chromatographic techniques, and the fractions examined further for specific compounds.
3. The process conditions should be recorded whenever future source samples are taken.
4. Material balances should be developed to more precisely define and confirm emissions rates.
5. Fugitive emissions should be sampled and tested using evacuated containers for "grab" samples.

Further sampling and testing of emissions sources is needed to determine what specific substances there may be in those gross emissions of organic compounds now identified only as classes of compounds. Distinction between  $\text{NO}_2$  and  $\text{NO}$  is desirable if the air chemistry is to be better defined.

The fact that mobilization rates may not be attained need not be an obstacle to further definition of emissions. Most of the process steps are performed with several similar units, all of which would be operating at mobilization. At least one of these units is frequently operated at its anticipated rate under mobilization. Where all the units have similar emissions, sources, and controls, the one unit could usually be sampled so as to be representative of the others.

#### Environmental Consequences

In the present study, the emissions from HAAP were identified to the extent available data permitted and their emission rates were estimated. With this information in hand, a literature review was conducted to determine the known or potential atmospheric chemistry of these emissions and a meteorological dispersion analysis was performed to estimate their ambient air concentrations. If the identified emissions and the estimated rates are comprehensive and reflect reality, then the literature review of the atmospheric chemistry and the dispersion analysis will also reflect reality. From the available data, it appears that the emission rates of air pollutants, especially of the nitrogen oxides, from HAAP are of sufficient magnitude to have a significant impact on the local environment. Therefore, it is recommended that action be taken along several lines.

It is clear from the emission inventory portion of this investigation that definitive data are lacking in several instances. In particular, the nitrogen oxide emission rate from HAAP is excessive. A sizeable quantity of the reported  $\text{NO}_x$  emission may actually consist of nitrous oxide, a relatively unreactive species. It is recommended that a source sampling program be initiated to define the emission rate of each nitrogen oxide species ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ ) from the ammonia oxidation, nitric acid concentrators, RDX/HMS manufacturing, and steam generation processes.

Dispersion modeling analysis was employed to elucidate the impact of the identified species on the local air quality. However, this is only an initial step. Further modeling studies which couple both meteorology and chemistry are necessary to assess the hundreds of potential reactions occurring over a diurnal cycle.

To rank reactions on the basis of importance is difficult in such an interactive, dynamic system. For example, the photolytic reactions which are significant during the daylight hours are unimportant at night. Furthermore, secondary reactions involving products of photolytic reactions assume roles of various importance at night. Even within a daylight or nighttime period, different reactions may assume roles of different importance depending on the reaction time of "state of progression" for the reacting matrix.

For computer modeling to serve as a valid approach, it is necessary that the relevant individual reactions be identified in terms of both reactants and products and that the rate expressions include known rate constants. The present review of atmospheric chemistry of emissions from RDX installations revealed several cases in which this information was lacking and the literature provided little guidance in estimating the desired information. In spite of these shortcomings, computer modeling is nevertheless recognized as a valid approach for bounding atmospheric chemistry problems. Computerized models of atmospheric chemistry should be adapted to the explosives plants atmosphere and employed to identify the significant reactions under various scenarios (mobilization, non-mobilization, day, night). This is a first priority need.

Laboratory experiments should be conducted in those cases where the atmospheric chemistry of emitted species is lacking. Unfortunately, there are many compounds which fall into this category. Therefore, the compounds which have

the greatest concentration in the atmosphere should be given precedence. Organic compounds with estimated plant boundary concentrations greater than 10 percent of the NAAQS (0.024 ppm carbon) include acetone, cyclohexanone, acetic acid, propyl acetate, and methyl nitrate.\* These compounds occur in sufficient concentration to warrant further investigation. Experiments can be conducted in large reaction vessels designed to simulate ambient conditions and define the reaction mechanisms needed for accurate simulation of the plant atmosphere.

The needs for further work are ranked below in order of priority, first to last.

1. Chemical kinetics modeling of the RDX/HMX air chemistry, to guide all subsequent efforts.
2. Source sampling with subsequent specialized analyses as described in EPA's Level I-Level II Assessment Methodology to identify organic pollutants which have not been identified in compliance testing to date.
3. Engineering analysis of the normal and abnormal operation of emissions controls systems to reassess emission rates based on data from 2.
4. Dispersion modeling of plant sites to give rough estimates of expected plant-boundary concentrations of pollutants.
5. Laboratory experiments to delineate the chemical and photochemical behavior of the organic solvents emitted here which have not been sufficiently examined and reported in the chemical literature.
6. Ambient sampling at plant boundaries after reiteration of the chemical kinetics modeling and dispersion modeling to give rough estimates of expected concentrations of harmful pollutants.

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\* Acetic anhydride also falls into this category; however, it is believed by the authors that this compound will quickly hydrolyze to form acetic acid.

### 3.0 TNT STUDY

#### FINDINGS

A summary of the emissions and emission rates from VAAP is presented in Table 10. These primary pollutants are classified into three groups. The first classification is comprised of those species designated as air pollutants by the U.S. Environmental Protection Agency (EPA). The second group consists of organic compounds such as solvents or byproducts released during TNT manufacturing processes. The third and final group includes miscellaneous species

TABLE 10. EMISSIONS SUMMARY FROM TNT MANUFACTURING AT VAAP<sup>a</sup>

Compound	Emission Rate	
	lb/day	ton/year
Group 1. EPA Criteria Pollutants		
Particulates	200	37
Sulfur Oxides	2,894	528
Carbon Monoxide	75	14
Nitrogen Oxides	6,855	1,251
Nonmethane Hydrocarbons	123	22
Group 2. Organics		
Tetranitromethane	b	b
Trinitrobenzene	b	b
Isomers of Trinitrotoluene	b	b
Nitrocresols <sup>c</sup>	b	b
Trinitrobenzaldehyde	b	b
Mononitrotoluenes	b	b
Toluene	b	b
Group 3. Miscellaneous		
Sulfuric Acid Mist	599	109
Nitric Acid Mist	b	b
Ammonia	d	d

<sup>a</sup>Assumes plant operation at six 50 TPD.

<sup>b</sup>Emission rates not available although they are believed to be small.

<sup>c</sup>High toxic

<sup>d</sup>Ammonia emissions are suspected, with data to confirm.

not considered in the first two groups. Data were not available in sufficient detail to allow the construction of a similar table for RAAP. However, it appears that the emission rates of particulates, sulfur dioxide, carbon monoxide, nitrogen oxides, and hydrocarbons at RAAP are even greater than those at VAAP.

#### EPA Criteria Pollutants

A qualitative evaluation of the impact of the EPA-designated air pollutants on the local environment can now be made by comparing the emission rates from the TNT installations with county-wide emission rates. Emission rates from RAAP and VAAP along with the county-wide emission rates are presented in Table 11. From the available data, it appears that a large fraction of sulfur oxides

TABLE 11. COMPARISON OF RAAP AND VAAP EMISSIONS TO COUNTY-WIDE EMISSIONS (TONS/YEAR)

Location	Particulates	SO <sub>2</sub>	CO	NO <sub>x</sub>	HC
RAAP <sup>a,b</sup>	13,883	6,357	294	7,933	360
Montgomery Co. <sup>a,c</sup>	16,449	7,924	21,251	11,130	4,349
% <sup>d</sup>	85	80	14	72	8
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VAAP <sup>a</sup>	36	74	---	177	---
(RTI Estimate) <sup>e</sup>	37	528 <sup>f</sup>	14	1,251	22
Hamilton Co. <sup>a,c</sup>	14,392	10,165	119,070	16,002	24,545
% <sup>d</sup>	0.2	0.7	0	1.1	0

<sup>a</sup>Data were retrieved from EPA's National Emissions Data System (NEDS) on June 7, 1977 (Reference 15). NEDS is a computerized data bank which holds detailed emissions inventory data for each county in the country. It should be noted that differences in practices of reporting and updating emissions data may prevent comparisons on the same basis.

<sup>b</sup>Emission rate is for 1972.

<sup>c</sup>Emission rate as of June 2, 1971.

<sup>d</sup>This value is the percent contribution of the army installation to county-wide emissions.

<sup>e</sup>RTI's emissions estimate at six 50 TPD operations.

<sup>f</sup>An additional 109 tons/year of H<sub>2</sub>SO<sub>4</sub> mist are also indicated.

and particulate emissions of Montgomery County, Virginia, are comprised of emissions from RAAP, in particular, from the power plant at RAAP. In contrast, the emissions from VAAP make up a small fraction of the total emissions of the highly industrialized Hamilton County, Tennessee. Since the county emission rates in Table 11 were developed for TNT plant operation at less than full capacity, the impact of emissions under full mobilization would result in an increase in the county-wide emission rates. The fraction of the county-wide emissions due to the TNT plants would also change. It should be noted that the above comparison of NEDS data does not assess the possibility of elevated ambient pollutant concentrations in the vicinity of or downwind from the plants.

EPA has established source performance standards (SPS) which specify the maximum permissible emission rates for several types of industries. Currently, these regulations have not been established for the explosives manufacturing industry. To set the TNT plant emissions rates (Table 10) into perspective, capacities of sources subject to EPA SPS with emissions equivalent to VAAP are presented in Table 12. The nitrogen oxide emissions from VAAP are equivalent to those from a coal fired boiler in a power plant having a capacity of 38 megawatts or a nitric acid plant which produces 2285 TPD. On this basis, the nitrogen oxide emissions appear to be significant and are expected to have a noticeable impact on the local environment.

A major issue for EPA criteria pollutants (Group 1 in Table 10) is the question of compliance with air quality standards (National Ambient Air Quality Standards (NAAQS) are given in Table 13) and nondegradation guidelines (given in Table 14). Although it is outside the scope of the present study, an estimate of ground level concentrations could be made for the primary pollutants\* using meteorological dispersion models as was done for the RDX/HMX plant. For secondary pollutants (pollutants that are formed in atmospheric

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\* Meteorological dispersion models can be applied to primary pollutants only if these pollutants are assumed to be nonreacting.

TABLE 12. CAPACITIES OF SOURCES SUBJECT TO EPA PERFORMANCE STANDARDS WITH EMISSIONS EQUIVALENT TO THE VAAP TNT INSTALLATIONS

Pollutant	Emission Rate lb/day	Source Category	Emission Regulation <sup>a</sup>	Equivalent Capacity
Particulate	200	Coal Fired Boiler	0.1 lb/10 <sup>6</sup> BTU	7.8 MW <sup>b</sup>
SO <sub>2</sub>	2894	Coal Fired Boiler	1.2 lb/10 <sup>6</sup> BTU	9.4 MW
		Sulfuric Acid Plant	4 lb/ton	724 TPD
Acid Mist	597	Sulfuric Acid Plant	.15 lb/ton	3980 TPD
CO	75	---	---	---
NO <sub>x</sub>	6855	Coal Fired Boiler	.70 lb/10 <sup>6</sup> BTU	38 MW
		Nitric Acid Plant	3.0 lb/ton	2285 TPD
HC	123	---	---	---

<sup>a</sup>See Reference 3.

<sup>b</sup>MW = megawatt; conversion assumes power plant efficiency of 32%.

reactions), dispersion models coupling both chemistry and meteorology are required. Because of the inaccuracies inherent to dispersion modeling and the many assumptions that are made (e.g., assumptions involving the plant location, the plant characteristics, and the emission characterization), ambient air concentration estimates from such meteorological models may be in error by a two or three-fold multiplier or divisor. This dispersion analysis does, however, give a general feeling for the effect that an industry has on air quality such that a comparison with the applicable air quality standards and an assessment of the environmental impact of new facilities can be made.

Once in the atmosphere, the ultimate fate of these EPA criteria pollutants is fairly straightforward. The particulate material will be deposited on the earth's surface. The sulfur dioxide will be oxidized to sulfates and sulfuric

TABLE 13. NATIONAL AMBIENT AIR QUALITY STANDARDS<sup>a</sup>

Pollutant	Averaging Time	Maximum Concentration	
		Primary Standard <sup>b</sup>	Secondary Standard <sup>c</sup>
Suspended particulate matter	Annual	75 $\mu\text{g}/\text{m}^3$	60 $\mu\text{g}/\text{m}^3$
	24 hr	260 $\mu\text{g}/\text{m}^3$	150 $\mu\text{g}/\text{m}^3$
Sulfur oxides	Annual	0.03 ppm	0.02 ppm
	24 hr	0.14 ppm	0.10 ppm
	3 hr		0.5 ppm
Carbon monoxide	8 hr	9 ppm	9 ppm
	1 hr	35 ppm	35 ppm
Nitrogen oxides	Annual	0.05 ppm	0.05 ppm
Nonmethane hydrocarbons	3 hr (6-9 am)	0.24 ppm	0.24 ppm
Photochemical oxidants as ozone	1 hr	0.08 ppm	0.08 ppm

Additional standards have been proposed for asbestos, beryllium, mercury, and lead; they are being prepared for fluorides, polycyclic organic compounds, odors (including hydrogen sulfide), chlorine, hydrogen chloride, arsenic, cadmium, copper manganese, nickel vanadium, zinc, barium, boron, chromium, selenium, pesticides, radioactive substances, and aeroallergens.

<sup>a</sup>See Reference 4.

<sup>b</sup>Primary standards have been established to protect public or human health.

<sup>c</sup>Secondary standards have been established to protect soil, water, vegetation, materials, and animals as well as to maintain personal comfort, weather, and visibility.

TABLE 14. MAXIMUM ALLOWABLE INCREASE IN CONCENTRATION FOR SO<sub>2</sub> AND PARTICULATE MATTER<sup>a</sup>

Pollutant	Class I ( $\mu\text{g}/\text{m}^3$ )	Class II ( $\mu\text{g}/\text{m}^3$ )	Class III <sup>b</sup> ( $\mu\text{g}/\text{m}^3$ )
Particulate matter			
Annual average	5	10	60
24 hour maximum	10	30	150
Sulfur dioxide			
Annual average	2	15	(0.02 ppm)
24 hour maximum	5	100	(0.10 ppm)
3 hour maximum	25	700	(0.5 ppm)

<sup>a</sup>See Reference 5. The recently promulgated nondegradation regulations affect only new sources, in contrast to NAAQS which affect both existing and new sources. These regulations require weighing the incremental deterioration against social and economic considerations and limiting increases in sulfur dioxide and particulate matter concentrations within each of three classification areas. The nondegradation guidelines will not allow industrial development in areas designated Class I, will permit a modest increase in industrial development in Class II areas, and will allow industrial development in Class III areas as long as NAAQS are met.

<sup>b</sup>Federal Secondary Ambient Air Quality Standard.

acid which will form aerosols. The fate of these aerosols will then include rainout or dry deposition. The carbon monoxide in the atmosphere will be oxidized to carbon dioxide. The nitrogen oxides in the atmosphere will be converted to nitric acid and nitrates with subsequent removal by rainout and dry deposition. The hydrocarbons will be oxidized into carbon dioxide, water, and aerosols.

In addition, the hydrocarbons and nitrogen oxides are also precursors of the secondary pollutant, ozone (photochemical oxidant). Ozone is generated and accumulates in the cyclic process illustrated in Volume 3. In the cycle, free radicals (R) are generated from organic compounds by processes following the photolysis of nitrogen dioxide. These free radicals combine with atmospheric oxygen to form peroxy radicals ( $RO_2$ ) which are capable of oxidizing nitric oxide to nitrogen dioxide. For each molecule of nitric oxide oxidized to nitrogen dioxide by a nonozone species, a molecule of ozone accumulates in the atmosphere. At high hydrocarbon and nitrogen oxide concentrations representative of urban atmospheres, the concentration of hydrocarbons is more influential than that of nitrogen oxides in dictating the resulting ozone concentration. At lower hydrocarbon and nitrogen oxide concentrations, representative of nonurban atmospheres, the ozone concentration is thought to be influenced more strongly by the nitrogen oxide concentration. Thus, injection of nitrogen oxides into nonurban air may enhance the ozone generative potential of the air mass. It should be noted, however, that under conditions where the concentration of nitrogen oxides is in substantial excess of the concentration of hydrocarbons, oxidant formation is inhibited and any ozone that may enter such an atmosphere is quickly destroyed by its reaction with the nitrogen oxides.

Since explosives plants are sources of both organic and nitrogen-containing compounds, the setting of the facility as well as the magnitude of the emissions relative to the local emissions will determine the impact on both the local and downwind oxidant levels. The data in Table 10 show that the emission rate of nitrogen oxides is much greater than that of any other pollutant and that the ratio of the emission rates of nitrogen oxides to hydrocarbons ranges from 20 to 60. The dominant impact of this emissions profile in the immediate vicinity of the TNT facility will be to destroy any ozone which may enter the plume and to inhibit its formation until atmospheric processes facilitate attainment of a more favorable nitrogen oxide-hydrocarbon ratio. Thus, the concentration of ozone in the plume should be less than that in the surrounding air parcels. In the atmosphere downwind from the TNT facilities, the ratio may be more favorable to ozone production. However, it is difficult to ascertain the contribution of a single source to rural oxidant levels at long distances downwind because the ozone precursors may be emitted by many sources within the region.

### Non-EPA Criteria Pollutants

Other atmospheric emissions also are associated with the TNT facilities. They include such compounds as tetranitromethane, toluene, and nitrotoluenes. Unfortunately, data that would allow an estimate of emission rates for these compounds are not available (see Table 10). Although the source strengths of these compounds are thought to be low, they should not be dismissed simply because their emission rates are currently undefined. Instead, this issue should be addressed by a comprehensive sampling program. The resulting data base could then be used to develop a list of pollutants prioritized on the basis of emission rates and also an estimate of ambient air concentrations.

A discussion of the potential atmospheric chemistry of the emitted compounds was presented in the previous sections. In general, the literature revealed little information on the atmospheric chemistry of these compounds; therefore, mechanisms were proposed by analogy. Although the details of the atmospheric decomposition of tetranitromethane are currently undefined it is believed that the TNM will decompose into carbon oxides and nitrogen oxides.

In the atmosphere, the tonuele may degrade to carbon monoxide, carbon dioxide, and organic species such as acids, aldehydes, and alcohols. These organic oxidation products may then form aerosols. The toluene may also be nitrated to form a variety of nitro-substituted aromatics such as the nitro-cresols. Nitrotoluenes may be oxidized or nitrated in a similar fashion. The nitro group of the nitrotoluenes may also dissociate from the ring. In addition to numerous oxidized and nitrated products, peroxyacetyl nitrate and peroxybenzoyl nitrate, known eye irritants, may be produced.

### Atmospheric Chemistry

In the atmosphere, the lifetime of an air contaminant is largely determined by the propensity of the compound to photodissociate and by its reactivity with species such as ozone and hydroxyl radicals. A compilation of half-lives ( $t_{1/2}$ ) has been assembled in Table 15 for selected air contaminants associated with TNT installations. These half-lives consider each pathway to be independent of the others and do not consider secondary or competitive pathways. The photolytic half-life assumes a first order reaction with the light intensity

equivalent to that with the sun at a zenith angle of  $40^\circ$  ( $z = 40^\circ$ ).<sup>11,10</sup> The half-life in the presence of ozone assumes a constant ozone concentration equal to the NAAQS,  $[O_3] = 0.08$  ppm (see Table 13). A range of half-lives is presented for the compound in the presence of hydroxyl radicals, because the mean ambient hydroxyl radical concentration currently is not well established. Since it is believed to lie between  $0.5$  and  $5.0 \times 10^{-7}$  ppm ( $0.5 \times 10^{-7} < [OH] < 5 \times 10^{-7}$  ppm),<sup>9</sup> these two values were chosen to bound the disappearance rate due to hydroxyl radical attack.

It can be seen that the nitrogen oxides are the most reactive species in the atmosphere. Half of the nitric oxide in the atmosphere may react within minutes with ozone to form nitrogen dioxide and within hours with hydroxyl radicals to form nitrous acid. In the atmosphere, half of the nitrogen dioxide may photodissociate into nitric oxide and atomic oxygen within one minute. The nitrogen dioxide may also react with ozone or hydroxyl radical within hours. Similarly, the secondary pollutant, nitrous acid, also photodissociates rapidly into nitric oxide and hydroxyl radicals. Within six minutes, half of this acid may photodissociate. Nitric acid photodissociates at a negligible rate relative to nitrous acid; it has a half-life of approximately fifty-five hours. Half of the toluene in the atmosphere may react with hydroxyl radicals within two to twenty-one hours. In general, the half-lives of the remaining reactions between the air contaminants and light, ozone, or hydroxyl radicals are either much longer or not available.

To determine the total effect of the emissions from RAAP and VAAP on the atmosphere, the secondary pollutants must also be considered. Two of the chief secondary pollutants in this atmosphere include ozone and nitrous acid. The formation and chemistry of ozone as well as the potential effects of munition emissions on its formation and destruction were discussed earlier. Nitrous acid, a secondary pollutant, is formed in an equilibrium reaction involving nitric oxide, nitrogen dioxide, and water and also in the reaction between nitric oxide and hydroxyl radicals. Nitrous acid in the presence of secondary amines can lead to the formation of carcinogenic nitrosamines either in ambient air or in the work place. Based on the findings of this study, nitrosamine

TABLE 15. HALF-LIVES OF SELECTED AIR CONTAMINANTS ASSOCIATED WITH THE MANUFACTURE OF TNT<sup>a,b</sup>

Compound (A)	A + h → t <sub>1/2</sub>	A + O <sub>3</sub> → t <sub>1/2</sub>	A + OH → t <sub>1/2</sub>
Carbon monoxide	---	1 x 10 <sup>7</sup> days	4.6-46 days
Methane	---	9.4 x 10 <sup>5</sup> days	87-870 days
Toluene	---	330 days	2.1-21 hr
Nitric oxide	---	0.33 min	2.8-28 hr
Nitrogen dioxide	1.1 min	3.0 hr	3.5-35 hr
Nitrous acid	5.8 min	---	7.0-70 hr
Nitric acid	55 hr	---	6.9-69 days
Tetranitromethane	?	?	?
Mononitrotoluenes	?	?	157-1570 days
Sulfur dioxide	102 hr	6 x 10 <sup>4</sup> days	26-260 hr
Sulfuric acid	---	---	---

<sup>a</sup>The half-life of a reactions is defined by the equation,  $t_{1/2} = 0.693/k$  sec. Except for the photolyses of nitrous acid and sulfur dioxide, the rate constants are those reported in the preceding sections. The rate constant for the photolysis of nitrous acid is from Reference 20, and that for the photolysis of sulfur dioxide is from Reference 19.

<sup>b</sup>A blank space (---) designates that the reaction between a particular pollutant and light, ozone, or hydroxyl radical is unimportant in the atmosphere. A question mark (?) indicates that the rate constant for the reaction between a pollutant and light, ozone, or hydroxyl radical is unavailable.

formation is not anticipated. However, if future sampling programs reveal amine emissions, then the potential would exist for nitrosamine formation.

## Toxicity

None of the compounds emitted from RAAP and VAAP are known to be carcinogenic; however, some are toxic. Previously, it was mentioned that 4,5-dinitro-o-cresol and 3,5-dinitro-p-cresol are toxic. The nitrogen oxides, nitric acid, tetranitromethane, sulfur dioxide, and sulfuric acid are known to irritate the eyes and upper respiratory tract. In addition, TNM is known to damage the liver; nitric and sulfuric acids are known to corrode teeth. Permissible threshold level values (TLV) for the emitted compounds have been established and are presented in Table 16.<sup>13</sup>

TABLE 16. PERMISSIBLE THRESHOLD LEVEL VALUES OF EMISSIONS FROM TNT INSTALLATIONS<sup>13</sup>

Compound	TLV <sup>a</sup>
Carbon Monoxide	50
Methane	---
Toluene	100
Nitric Oxide	25
Nitrogen Dioxide	5
Nitrous Acid	---
Nitric Acid	2
Tetranitromethane	1
Nitrotoluene <sup>b</sup>	5
Dinitrotoluene <sup>b</sup>	1.5 mg/m <sup>3</sup>
Trinitrotoluene <sup>b</sup>	0.2
Sulfur Dioxide	5
Sulfuric Acid	1 mg/m <sup>3</sup>

<sup>a</sup>Unless otherwise stated, the units of the threshold level values are ppm.

<sup>b</sup>Threshold level values for this compound refers to the recommended upper limit in concentration which should contact the skin.

## RECOMMENDATIONS

### Process and Source Emissions

The TNT process emissions inventory should be considered as preliminary until further sampling and testing more adequately define the pollutants. Without more data, the emissions cannot be identified properly or their concentrations projected for assessment as was done for the RDX process. Although quantitative data are lacking, suspected non-EPA criteria pollutants have been included in the study of the air chemistry. However, no meteorological dispersion modeling was attempted. Instead, the effort for the present study was concentrated on the RDX process, which had more data and appeared to have more urgent problems.

Source sampling of a single continuous process line (e.g., the computer-controlled line at NAAP, or one line at VAAP) should be conducted in depth to provide data on the pollutants and the process parameters plus the condition of the controls. The continuous TNT process has potential for minimizing emissions only if the controls are properly functioning.

### Environmental Consequences

If the emissions identified and estimated in the engineering process analysis of the current study were comprehensive and precise, then emission rates of air pollutants from the TNT facility at VAAP could be considered too low to have a significant impact on the local environment. On this basis, no additional action can be recommended.

It should be remembered, however, that the present study is primarily a literature review. If major emissions do exist, were not documented, and therefore were overlooked, then a comprehensive investigation is appropriate. The following is a discussion of an ordered prioritized approach to dealing with such a problem. In this situation, the suggested approach is iterative and involves:

1. Sampling (both source and ambient).
2. Computer modeling (dispersion and photochemical).
3. Laboratory experiments.

To determine the impact of TNT plants on the atmospheric environment, two pieces of information are required: pollutant identity and pollutant emission rate. The engineering process analysis portion of the current study has addressed these points and has shown definitive data to be lacking in many instances. A source sampling program should be initiated to define the emitted species and their emission rates.

On completion of the sampling study, specific programs can be undertaken to elucidate the impact of the identified species on local air quality. The first step includes dispersion modeling to define the range of expected concentrations. Pollutant concentrations are needed for several reasons:

1. To enable an assessment of compliance for the EPA primary criteria pollutants.
2. To estimate bounds for ambient air contaminant concentrations which correspond to the uncertainty range for the corresponding emissions rates.
3. To evaluate the sensitivity of ambient air quality to varying degrees of emissions control.
4. To facilitate an evaluation of the hazard that could result from non-EPA pollutants in the local environs.
5. To provide concentration estimates for designing and air monitoring system (instrumentation and siting).
6. To make possible a detailed assessment of the atmospheric chemistry of both primary and secondary air pollutants.

Formation of secondary pollutants will occur as the plume from emissions sources travel to ground-based receptors. The dispersion model employed should be capable of resolving both primary pollutant concentrations aloft and at ground level. This would help to estimate the rate of destruction of primary pollutants and the concurrent formation rate of secondary species. Presently available dispersion/kinetics models should be employed to define the expected range of air contaminant concentrations within the zone of influence of plant facilities.

Without modeling effort, it is unlikely that much insight can be gained as to the air chemistry of the plant emissions. The matrix of air contaminants above the TNT plant is highly complex. The individual reactions that may be

occurring over a diurnal cycle number into the hundreds. Many of these reactions may be involved in chain reactions. To rank reactions on the basis of importance is difficult in such an interactive, dynamic system.

The importance of many reactions varies nonlinearly with reactant concentration. A good example is the thermal oxidation of nitric oxide to nitrogen dioxide, which is second order in NO concentration. This reaction is important at high nitric oxide concentrations such as exist in power plant plumes and automobile exhaust. At ambient NO levels, however, thermal oxidation exerts a minor role.

Existing illumination determines the importance of various reactions. It is evident that photolytic reactions which are significant during the daylight hours are unimportant at night. Furthermore, secondary reactions involving products of photolytic reactions assume roles of various importance at night. Even within a daylight or nighttime period, different reactions may assume roles of different importance depending on the reaction time or "state of progression" for the reacting matrix.

Two points implicit in the modeling approach are also potential shortcomings. The individual reactions must be identified in terms of both reactants and products. Secondly, the rate expressions including rate constants must be known. The present review of atmospheric chemistry of emissions from TNT installations revealed several cases in which this information was lacking and for which the literature provided little guidance in estimating the desired information. In spite of the shortcomings of the modeling approach, it nevertheless appears to be the best approach for bounding atmospheric chemistry problems. Computerized models of atmospheric chemistry should be employed to identify the significant reactions under various scenarios.

Laboratory experiments should be conducted in those cases where the mechanisms of atmospheric chemical reaction of emitted species is lacking. Two compounds so identified in the current study are tetranitromethane and nitrotoluene. Experiments can be conducted in large reaction vessels designed to simulate ambient conditions and known as smog chambers.

## 4.0 OPEN BURNING AND INCINERATION OF WASTE MUNITIONS

### FINDINGS

#### Problem Statement

In the interest of national security, enormous inventories of propellants, explosives, and pyrotechnics are maintained. Because the items held in the stockpile are subject to deterioration and obsolescence, leading to potential safety hazards, safe procedures for their removal have to be developed. There are a number of options presently available for disposing of waste munitions. The materials may be sold, recycled or salvaged as much as possible, and incineration technology is being developed. However, open burning still is and will continue for some time to be a method of disposal for practically all waste explosives. There are several undesirable features associated with this method. For example, it is a source of serious air pollution and a fire hazard to operating personnel; disposition is limited by weather conditions, and efficient disposal of large quantities of waste explosives is involved.

#### Current Status of Munitions Disposal at RAAP, VAAP, and HAAP

Open burning is practiced at three munitions plants, RAAP, VAAP, and HAAP. Of these plants, only RAAP also has an air curtain incinerator (built in 1976) and a prototype rotary kiln incinerator (250 pounds per hour) which has been evaluated since 1975. Two full size rotary kilns (550 pounds per hour) are scheduled for completion at RAAP in 1978. The air curtain incinerator is used mainly for disposal of explosives contaminated materials, packaging, paper, rags, and other contaminated waste.

#### Estimated Quantities of Materials Burned By All Army Installations

Thirty-two Army installations, located in 25 States, conducted open burning of waste explosives and explosives contaminated materials periodically during 1975.<sup>16</sup> The quantities of waste explosives and explosives contaminated

materials open burned by these installations are shown in Tables 17 and 18, respectively.

TABLE 17. QUANTITIES OF WASTE EXPLOSIVES OPEN BURNED BY ARMY INSTALLATIONS\*

INSTALLATION	Tons per Year	
	1974	1975
<b>ARMY AMMUNITION PLANTS</b>		
Radford	1080.0	720.0
Iowa	498.0	518.4
Longhorn	355.2	355.2
Milan	289.2	289.2
Louisiana	252.2	165.6
Volunteer	244.8	244.8
Holston	214.8	228.0
Joliet	213.6	133.2
Lone Star	75.6	42.0
Lake City	69.6	69.6
Indiana	67.2	74.4
Kansas	46.8	46.8
Twin Cities	1.2	1.2
<b>ARSENALS</b>		
Pine Bluff	164.6	164.6
Redstone	116.4	139.2
Picatinny	63.6	63.6
Edgewood	4.8	4.8
<b>DEPOTS/DEPOT ACTIVITIES</b>		
Seneca	1312.8	816.0
Anniston	637.2	396.0
Lexington-Blue Grass	584.4	363.6
Letterkenny	582.0	361.2
Tooele	220.8	136.8
Red River	188.4	116.4
Sierra	184.8	115.2
Savanna	162.0	100.8
Navajo	74.4	45.6
Pueblo	9.6	6.0
Umatilla	2.4	1.2
Wingate	1.2	1.2

TABLE 17. (cont'd)

INSTALLATION	Tons per Year	
	1974	1975
OTHER		
Fort Sill	230.4	230.4
	<hr/>	<hr/>
TOTAL	7947.6	5950.8

\*From AMCPA-E Draft Memorandum, Subj: Open Burning of Waste Munitions, of 7 January 1976.

TABLE 18. QUANTITIES OF EXPLOSIVES-CONTAMINATED WASTES OPEN BURNED BY INSTALLATIONS\*

INSTALLATION	Tons per Year	
	1974	1975
ARMY AMMUNITION PLANTS		
Holston	31620.0	14268.0
Kansas	1560.0	1560.0
Lone Star	1560.0	780.0
Milan	936.0	936.0
Radford	540.0	372.0
Joliet	288.0	96.0
Iowa	240.0	240.0
Badger	204.0	120.0
Sunflower	132.0	204.0
Louisiana	96.0	36.0
Indiana	96.0	180.0
Volunteer	84.0	84.0
Longhorn	48.0	48.0
Lake City	12.0	12.0
ARSENALS		
Pine Bluff	456.0	456.0
Picatinny	192.0	192.0
Redstone	36.0	48.0
Edgewood	24.0	24.0

TABLE 18. (cont'd)

INSTALLATION	Tons per Year	
	1974	1975
DEPOTS/DEPOT ACTIVITIES		
Seneca	7440.0	4620.0
Savanna	1152.0	720.0
Letterkenny	900.0	564.0
Red River	336.0	204.0
Lexington-Blue Grass	288.0	180.0
Sierra	228.0	144.0
Anniston	192.0	120.0
Tooele	6.0	6.0
Umatilla	6.0	6.0
TOTAL	48,672.0	26,172.0

\*From AMCPA-E Draft Memorandum, Subj: Open Burning of Waste Munitions, 7 January 1976.

#### Combustion Products Generated

#### Combustion Products Sampled

From discussions with the personnel at RAAP, HAAP, and VAAP, it became apparent that no sampling of combustion products generated in the open burning of explosives has been conducted. Attempts at locating any pertinent information on this point resulted in the discovery of some work that the Ammunition Equipment Office at Tooele had done.<sup>17</sup> According to a report by Ralph W. Hayes, only minimal previous work had been conducted in the Soviet Union and in this country by the Burlington and Pantex AEC Plants.

The previous work, as well as that conducted by the Ammunition Equipment Office, has been very small scale (25 g maximum charge) and is thus open to questions as to its relevance to large scale open burning. Only the following gaseous components were sampled for:

O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, NO<sub>x</sub>, CH<sub>4</sub>, HCl, HF, P<sub>2</sub>O<sub>5</sub>, and soot.

Burlington has conducted gas sampling tests by burning 6 g of various explosives and then extrapolating the results to a large scale open burning of 3.8 tons (the average daily amount burned) of explosives for the purposes of estimating daily pollution emissions. Some of the data are tabulated in Table 19.

TABLE 19. ESTIMATED DAILY POLLUTION EMISSIONS FROM BURNING EXPLOSIVES

Pollutant	Burning 3.8 Tons PBX-9404	Burning 3.8 Tons LX-09	Burning 3.8 Tons Comp B-3	Burning 3.8 Tons TNT
Carbon Monoxide (lbs)	23	4	19	213
Oxides of Nitrogen (lbs)	144	110	141	570
Hydrocarbons (lbs)	0	0	0	4
Phosphorous Pentoxide (lbs)	49	0	0	0
Hydrochloric Acid (lbs)	87	0	0	0
Hydrofluoric Acid (lbs)	0	23	0	0
Soot (lbs)	0	0	0	684

Mason and Hanger, Silas Mason Co., Inc., have also conducted experimental burns of several explosives to determine "typical" emission factors for the open burning of these materials.<sup>18</sup> A summary of some of their results is presented in Table 20. However, the burns were made again on very small quantities (of the order of one gram) of these materials. The test apparatus supposedly was designed to simulate open burning conditions. However, because of the differences in the quantities burned and the wide variety of conditions encountered in actual practice, such simulations can never be completely representative of actual opening burning. Thus, any such calculations are highly tenuous at best.

TABLE 20. EMISSION FACTORS FOR THE OPEN BURNING OF SOME EXPLOSIVES (LBS OF POLLUTION PER TON OF EXPLOSIVE OPEN BURNED)

Explosive	Carbon Monoxide	Oxides of Nitrogen (NO <sub>x</sub> )	Fluorocarbons & Hydrocarbons	Phosphorus Pentoxide	Hydrochloric Acid	Hydrofluoric Acid	Soot
TNT	56.0	150.0	1.1	0	0	0	180.0
Comp B-3	5.0	37.1	0	0	0	0	0
PBX 9404	6.1	37.9	0	4.0	22.9	0	0
LX-07	1.3	27.9	4.0	0	0	54.0	0
LX-09	1.1	27.9	0	0	0	6.1	0

#### Combustion Products not Sampled but Expected to be Present as Deduced From Other Work

In addition to the more prevalent air pollutants listed above, the open burning of waste explosives and propellants may result in the emission of lesser amounts of a number of other potentially harmful substances. Table 21 lists some additional air pollutants which can arise from the open burning of waste explosives and propellants which may pose potential environmental and/or personal hazards.<sup>16</sup> Generally, these secondary substances comprise only a very minor amount of the total open burning emissions, since they arise from a small portion of the waste explosives and propellants being open burned. However, many of the emissions resulting from the opening burning of pyrotechnic materials either are known or suspected to be potentially quite hazardous. Pyrotechnics account for only approximately three percent of the current Navy inventory of waste explosives and propellant materials awaiting disposal, and only a portion of these pyrotechnics are being open burned.

It is well known that polycyclic aromatic hydrocarbons may be produced during the incomplete combustion of wood, oil, petroleum, cellulose, and a large variety of hydrocarbons.<sup>19,20</sup> Both the fuel/air equivalence ratio and temperature have a direct effect on the production of polycyclic aromatic hydrocarbons. High equivalence ratio or low temperature or both contribute to high polycyclic aromatic hydrocarbon production.

#### Combustion Products not Sampled but Probably Present as Deduced from Relevant Chemistry

##### Nitrosamines --

The environmental distribution of N-nitroso compounds has been placed in a new perspective since N-nitrosodimethylamine (DMN) was found in the air in two U.S. cities.<sup>21,22</sup> Using a new sensitive and selective detection system for N-nitroso compounds,<sup>23-25</sup> Fine et al. found DMN at the 3.0 to 320 ng/m<sup>3</sup> level in the air in Baltimore, Maryland, at the 5.0 to 170 ng/m<sup>3</sup> level in the

TABLE 21. SECONDARY AIR POLLUTANTS WHICH MAY RESULT FROM THE OPEN BURNING OF WASTE MUNITIONS<sup>a</sup>

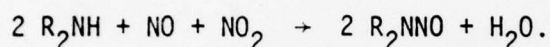
Name of Chemical Element or Compound	Present in (Some)	Potentially Hazardous Emission Products From Open Burning <sup>b</sup>
Aromatic Dyes	Colored smoke - producing pyrotechnics	Dyes & decomposition products
Asbestos	Pyrotechnics	Asbestos
Barium	Pyrotechnics	BaO
Boron	Liquid propellants	Decomposition Products, B <sub>2</sub> O <sub>3</sub>
Bromine	Pyrotechnics	HBr, Br <sub>2</sub>
Chlorine	Pyrotechnics, propellants	HCL, Cl <sub>2</sub> , COCl <sub>2</sub>
Chromium	Pyrotechnics, decay elements	Cr <sub>2</sub> O <sub>3</sub>
Copper	Pyrotechnics, propellants	CuO
Fluorine	Propellants	HF
Lead	Propellants	PbO
Phosphorus (white)	Pyrotechnics (tracers & incendiaries) & ordance	P <sub>2</sub> O <sub>5</sub>
Phosphorus (red)	Pyrotechnics	P <sub>2</sub> O <sub>5</sub>
Selenium	Delay elements	SeO <sub>2</sub>
Strontium	Pyrotechnics	SrO
Sulfur	Explosives, pyrotechnics	SO <sub>2</sub> , SO <sub>3</sub>
Trinitrotoluene	Explosives	HCN

<sup>a</sup>Effluents which are expected to be emitted only in limited quantities.

<sup>b</sup>Emissions may be from airborne (vaporized, aerosolized, etc.) uncombusted materials as well as partially or completely combusted materials. Emissions listed are not all inclusive.

air in Belle, West Virginia. DMN has also been reported in nearby Curtis Bay and in the Kanawha River in Belle.<sup>26</sup> Because N-nitrosamines have been absent in aquatic and atmospheric environments, the possibility that a compound as carcinogenic as DMN may be an air pollutant had not been considered previously.

The chemical formation of nitrosamines has been the subject of numerous studies that have recently been reviewed by Mirvish.<sup>27</sup> Although most of the reported studies have been concerned with condensed-phase reaction systems, the formation of nitrosamine in the gas phase has been demonstrated.<sup>28,29</sup> Neurath *et al.*<sup>29</sup> showed that the formation of nitrosamines from secondary amines requires an equimolar mixture of nitrogen oxides. This reaction, which occurs in the gaseous phase, can be represented as follows:



Bretschneider and Matz<sup>28</sup> showed that diethylamine and nitrogen dioxide (NO<sub>2</sub>) at concentrations of 50 to 100 parts per million (ppm) reacted within seconds to form measurable levels of nitrosamine.

Some work with gas-phase systems is currently being conducted by EPA.<sup>30</sup> In this study, gaseous dimethylamine, (CH<sub>3</sub>)<sub>2</sub>NH, has been shown to react with gaseous nitrous acid, HONO, in air to yield N-nitrosodimethylamine, (CH<sub>3</sub>)<sub>2</sub>N-NO. This on-going research has shown that, in a humid atmosphere containing dimethylamine, NO, NO<sub>2</sub>, and HONO at concentrations of 0.5 to 2 ppm, the amine reacted at a rate of about 4 percent per minute yielding N-nitrosodimethylamine as the major reaction product. In the absence of HONO and humidity, the rate was lower by a factor of four, approximately. It now appears that a much more intense look will have to be taken at the concentrations of nitrosamine precursors in pollutant atmospheres. Thus, knowledge of the environmental concentrations of nitric oxide, nitrogen dioxide, nitrous acid, nitrites, nitrates, and primary, secondary, tertiary, and quaternary amines will be required.

The nitric acid manufacturing area at HAAP had a very high ambient NO<sub>x</sub> concentration. Just east of this area, in the path of prevailing winds, is the "B Line" area. In this area, ammonia along with other low molecular weight amines is recovered from the spent acetic acid. Thus all the ingredients for ambient nitrosamine formation appear to be present in this locale and their formation should be investigated.

Red Water

Concentration and/or incineration of red water can become quite a significant activity at a plant especially when there are no outside customers to sell it to. Thus, RAAP, VAPP, JAAP, and NAAP all concentrate or incinerate red water. Thus, in the 1969-1971 production period approximately 45 million lbs of TNT per month were produced. The capacity production at the three facilities is projected to be:

VAAP	500,000 lbs/day
RAAP	150,000 lbs/day
NAAP	530,000 lbs/day

Using 340 production days per year as a basis, these amounts translate into the following yearly capacities:

VAAP	204 MM lbs/year
RAAP	51 MM lbs/year
NAAP	180.2 MM lbs/year

Using the NAAP facilities standard operating manual data for production of 180.2 MM lbs of TNT per year, the following amounts of red water generated can be projected:

	M lbs/day		MM lbs/year	
	100%	120% of Capacity	100%	120% of Capacity
VAAP	415	---	141.2	---
RAAP	104	---	35.3	---
NAAP	367	439	124.6	149.5

According to the NAAP facilities standard operating manual data red water consists of:

Water	77.6%
Inorganic Salts	8.1%
Organics	14.3%

Thus, at the projected full capacity operation, the following amounts of "organics" in red water are generated:

VAAP	59,000 lbs/day
RAAP	15,000 lbs/day
NAAP	53,000 lbs/day

These amounts of organics are, therefore, subject to potential concentration or destruction by the plants. From all the literature that we have seen, there appears to be entirely too little attention paid to the details of disposal of these large quantities of organics.

For example, a brief general description of how red water is processed at JAAP is as follows:<sup>31</sup> There are six four-stage evaporators with a total capacity of 531 gpm and 12 rotary kiln incinerators with a total capacity of 50 gpm. The evaporators concentrate the red water to about 35 percent solids content for incineration in the rotary kilns. The ash from the incinerator is accumulated in an open area within the manufacturing area. The condensate for the evaporation step has a characteristic pale yellow color, contains a small amount of nitrobenzenes and is discharged to the TNT ditch which empties into a creek. The incineration of the concentrated red water generates air pollutants including particulates and nitrogen and sulfur oxides. Based on average discharge data, 3.8 lbs of particulates and 28 lbs of nitrogen oxides (as NO<sub>2</sub>) per ton of TNT manufactured are generated.

Using the JAAP capacity TNT production rate as the basis, the following amounts of pollutants were projected to be emitted in red water incineration:<sup>32</sup>

NO <sub>x</sub>	16,800 lbs/day
Particulates	3,600 lbs/day
SO <sub>2</sub>	1,150 lbs/day.

The RAAP red water destruction complex utilizes four rotary kilns to evaporate the liquid waste. Red water is evaporated to dryness and the nitro-bodies are incinerated leaving behind ash. A summary of the Red Water Destructor No. 2 Unit data is given in Table 22.<sup>33</sup> These data again emphasize the need for closer attention to red water destruction techniques because of the emission of large quantities of NO<sub>x</sub>, particulates, and nitro-bodies. Furthermore, in none of the reports that we have seen has the composition of the emitted nitro-bodies from the red water destruction process been analyzed.

TABLE 22. EMISSIONS FROM THE RED WATER DESTROYER

	Average	Range
Stack temperature	170°F	155 - 180
Stack gas velocity	3150 ft/min	2020 - 4120
Stack flow	2920 scfm	1840 - 3750
Stack flow percent moisture	45 %	43 - 50
Particulate emission rate	0.2 lb/hr	0.1 - 0.4
SO <sub>x</sub> emission rate	2.7 lb/hr	2.0 - 4.2
NO <sub>x</sub> emission rate	52.6 lb/hr	27.2 - 84.9
NO <sub>2</sub> emission rate	44.6 lb/hr	35.0 - 61.8
Total nitrobody emission rate	2.3 lb/hr	1.6 - 3.2

#### Thermochemistry Computer Program

In addition to the sampling problems created because of the wide variety of explosives compositions incinerated, another set of problems is introduced because of the different burning characteristics of the different explosives compositions. Some munitions compositions may burn while others will detonate. They may burn or detonate at distinct intervals, at irregular intervals, or in flurries. As a result, exhaust temperatures will vary greatly and the

pollutant emissions may surge and subside as a function of the burning or detonating frequency. Thus, to design an effective sampling program, some prior knowledge or expectation of pollutants from specific explosives compositions is required. The Ammunition Equipment Office, Tooele Army Depot, Tooele, Utah has experimented with a computer program, developed initially for the study of rocket engines, in attempts to predict products of combustion of explosives in the deactivation furnace. The computer program was developed by the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base, California.<sup>34</sup>

The computer program simulates furnace operating conditions; evaluates the chemical compositions of such input data as fuel, air, and munitions consumption rates; considers all species of compounds that may be formed; and predicts the specific products that may exist at furnace stack exit conditions. These data were used to determine which pollutants to sample for.

The computer program is based on a system in equilibrium at a given temperature. The actual furnace process is, of course, a rapid process in which sufficient time for an equilibrium condition may not be provided. For this reason products such as  $\text{No}_x$ , which are very dependent on the cooling rate as well as the combustion temperature are not easily predicted.

A brief description of the kinds of data that can be generated by the computer program on incinerating TNT and a RDX/TNT mixture (Composition B) follows.<sup>35</sup> The combustion species considered by the program on incineration of TNT in the presence of air are listed in Table 23. A typical computer run is illustrated in Table 24. In Tables 25-27 are data that were extracted from the computer runs, converted into grams of species generated per 100 g of TNT incinerated and arranged in decreasing order of the amount generated. Only the species generated in better than  $10^{-5}$  mole per 100 g of TNT incinerated were considered. The effect of two experimental parameters: (1) the amount of air, and (2) the incineration temperature upon the composition of incineration products are examined here. In Tables 25 and 26 are listed the most prevalent species generated at TNT/air ratios of 440 and 1.27 respectively. Thus, the low and high air content incineration results may be summarized as follows: (Text continues on page 55.)

TABLE 23. SPECIES CONSIDERED

C	HNO
CH	HNO <sub>2</sub>
CHN	HNO <sub>2</sub>
CHNO	HNO <sub>3</sub>
CHO	HO
CH <sub>2</sub>	HO <sub>2</sub>
CH <sub>2</sub> O	H <sub>2</sub>
CH <sub>3</sub>	HCOOH
CH <sub>4</sub>	H <sub>2</sub> N
CH <sub>3</sub> OH	H <sub>2</sub> N <sub>2</sub>
CN	H <sub>2</sub> O
CNN	H <sub>2</sub> O <sub>2</sub>
CN <sub>2</sub>	H <sub>3</sub> N
CO	H <sub>4</sub> N <sub>2</sub>
CO <sub>2</sub>	N
C <sub>2</sub>	NO
C <sub>2</sub> H	NO <sub>2</sub>
C <sub>2</sub> H <sub>2</sub>	NO <sub>3</sub>
C <sub>2</sub> H <sub>4</sub>	N <sub>2</sub>
C <sub>2</sub> H <sub>4</sub> O	N <sub>2</sub> O
C <sub>2</sub> N	N <sub>2</sub> O <sub>3</sub>
C <sub>2</sub> N <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
C <sub>2</sub> O	N <sub>2</sub> O <sub>5</sub>
C <sub>3</sub>	O
C <sub>3</sub> O <sub>2</sub>	O <sub>2</sub>
C <sub>4</sub>	O <sub>3</sub>
C <sub>4</sub> N <sub>2</sub>	C (Graphite)
C <sub>5</sub>	H <sub>4</sub> N <sub>2</sub> (L)
H	N <sub>2</sub> O <sub>4</sub> (C)
HN	N <sub>2</sub> O <sub>4</sub> (L)

TABLE 24. TYPICAL COMPUTER RUN

COMPUTER RUN DATE JULY 25, 1973

Propellant	HF*	Density	Weight	Moles	Volume
TNT	13.0000	1.6000	10.0000	0.0440	6.2500
Air	0.0000	0.0200	50.0000	0.0347	2500.0000

Gram Atoms	C	H	O	N
/100 grams	0.5136	0.3669	1.6533	4.7836

Enthalpy = 0.95392

Density = 0.024

	Chamber
Pressure (PSIA)	13.000
Epsilon	0.000
ISP	0.000
ISP (Vacuum)	0.000
Temperature (K)	2242.350
Molecular Weight	30.088
Moles gas/100 g	3.324
CE	0.000
PEAE/M (Seconds)	0.000
Gamma	1.254
Heat Cap/Cal	32.572
Entropy (Cal)	219.192
Enthalpy (Kcal)	0.954
Density (g/cc)	1.44649E-04
Iterations	5

Moles/100 Grams

C	1.78497E-17	C <sub>2</sub> H	4.26154E-24	HO <sub>2</sub>	3.51577E-06
CH	8.16988E-19	C <sub>2</sub> H <sub>2</sub>	7.53907E-24	H <sub>2</sub>	1.09775E-03
CHN	2.41123E-12	C <sub>2</sub> H <sub>4</sub>	4.09242E-30	HCOOH	3.40479E-10
CHNO	1.13464E-10	C <sub>2</sub> H <sub>4</sub> O	1.82169E-32	H <sub>2</sub> N	9.44488E-10
CHO	7.91724E-09	C <sub>2</sub> N	3.73021E-24	H <sub>2</sub> N <sub>2</sub>	8.47502E-15
CH <sub>2</sub>	1.60100E-19	C <sub>2</sub> N <sub>2</sub>	5.38652E-23	H <sub>2</sub> O	1.76684E-01
CH <sub>2</sub> O	2.98939E-12	C <sub>2</sub> O	7.69076E-19	H <sub>2</sub> O <sub>2</sub>	1.62872E-07
CH <sub>3</sub>	9.48545E-19	C <sub>3</sub>	6.66476E-35	H <sub>3</sub> N	1.62872E-07
CH <sub>4</sub>	9.43391E-20	C <sub>3</sub> O	8.55680E-23	H <sub>4</sub> N <sub>2</sub>	2.14199E-10
CH <sub>3</sub> OH	5.90953E-20	H	4.56107E-04	N	6.08610E-08
CN	5.09288E-14	HN	7.22578E-09	NO	2.56389E-02
CNN	6.46187E-21	HNO	1.85799E-07	NO <sub>2</sub>	1.48150E-05
CN <sub>2</sub>	2.37280E-17	HNO <sub>2</sub>	1.15320E-07	NO <sub>3</sub>	1.56637E-11
CO	1.65518E-02	HNO <sub>2</sub>	1.00373E-07	N <sub>2</sub>	2.37895E+00
CO <sub>2</sub>	4.97095E-01	HNO <sub>3</sub>	1.87624E-11	N <sub>2</sub> O	1.15196E-06
C <sub>2</sub>	2.45395E-27	HO	1.87624E-02	N <sub>2</sub> O <sub>3</sub>	7.41238E-14

\*heat of formation

TABLE 25. INCINERATION PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0001 mole
TNT/Air	440
Temperature	1993°C
<hr/>	
CO	73.64 g /100 g TNT
N <sub>2</sub>	18.62 g
C, graphite	4.57 g
H <sub>2</sub>	2.12 g
HCN	0.845 g
HC≡CH	0.115 g
H	0.019 g
C <sub>2</sub> H	0.003 g
CHO	0.001 g
CN	0.0008 g
CH <sub>4</sub>	0.0007 g
CO <sub>2</sub>	0.0005 g
H <sub>2</sub> O	0.0005 g
CH <sub>3</sub>	0.0003 g

TABLE 26. INCINERATION PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0347 mole
TNT/Air	1.27
Temperature	1969°C
<hr/>	
N <sub>2</sub>	66.61 g /100 g TNT
CO <sub>2</sub>	21.87 g
O <sub>2</sub>	6.82 g
H <sub>2</sub> O	3.18 g
NO	0.769 g
CO	0.463 g
HO	0.185 g
O	0.050 g
H <sub>2</sub>	0.002 g
NO <sub>2</sub>	0.0007 g
H	0.0005 g

TABLE 27. INCINERATION PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0277 mole
TNT/Air	1.59
Temperature	2164°C
<hr/>	
N <sub>2</sub>	64.62 g /100 g TNT
CO <sub>2</sub>	23.87 g
O <sub>2</sub>	4.35 g
H <sub>2</sub> O	3.67 g
CO	2.07 g
NO	0.891 g
HO	0.365 g
O	0.120 g
H <sub>2</sub>	0.009 g
H	0.003 g
NO <sub>2</sub>	0.0005 g

---

LOW AIR

HIGH AIR

- |   |  |
|---|--|
| 1. Many exotic species generated in significant amounts.                              | No exotic species generated in significant amounts.                  |
| 2. Among the top six species, two very reactive species: HCN and HC≡CH are generated. | No very reactive species generated among the top six.                |
| 3. CO is the most abundant component.   | N <sub>2</sub> the most abundant; comparatively little CO generated. |
| 4. "Graphite" in significant amount.  | No graphite generated.   |
| 5. Molecular and atomic hydrogen generated in significant amounts.                    | Molecular and atomic hydrogen generated in very low amounts.         |

In Tables 26 and 27 are listed the most prevalent incinerator species at 1969°C and 2164°C respectively. Thus, the low and high temperature incineration results at the lower TNT/Air ratios may be summarized as follows:

1. Nitrogen is the most prevalent component at both temperatures.
2. The same eleven most abundant species are generated at both of these temperatures.
3. At the higher temperature, almost 5 times more CO generated; 6 times more atomic hydrogen generated; 4 times more molecular hydrogen generated; about 2.5 times more atomic oxygen generated; and about 2 times more hydroxyl radical (HO<sup>•</sup>) generated.

In summary of these results, it is easily seen how important the air concentration (O<sub>2</sub> concentration) is, even in incineration, in decreasing the multiplicity of possible combustion products. This, in turn, indicates the important role fuel-air mixing (turbulence) plays even in the incineration if efficient combustion is to be achieved. The available data on the temperature effect is not sufficiently broad to make any significant generalizations. Furthermore, the indicated temperatures are probably unrealistically high as incinerator operating temperatures go.

We were not able to obtain computer modeling data on pure RDX; however, data on Composition B (60:40 RDX:TNT) were obtained. In Table 28 are listed all the species considered by the program. In Table 29, we have extracted and calculated the amounts of the most prevalent species (larger than 10<sup>-6</sup> mole amounts) generated in the incineration of Composition B in the absence of air.

TABLE 28. SPECIES CONSIDERED, COMPOSITION B

C	CN	C <sub>2</sub> N	HNO	H <sub>2</sub> O	N <sub>2</sub> O <sub>3</sub>
CH	CNN	C <sub>2</sub> N <sub>2</sub>	HNO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
CHN	CN <sub>2</sub>	C <sub>2</sub> O	HNO <sub>2</sub>	H <sub>3</sub> N	N <sub>2</sub> O <sub>5</sub>
CHNO	CO	C <sub>3</sub>	HNO <sub>3</sub>	H <sub>4</sub> N <sub>2</sub>	O
CHO	CO <sub>2</sub>	C <sub>3</sub> O <sub>2</sub>	HO	H	O <sub>2</sub>
CH <sub>2</sub>	C <sub>2</sub>	C <sub>4</sub>	HO <sub>2</sub>	NO	O <sub>3</sub>
CH <sub>2</sub> O	C <sub>2</sub> H	C <sub>4</sub> N <sub>2</sub>	H <sub>2</sub>	NO <sub>2</sub>	C (graphite)
CH <sub>3</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>5</sub>	HCOOH	NO <sub>3</sub>	H <sub>4</sub> N <sub>2</sub> (L)
CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	H	H <sub>2</sub> N	N <sub>2</sub>	N <sub>2</sub> O <sub>4</sub> (G)
CH <sub>3</sub> OH	C <sub>2</sub> H <sub>4</sub> O	HN	H <sub>2</sub> N <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub> O <sub>4</sub> (L)

TABLE 29. INCINERATION PRODUCTS OF 60/40 RDX/TNT

	RDX	0.2701 mole	
	TNT	0.1761 mole	
	Temperature	2305°C	
CO	52.32 g	/100 g	Composition B
N <sub>2</sub>	30.075 g		O 0.009 g
H <sub>2</sub> O	8.081 g		O <sub>2</sub> 0.004 g
CO <sub>2</sub>	7.674 g		CHO 0.001 g
H <sub>2</sub>	1.525 g		N 0.0002 g
HO	0.158 g		HN 0.00002 g
H	0.070 g		H <sub>2</sub> N 0.00002 g
NO	0.024 g		H <sub>3</sub> N 0.00002 g

As shown in these tables, numerous very reactive species are generated similarly to TNT combustion using low air concentration. Likewise, CO is the most prevalent species generated. Differently from TNT/low air, large concentrations of CO<sub>2</sub>, H<sub>2</sub>O, HO<sup>•</sup>, and NO are generated. Likewise, numerous hydrogen-nitrogen reactive species are also generated.

Perhaps the strongest signal that this examination of very limited computer modeling data gives is the potential for a very "rich" gas phase chemistry between the various indicated reactive species generated. On the basis of this preliminary examination of computer modeling data, it is strongly suggested that the approach be explored in more detail in future explosives incineration work.

#### CONCLUSIONS AND RECOMMENDATIONS

1. Open burning of explosives and propellants should be discontinued as soon as possible because of the potential of generating large quantities of toxic combustion products.
2. In general, only a limited amount of information could be found on explosives and propellants combustion products from open burning.
3. Computer modeling is a desirable approach to optimizing incinerator operation and minimizing pollutant emissions.

The limited amount of incineration work that the Army has done to date with pollution abatement equipped incinerators does indicate that there are at least two systems: SITPA II and the Rotary Kiln of RAAP, that would meet the existing emissions standards and would presumably eliminate the other objectionable emissions. Having seen both systems, we would favor the SITPA II over the Rotary Kiln on grounds of economics and ease of operation.

A strong effort in computer modeling of combustion product generation in the incineration of explosives and propellants is needed.

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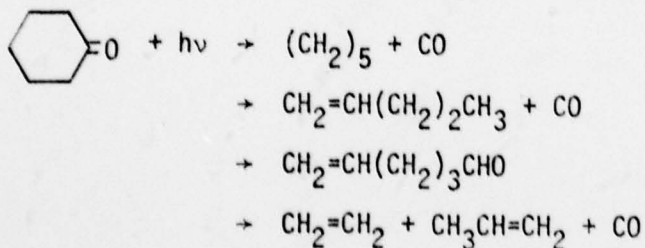
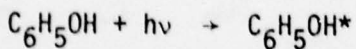
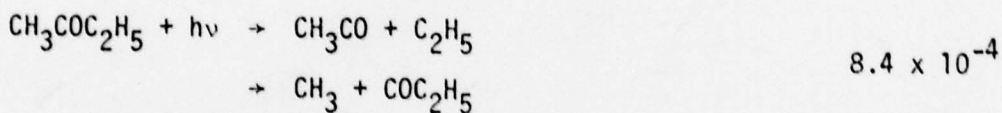
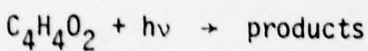
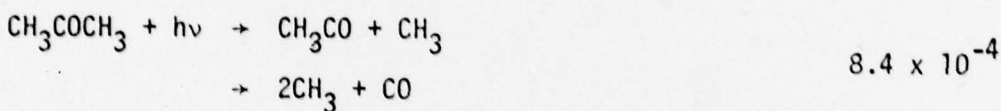
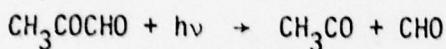
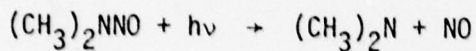
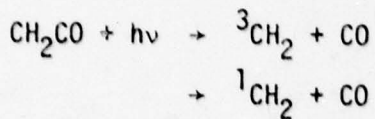
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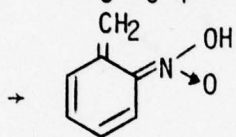
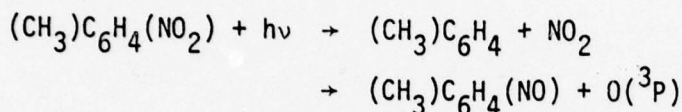
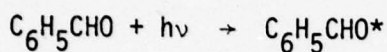
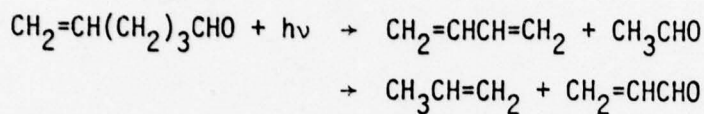
APPENDIX 1  
 CHEMICAL REACTIONS OF AIR POLLUTANTS  
 RATES AND RATE CONSTANTS

Included in this Appendix is a complete listing of the reactions cited in the text and tables of Volumes 2 and 3 of this report. For convenience, the reactions are classified into reactions with light, hydroxyl radicals, hydroperoxy radicals, water, nitric oxide, nitrogen dioxide, ground state atomic oxygen, molecular oxygen and ozone, as well as fragmentation and miscellaneous reactions. For each reaction, the units for the rate constants are given. The literature references for these reactions may be found within the two previously mentioned Volumes.

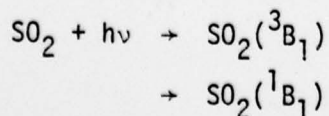
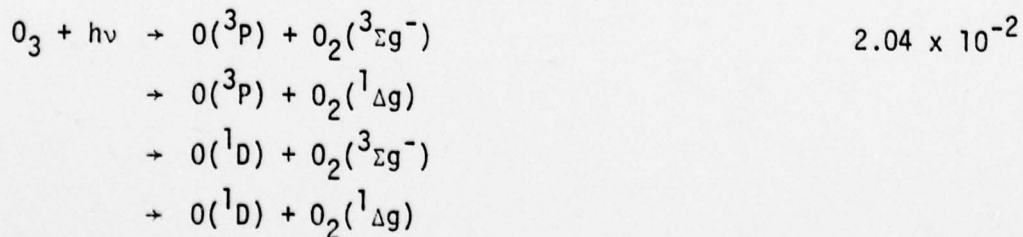
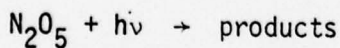
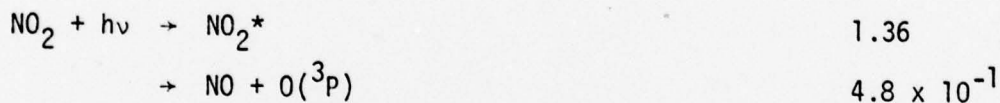
1. Photolyses

	<u>k (min<sup>-1</sup>)</u>
CHO + hν → H <sub>2</sub> + CO	5.2 × 10 <sup>-3</sup>
→ H + CHO	1.8 × 10 <sup>-3</sup>
 CH <sub>3</sub> NO <sub>2</sub> + hν → CH <sub>2</sub> O + HNO	 2.7 × 10 <sup>-3</sup>
→ CH <sub>3</sub> + NO <sub>2</sub>	
 CH <sub>3</sub> ONO + hν → CH <sub>3</sub> O + NO	 9.85 × 10 <sup>-2</sup>
 CH <sub>3</sub> ONO <sub>2</sub> + hν → CH <sub>2</sub> O + HONO	
→ CH <sub>3</sub> O + NO <sub>2</sub>	1.3 × 10 <sup>-4</sup>
→ CH <sub>3</sub> ONO + O( <sup>3</sup> P)	



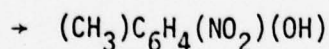
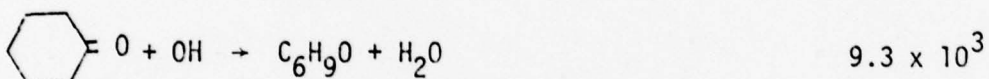
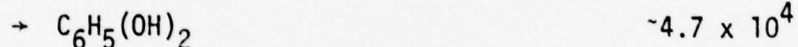
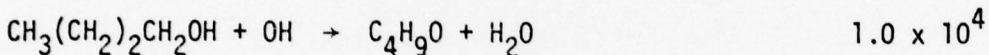
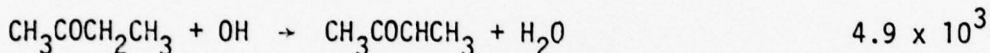
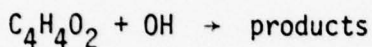
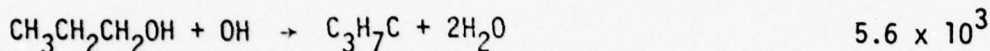
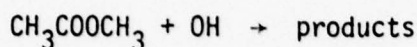
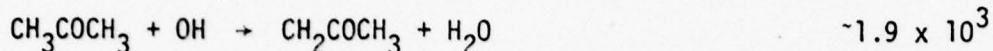
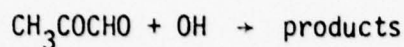


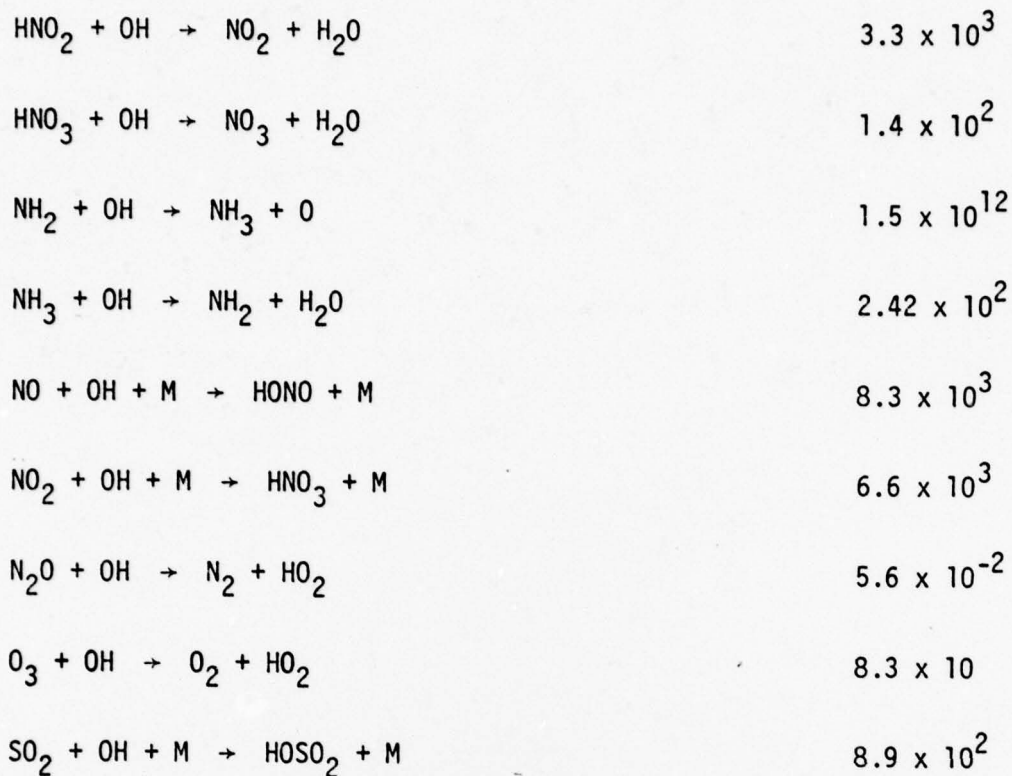
(ortho isomer only)



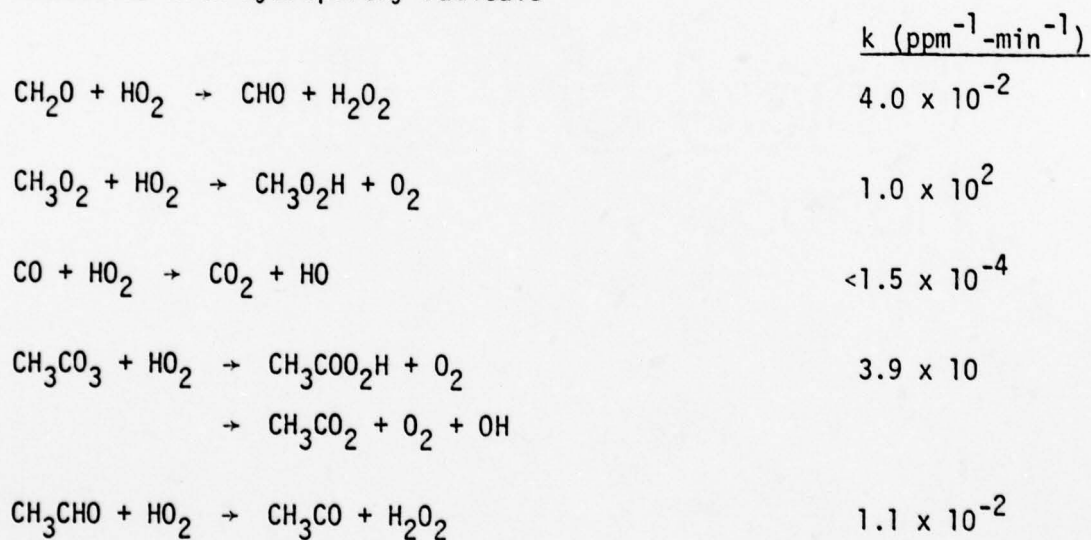
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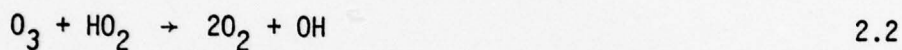
	<u>k (ppm<sup>-1</sup>-min<sup>-1</sup>)</u>
$\text{COOH} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	
$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$	$2.1 \times 10^4$
$\text{HCOOH} + \text{OH} \rightarrow \text{products}$	$3.4 \times 10^2$
$\text{CH}_3\text{NO}_2 + \text{OH} \rightarrow \text{CH}_2\text{NO}_2 + \text{H}_2\text{O}$	$1.4 \times 10^3$
$\text{CH}_3\text{ONO}_2 + \text{OH} \rightarrow \text{products}$	
$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	$1.1 \times 10$
$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}$	$1.4 \times 10^3$
$\text{CH}_3\text{NH}_2 + \text{OH} \rightarrow \text{CH}_2\text{NH}_2 + \text{H}_2\text{O}$	$3.26 \times 10^4$
$\text{C}(\text{NO}_2)_4 + \text{OH} \rightarrow \text{C}(\text{NO}_2)_3 + \text{HNO}_3$	
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	$2.07 \times 10^2$
$\text{CH}_2\text{CO} + \text{OH} \rightarrow \text{products}$	$\sim 2.5 \times 10^3$
$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	$3.0 \times 10^4$
$\text{CH}_3\text{COOH} + \text{OH} \rightarrow \text{products}$	$4.7 \times 10$
$\text{HCOOCH}_3 + \text{OH} \rightarrow \text{products}$	
$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	$3.9 \times 10^2$
$(\text{CH}_3)_2\text{NH} + \text{OH} \rightarrow \text{products}$	$> 3.3 \times 10^4$



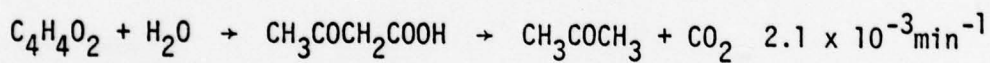
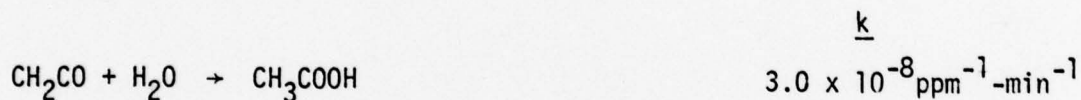


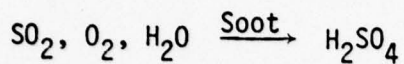
3. Reactions with hydroperoxy radicals



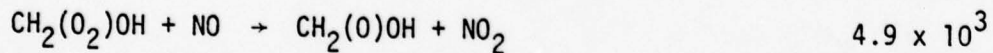
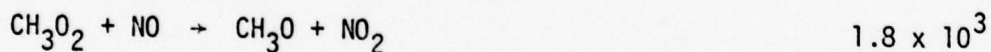
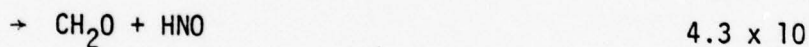
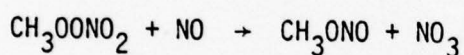


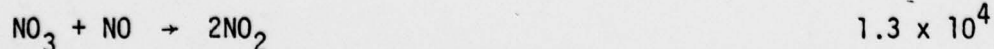
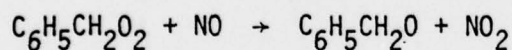
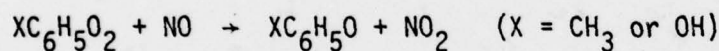
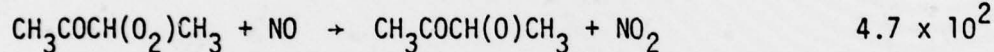
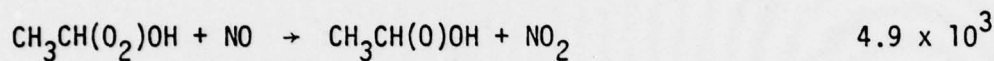
#### 4. Reactions with water





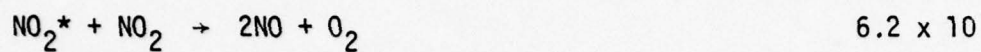
5. Reactions with nitric oxide





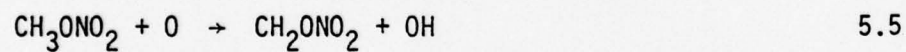
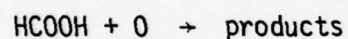
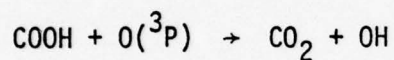
6. Reactions with nitrogen dioxide

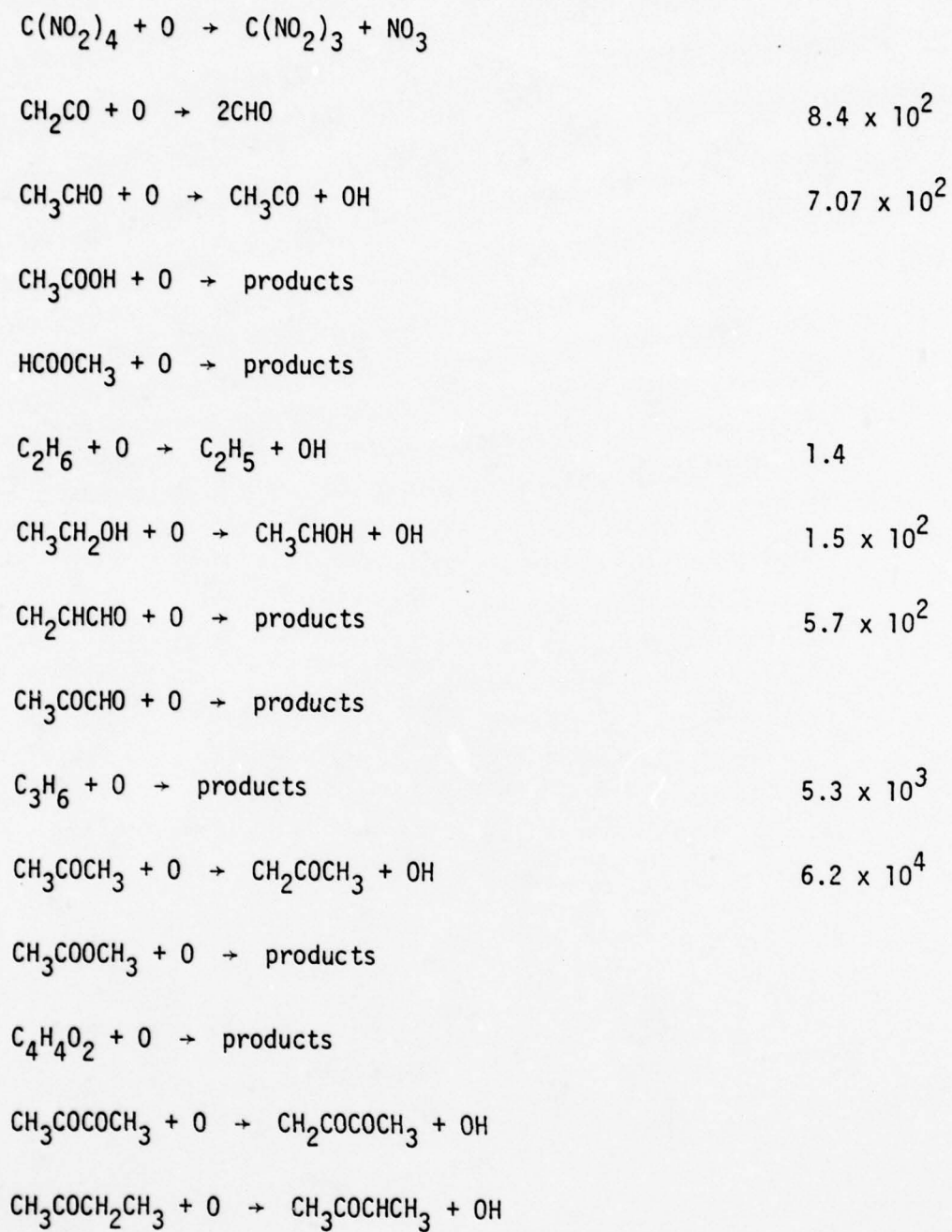
	$k$ (ppm <sup>-1</sup> -min <sup>-1</sup> ) <sup>a</sup>
$\text{HCO}_3 + \text{NO}_2 \rightarrow \text{HCOO}_2\text{NO}_2$	$4.9 \times 10^2$
$\text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}$	$4.9 \times 10^4$
$\text{CH}_3\text{O}_2\text{NO}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2 + \text{NO}_3$	
$\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$	$4.9 \times 10^2$
$\rightarrow \text{CH}_2\text{O} + \text{HONO}$	$4.9 \times 10$
$\text{CH}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{HONO}_2$	
$\rightarrow \text{CH}_3\text{O}_2\text{NO}_2$	$1.8 \times 10^3$
$\text{CH}_3\text{COO}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{COO}_2\text{NO}_2$	$7.4 \times 10^2$
$\text{C}_2\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{ONO}_2$	$3.0 \times 10^2$
$\rightarrow \text{CH}_3\text{CHO} + \text{HONO}$	$6.0 \times 10$
$\text{C}_6\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{C}_6\text{H}_5\text{ONO}_2$	
$\text{XC}_6\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{XC}_6\text{H}_5\text{ONO}_2$ (X = CH <sub>3</sub> or OH)	
$\text{C}_6\text{H}_5\text{O}_2 + \text{NO}_2 \rightarrow \text{C}_6\text{H}_5\text{OONO}_2$	
$\text{XC}_6\text{H}_5(\text{OH}) + \text{NO}_2 \rightarrow \text{XC}_6\text{H}_5(\text{OH})(\text{NO}_2)$ (X = H, CH <sub>3</sub> , or OH)	
$\text{C}_6\text{H}_5\text{CO}_3 + \text{NO}_2 \rightarrow \text{C}_6\text{H}_5\text{COO}_2\text{NO}_2$	
$\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$9.6 \times 10^{-8} \text{ ppm}^{-2} \text{ min}^{-1}$

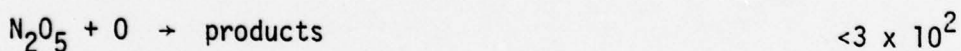
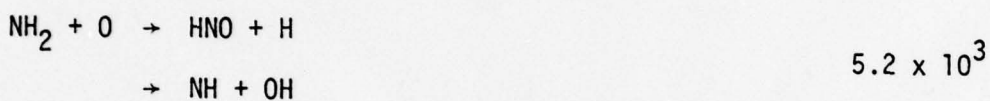
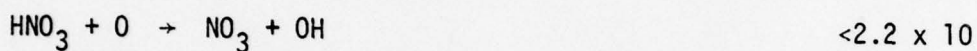
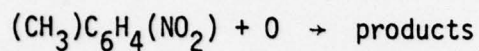
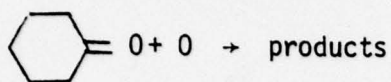
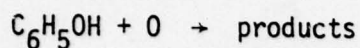


7. Reactions with ground state atomic oxygen

$k$  (ppm<sup>-1</sup>-min<sup>-1</sup>)<sup>a</sup>







8. Reactions with molecular oxygen

	$k$ (ppm <sup>-1</sup> -min <sup>-1</sup> ) <sup>a</sup>
$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	$2.5 \times 10^2$
$\text{CHO} + \text{O}_2 + \text{M} \rightarrow \text{HCO}_3 + \text{M}$	$1.0 \times 10^2$
$\text{CHO}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2$	$4.8 \times 10$
$\text{COOH} + \text{O}_2 \rightarrow \text{O}_2\text{COOH}$	
$\text{CH}_2\text{NO}_2 + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{NO}_2$	
$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	$1.8 \times 10^3$
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	2.7
$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{OH}$	$1.0 \times 10^4$
$\text{CH}_2(\text{O})\text{OH} + \text{O}_2 \rightarrow \text{HCOOH} + \text{HO}_2$	3.8
$\text{CH}_2\text{NH}_2 + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{NH}_2$	
$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_3$	$8.9 \times 10^3$
$\text{CH}_2\text{COOH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{COOH}$	
$\text{CH}_3\text{COCO} + \text{O}_2 \rightarrow \text{CH}_3\text{COCO}_2$	
$\text{CH}_3\text{CHO}^* + \text{O}_2 \rightarrow \text{CH}_3 + \text{CO} + \text{HO}_2$	$5.2 \times 10^{-4}$
$\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$	$1.0 \times 10^4$

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SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING AND THEIR ATM--ETC(U)

JAN 78 B H CARPENTER, R LIEPINS, J SICKLES

DAMD17-76-C-6067

UNCLASSIFIED

RTI/1342/00-01F

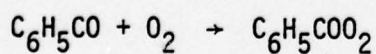
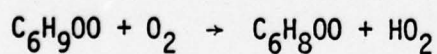
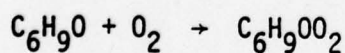
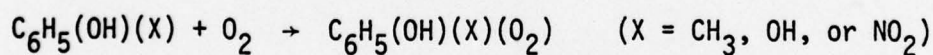
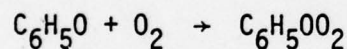
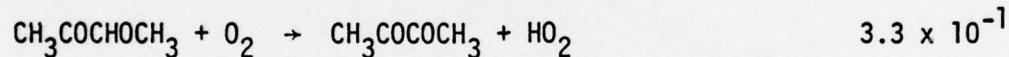
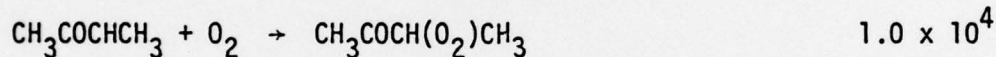
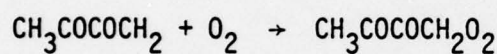
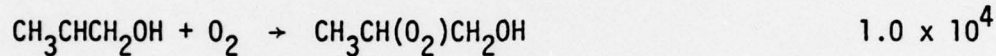
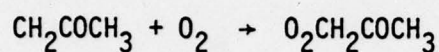
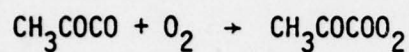
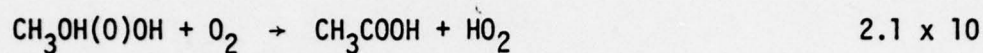
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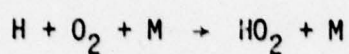
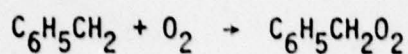
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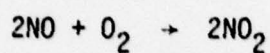




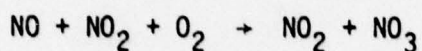
$$1.7 \times 10^{-3} \text{ ppm}^{-2} \text{ min}^{-1}$$



$$< 3 \times 10^{-5}$$



$$7.1 \times 10^{-1} \text{ ppm}^{-2} \text{ min}^{-1}$$



$$1.1 \times 10^{-10} \text{ ppm}^{-2} \text{ min}^{-1}$$



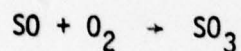
$$4.1 \times 10^{-34}$$



$$7.2 \times 10^{-11} \text{ min}^{-1}$$



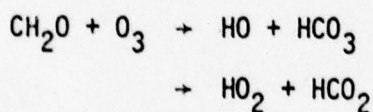
$$1 \times 10^{-18}$$



$$< 1 \times 10^{-1}$$

#### 9. Reactions with ozone

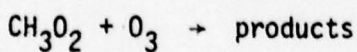
k (ppm<sup>-1</sup> min<sup>-1</sup>)



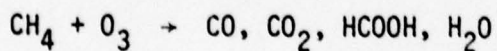
$$3.1 \times 10^{-9}$$



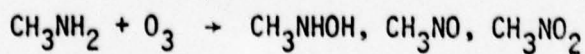
$$2.4 \times 10^2$$

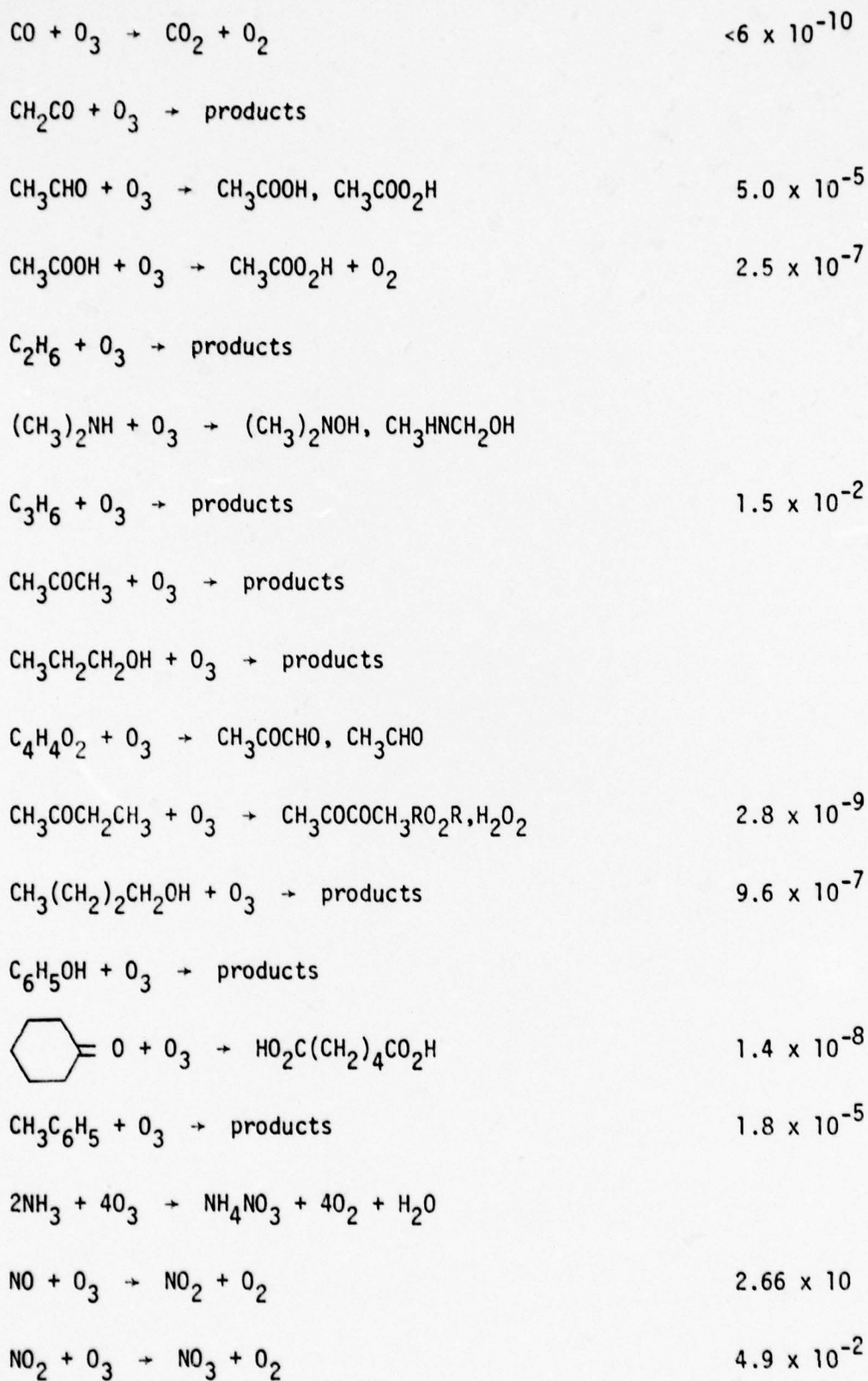


$$3.6 \times 10^{-2}$$



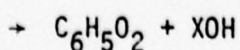
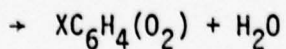
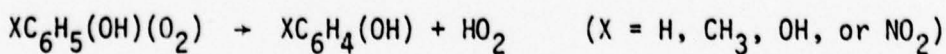
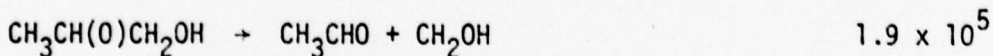
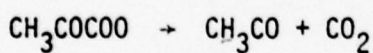
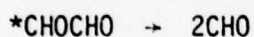
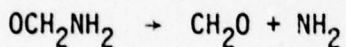
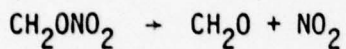
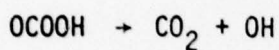
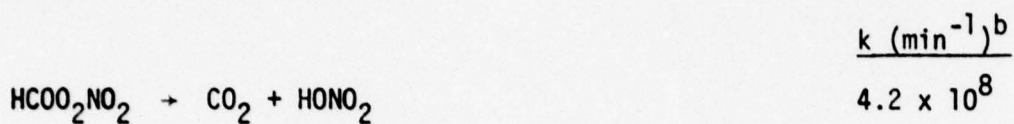
$$6.4 \times 10^{-19}$$

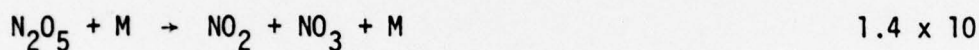
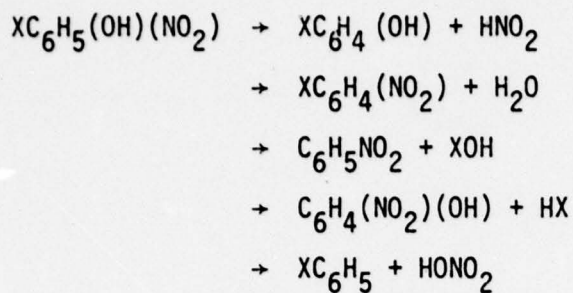




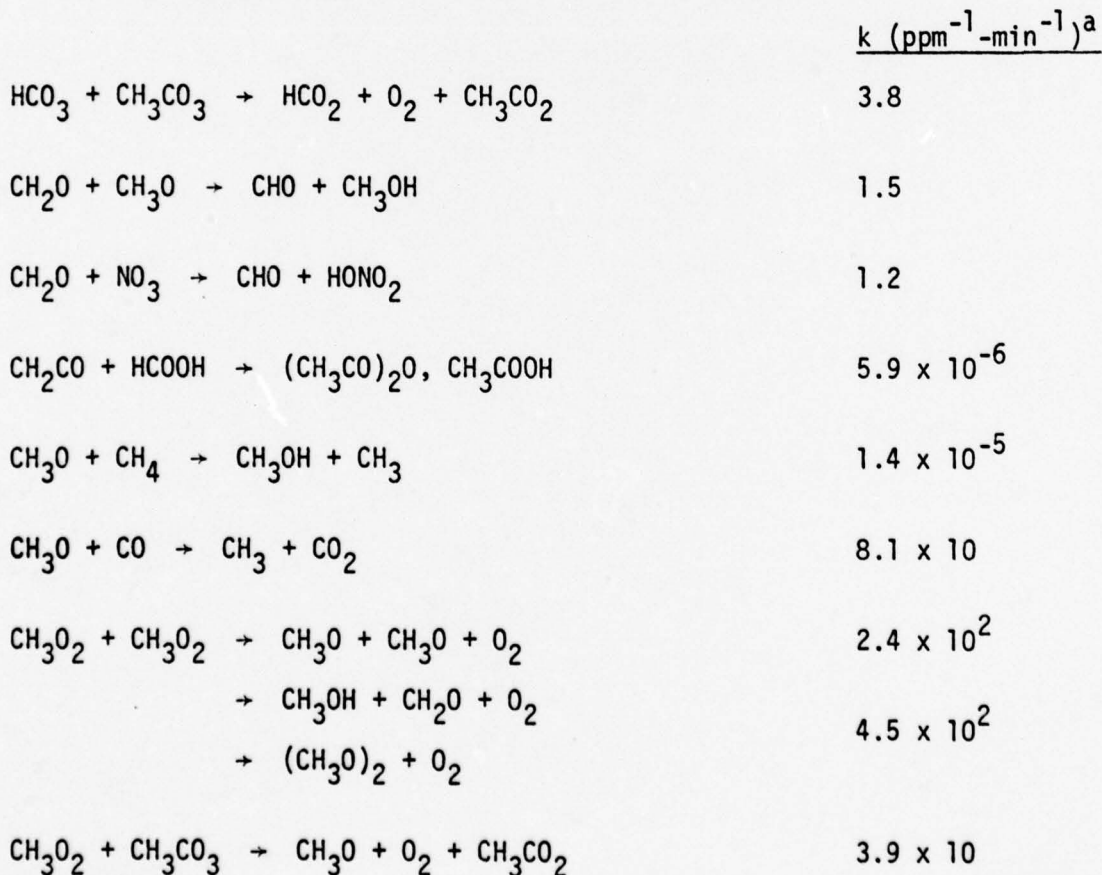


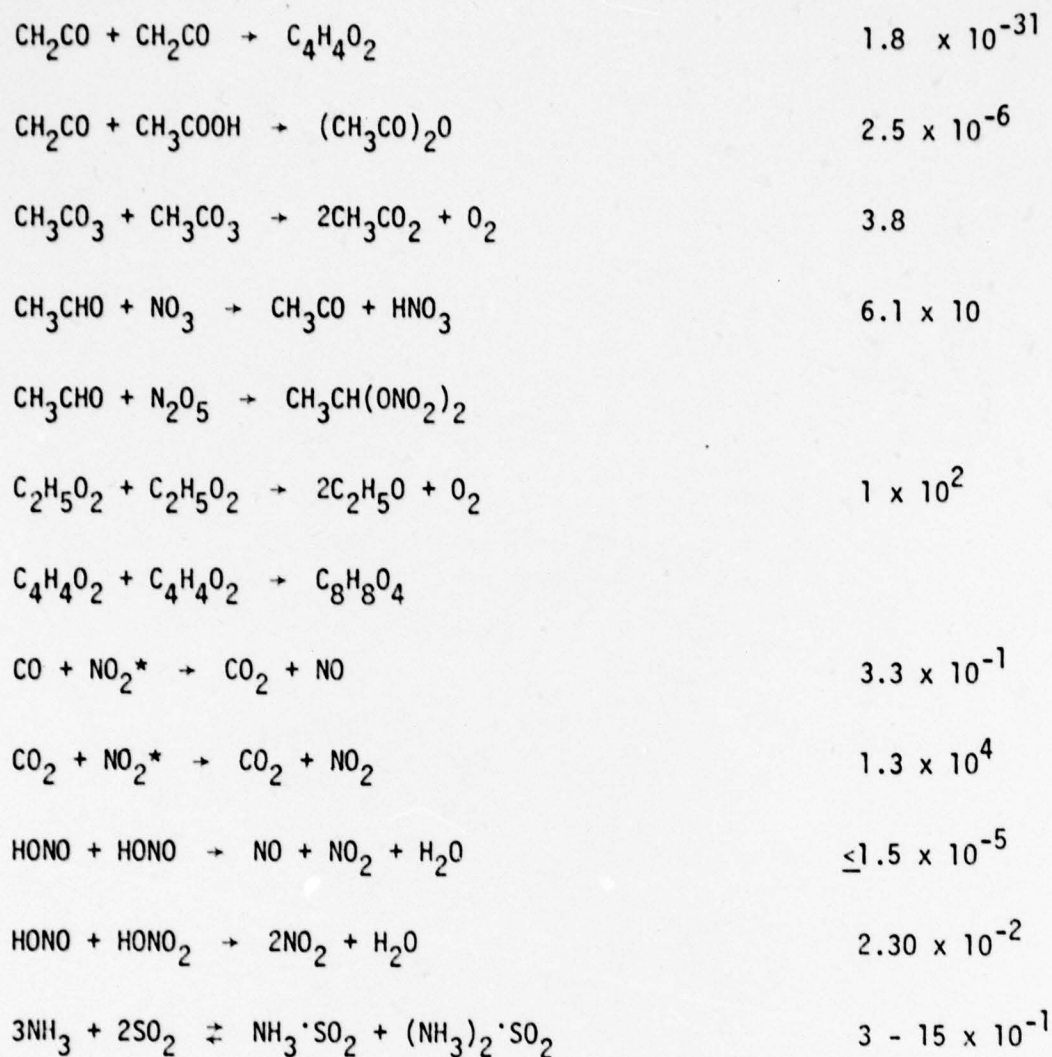
10. Fragmentation Reactions





#### 11. Miscellaneous Reactions





[Depending on the surrounding oxygen and water concentrations, these compounds condense to form aerosols composed of such compounds as ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ ; ammonium sulfamate,  $\text{NH}_4\text{NH}_2\text{SO}_3$ ; sulfamic acid,  $\text{NH}_2\text{SO}_3\text{H}$ ; ammonium azide,  $\text{NH}_4\text{N}_3$ ; ammonium amidosulfate,  $\text{NH}_4\text{NH}_2\text{SO}_2$ ; ammonium pyrosulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_7$ ; and amidosulfate hydrazine,  $\text{N}_3\text{H}_7\text{SO}_4$ .]

$\text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$	$3.3 \times 10^{-1}$
$\text{NO}_3 + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3$	$<1 \times 10^{-5}$
$\text{N}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{N}_2\text{O}_4 + \text{SO}_3$	$<6 \times 10^{-8}$
$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P}) + \text{M}$	$8.0 \times 10^4$
$\text{SO} + \text{SO} \rightarrow \text{S} + \text{SO}_2$ [or $(\text{SO})_2$ ]	$<4$
$\text{SO} + \text{SO}_3 \rightarrow 2\text{SO}_2$	3
$\text{SO}_2^*(^3\text{B}_1) \rightarrow \text{SO}_2 + h\nu$	$8.4 \times 10^3 \text{min}^{-1}$
$\quad \quad \quad \rightarrow \text{SO}_2$	$7.8 \times 10^3 \text{min}^{-1}$
$\text{SO}_2^*(^1\text{B}_1) \rightarrow \text{SO}_2 + h\nu$	$1.3 \times 10^6$
$\quad \quad \quad \rightarrow \text{SO}_2^*(^3\text{B}_1)$	$9 \times 10^4$
$\text{SO}_2^*(^3\text{B}_1) + \text{M} \rightarrow \text{SO}_2 + \text{M}$	$2 \times 10^2$
$\text{SO}_2 + \text{SO}_2^*(^3\text{B}_1) \rightarrow \text{SO}_3 + \text{SO}(^3\Sigma^-)$	$1 \times 10^2$
$\text{SO}_2 + \text{SO}_2^*(^1\text{B}_1) \rightarrow \text{SO}_3 + \text{SO}$	$5.4 \times 10^3$
$\quad \quad \quad \rightarrow \text{SO}_2^*(^3\text{B}_1) + \text{SO}_2$	$4.4 \times 10^3$

<sup>a</sup>Unless otherwise stated, the units of the rate constants in this section are in  $\text{ppm}^{-1}\text{-min}^{-1}$ .

<sup>b</sup>Unless otherwise stated, the units of the rate constants in this section are in  $\text{min}^{-1}$ .

## APPENDIX 2

### TOXICITY

#### Introduction

Many of the air pollutants from explosives manufacturing have been tested for toxicity and toxic effects. A list of substances emitted as pollutants during the manufacture of RDX, HMX, and the incineration of wastes is presented in Table 30. The importance of the results of these tests is difficult to evaluate because of the variety of testing methods, animals, and routes of exposure and the lack of data on some substances.

The prioritization of pollutants according to toxicity is further complicated by the need to translate results from one animal species to another. This is especially critical when humans are involved.

At this time, the best available means of prioritizing pollutants appears to be to rank them by mortality, threshold limit value, and toxic effects.

#### Prioritization by Mortality

A scheme proposed by Hodge and Steiner is used for ranking pollutants by mortality.<sup>36</sup> The scheme is based on the administration of either a single oral dose or a 4-hour inhalation dose to rats. The single oral dose is reported in mg/kg of body weight based on the lethality to 50 percent of the rats ( $LD_{50}$ ). The inhalation dose is reported in parts per million (ppm) based on the lethal concentration to 50 percent of the rats ( $LC_{50}$ ). The rating system is shown in Table 31. It should be noted that the limits on the rating classes are not rigid but are set to allow evaluation of relative toxicity.

Of the 131 substances identified as either pollutants or reaction products of pollutants from explosives manufacturing, only 42 fit into the Hodge and Steiner scheme based on oral dosages. A listing of these substances follows. The substances are listed in alphabetical order in each rating class with the  $LD_{50}$  in parentheses.

TABLE 30. SOURCES OF POLLUTANTS FROM EXPLOSIVES MANUFACTURING

Substance	SOURCE		
	TNT	RDX	Open Burning and Incineration
Acetaldehyde		x	
Acetic acid		x	
Acetic anhydride		x	
Acetoacetic acid esters (methylacetoacetate)		x	
Acetone		x	
Acetylene			x
Adipic acid		x	
Aldehydes			x
Alkenes			x
Allene		x	
Amidosulfate hydrazine		x	
Amidosulfurous acid		x	
Ammonia		x	x
Ammonium amido sulfate		x	
Ammonium amido sulfite		x	
Ammonium azide		x	
Ammonium nitrate		x	
Ammonium pyrosulfate		x	
Ammonium sulfamate		x	
Ammonium sulfate		x	
Asbestos			x
Barium oxide (BaO)			x
Benzaldehyde	x		
Biacetyl		x	
Boron oxide (B <sub>2</sub> O <sub>3</sub> )			x
Bromine gas			x
Butene			x
Butyl alcohol (n-butanol)		x	
Carbon dioxide	x	x	x
Carbon disulfide			x
Carbon monoxide	x	x	x
Carbonyl sulfide			x
Chlorine gas			x
Chromium (III) oxide			x
Copper (II) oxide			x
Cresol isomers	x		
Cyanides			x
1,2-cyclohexadione		x	
1,3-cyclohexadione		x	
1,4-cyclohexadione		x	
Cyclohexanone		x	

TABLE 30. (cont'd)

Substance	SOURCE		
	TNT	RDX	Open Burning and Incineration
Cyclonite		x	
Cyclopentane		x	
Cyclopentanone		x	
Dehydroacetic acid		x	
2,2'-dicarboxy-3,3',5,5'-tetranitroazoxy- benzene (white compound)	x		
Diketene		x	
Dimethyl peroxide		x	
Dinitrogen pentoxide	x	x	
Dinitrogen trioxide	x	x	
4,6-dinitro- <i>o</i> -cresol	x		
2,6-dinitro- <i>p</i> -cresol	x		
2,4-dinitrotoluene	x		
2,5-dinitrotoluene	x		
2,6-dinitrotoluene	x		
3,4-dinitrotoluene	x		
3,5-dinitrotoluene	x		
Ethane		x	x
Ethene			x
Ethylene		x	
Ethyl nitrate		x	
Ethyl nitrite		x	
Fluorine gas			x
Formaldehyde	x	x	
Formic acid	x	x	
Glyoxal		x	
Hexamine		x	
5-hexenal		x	
Hydrochloric acid			x
Hydrofluoric acid			x
Hydrogen bromide			x
Hydrogen cyanide			x
Hydrogen peroxide	x	x	
Hydrogen sulfide			x
Lead oxide (PbO)			x
Methane	x	x	x
Methanol	x	x	
Methyl acetate		x	
Methyl ethyl ketone		x	
Methyl formate		x	
Methyl nitrate	x	x	
Methyl nitrite	x	x	

TABLE 30. (cont'd)

Substance	SOURCE		
	TNT	RDX	Open Burning and Incineration
Nitric acid	x	x	
Nitric oxide	x	x	x
Nitrocresol isomers	x		
Nitrogen dioxide	x	x	x
Nitrogen trioxide	x	x	
Nitromethane		x	
Nitrosamines (N-nitrosodimethylamine)			x
o-nitrosobenzoic acid	x		
Nitrosomethane		x	
Nitrosotoluene isomers	x		
α-nitrotoluene	x		
2-nitrotoluene	x		
3-nitrotoluene	x		
4-nitrotoluene	x		
Nitrous acid	x	x	
Nitrous oxide		x	
Ozone	x	x	
4-pentenal		x	
1-pentene		x	
Peroxy acetyl nitrate	x	x	
Peroxy benzoyl nitrate	x		
Phenol		x	
Phosgene			x
Phosphorous pentoxide			x
Polycyclic aromatic hydrocarbons			x
n-propanol		x	
Propene			x
n-propyl acetate		x	
n-propyl formate		x	
Pyruvaldehyde		x	
Selenium dioxide			x
Soot			x
Sulfamic acid		x	
Sulfoacetic anhydride		x	
Sulfur dioxide	x	x	x
Sulfuric acid	x	x	x
Sulfur tioxide	x	x	x
Tetranitromethane	x		
Toluene	x	x	
Trinitrobenzaldehyde	x		
Trinitrobenzene	x		
Trinitrobenzoic acid	x		
2,4,6-trinitro-m-cresol (methyl picric acid)	x		

TABLE 30 (cont'd)

Substance	SOURCE		
	TNT	RDX	Open Burning and Incineration
Trinitromethane			x
Trinitromethylnitrite (unstable)	x		
Trinitronitrosomethane (unstable)	x		
2,3,4-trinitrotoluene	x		
2,3,5-trinitrotoluene	x		
2,4,5-trinitrotoluene	x		
2,4,6-trinitrotoluene	x		
TNT		x	

TABLE 31. THE TOXICITY RATING SYSTEM OF HODGE AND STEINER

Toxicity Rating	Descriptive Term	Dose	
		Oral LD <sub>50</sub> (mg/kg)	Inhalation LC <sub>50</sub> (ppm)
1	Extremely Toxic	≤ 1	< 10
2	Highly Toxic	1 - 50	10 - 100
3	Moderately Toxic	50 - 500	100 - 1000
4	Slightly Toxic	500 - 5000	1000 - 10,000
5	Practically Non-Toxic	5000 - 15,000	10,000-100,000
6	Relatively Harmless	>15,000	>100,000

1 - Extremely Toxic

None

2 - Highly Toxic

4,6-dinitro-o-cresol (25)

n-nitrosodimethylamine (26)

### 3 - Moderately Toxic

m-cresol	(242)
o-cresol	(121)
p-cresol	(207)
cyclonite	(200)
dehydroacetic acid	(500)
2,4-dinitrotoluene	(268)
2,6-dinitrotoluene	(177)
3,4-dinitrotoluene	(177)

### 4 - Slightly Toxic

Acetaldehyde	(1930)
Acetic Acid	(3310)
Acetic Anhydride	(1780)
Ammonium Sulfamate	(1600)
Ammonium Sulfate	(3000)
Benzaldehyde	(1300)
Biacetyl	(1580)
Cresol	(1454)
Cyclohexanone	(1620)
Diketene	(560)
2,5-dinitrotoluene	(707)
Formaldehyde	(800)
Formic Acid	(1210)
Hexanal	(4900)
Methylacetoacetate	(3000)
Methyl Ethyl Ketone	(3400)
2-nitro-p-cresol	(3360)
Nitromethane	(940)
2-nitrotoluene	(891)
3-nitrotoluene	(1072)
4-nitrotoluene	(2144)
4-pentanol	(3200)
n-propanol	(1870)
n-propyl formate	(3980)

Sulfamic acid	(1600)
Sulfuric acid	(2140)
Toluene	(5000)
Trinitrobenzene	(505)

5 - Practically Non-Toxic

Acetone	(9750)
Butyl Alcohol	(6480)
Methanol	(13,000)
n-propyl acetate	(9800)

6 - Relatively Harmless

None

A similar list follows for the inhalation route. The duration of the dosage is not the same throughout the data. The duration is given in parentheses after the LC<sub>50</sub>.

1 - Extremely Toxic

Ozone (4.8) (4H)

2 - Highly Toxic

Nitrogen Dioxide (88) (4H)  
n-nitrosodimethylamine (78) (4H)

3 - Moderately Toxic

Chlorine (293) (1H)  
Hydrogen Sulfide (713) (1H)

4 - Slightly Toxic

Hydrochloric Acid (3124) (1H)  
Hydrofluoric Acid (1276) (1H)  
Hydrogen Bromide (2858) (1H)  
Methyl Ethyl Ketone (2000) (4H)

5 - Probably Non-Toxic

None

6 - Relatively Harmless

None

The toxicity data were extracted from Reference 44.

### Prioritization by Toxic Effects

Many of the pollutants from explosives manufacturing produce toxic effects in humans and other animals. Some of these effects have been observed to occur at high levels of exposure over long periods of time. Others have been produced by exposure of lower animals and are difficult to translate into human effects. This presents difficulties in interpretation of the data.

Each substance is evaluated separately. A standard list of abbreviations and explanations used in the evaluations are presented in Table 32. The effects on humans are examined first (Table 33), followed by the effects on animals (Table 34).

TABLE 32. ABBREVIATIONS AND EXPLANATIONS

Abbreviation	Explanation
CAR	Carcinogenic effects - producing cancer
CNS	Central nervous system effects - such as headaches, tremor, drowsiness, convulsions, hypnosis, anesthesia
EYE	Eye effects - irritation, diplopia, cataracts, eye ground, or blindness
GIT	Gastrointestinal tract effects - diarrhea, constipation, ulceration
ham	Hamster
hmn	Human
ihl	Inhalation
ims	Intramuscular
ipl	Intrapleural - pleural cavity
ipr	Intraperitoneal - peritoneal cavity
IRR	Irritant effects - skin, eye, or mucous membrane
itr	Intratracheal - trachea
IVN	Intravenous
MAN	Man
MTH	Mouth effects
MUT	Mutagenic effects - transmissible changes produced in offspring
mus	Mouse
NEO	Neoplastic effects - tumor producing
orl	Oral
par	Parenteral - into the body through the skin

TABLE 32. (cont'd)

Abbreviation	Explanation
PNS	Peripheral nervous system effects
PSY	Psychotropic effects - mind effects
PUL	Pulmonary system effects - respiration and respiratory pathology
rat	Rat
rbt	Rabbit
SKN	Skin effects - erythema, rash, sensitization, and petechial hemorrhage
scu	Subcutaneous - under the skin
TER	Teratogenic effects - nontransmissible changes produced in the offspring
unk	Unreported route
wmn	Woman

The polycyclic organics are evaluated separately because of their varied toxic effects and because no specific compounds have been identified among the pollutants. The NAS Committee on Biological Effects of Atmospheric Pollutants has presented extensive information on this group of substances.<sup>38</sup> Some of the polycyclics were not shown to be carcinogens while others showed varied degrees of carcinogenicity. The results are presented in Table 33.

One polycyclic, benzo(e)pyrene (B(e)P), was listed as a non-carcinogen in this report. Later data described B(e)P as a suspect animal carcinogen.<sup>37</sup> This designation was the result of applying B(e)P to the skin of a mouse at 516 mg/kg for 43 weeks. This comparatively low toxic dose produced a carcinogenic effect.

#### Prioritization by Threshold Limit Values

The threshold limit values (TLV's)<sup>R</sup> represent levels of prolonged exposure to substances that are believed to produce no adverse effects on workers. There are three categories of TLV's<sup>R</sup>; the time weighted average concentration (TWA) for a normal 8 hour workday or 40 hour workweek, the short term exposure limit (STEL) which is a maximum 15 minute exposure level, and the ceiling concentration (C) that should not be exceeded for any duration.<sup>39</sup>

TABLE 33. TOXIC EFFECTS ON HUMANS

Substance	Effect	Route	Dosage	Remarks
Acetaldehyde	IRR	ihl	134 ppm	Unconsciousness  Many references to carcinogenic effects of asbestiform minerals <sup>45</sup> Asphyxiant and weak anesthetic <sup>45</sup> Suspected of causing miscarriages, sperm abnormalities, decreased libido, menstrual disorders, decreased fertility in women, and impotency in men. <sup>43</sup> Suspected of causing birth abnormalities. <sup>43</sup>
Acetic acid	IRR	ihl	816 ppm/3H	
Acetone <sup>5</sup>	EYE	ihl	500 ppm	
Acetylene	CNS	ihl	350,000 ppm/5M	
Ammonia	IRR	ihl	20 ppm	
Asbestos	PUL	ihl	1.2 fibers/cc/19YC	
Butene				
Carbon disulfide	CNS	ihl	50 mg/m <sup>3</sup> /74	
Carbon monoxide	CNS	ihl	650 ppm/45M	
Chlorine	PUL	ihl	15 ppm	Can cause convulsions, irritation, and dermatitis. <sup>45</sup> Dinitroresols are poisons and <sup>45</sup> can cause liver and kidney damage <sup>45</sup> Causes methemoglobin formation
Cyclohexanone	IRR	ihl	75 ppm	
Cyclonite				
4,6-Dinitro-o-cresol	CNS	ihl	1 mg/m <sup>3</sup>	
Ethyl nitrite	IRR	ihl	25 ppm/5M	
Fluorine	IRR	ihl	13.8 ppm	
Formaldehyde	IRR	ihl	32 ppm	
Hydrofluoric acid	IRR	ihl	5 ppm	
Hydrogen bromide				

TABLE 33. (cont'd)

Substance	Effect	Route	Dosage	Remarks
Lead compounds				Caused miscarriages, stillbirths, sperm abnormalities, chromosome aberrations, decreased libido, atrophy of testes, menstrual disorders and birth abnormalities. <sup>43</sup>
Methanol	EYE CNS	orl ihl	100 mg/kg 300 ppm	
Methyl ethyl ketone	PNS CNS	ihl ihl	300 ppm 398 ppm	
Methyl nitrate				In women Causes headaches in men at minimal doses between 117 and 470 mg
Nitrogen dioxide	PUL	ihl	64 ppm	Methemoglobin former <sup>45</sup>
p-Nitrosotoluene				Low grade methemoglobin formers <sup>45</sup>
Nitrotoluenes				Exposure of human tissues in a culture to 8 ppm ozone for 5 to 10 minutes produced chromatid breaks. <sup>44</sup>
Ozone	SKN CNS IRR PUL EYE GIT IRR	ihl ihl ihl ihl ihl orl ihl	100 ppm/1M 1860 ppb/75M 100 ppb 1 ppm 0.2 ppm/3H 14 mg/kg 25 ppm/30M	
Phenol				Corrosive irritant to mucous surfaces, eyes, and skin. <sup>46</sup>
Phosgene				See separate discussion
Phosphorous pentoxide				Human carcinogen <sup>47</sup>
Polycyclic hydrocarbons				
Soot				

TABLE 33. (cont'd)

Substance	Effect	Route	Dosage	Remarks
Sulfur dioxide	PUL	ihl	3 ppm/5D	In a man
Sulfuric acid mist	PUL	ihl	4 ppm/1M	
	MTH	ihl	3 mg/m <sup>3</sup> /24H	
	PUL	ihl	3 µg/m <sup>3</sup> /3M	
Toluene	CNS	ihl	200 ppm	Suspected to cause chromosome aberrations, menstrual disorders <sup>43</sup> birth abnormalities, and cancer. <sup>43</sup> May cause aplastic anemia and toxic hepatitis. Poison. <sup>45</sup> Described as "...highly toxic..."
Trinitrotoluene	PSY	ihl	100 ppm	

TABLE 34. TOXIC EFFECTS IN ANIMALS

Substance	Animal	Route	Dosage	Effect	Remarks	
Acetaldehyde	rat	ihl	12 mg/m <sup>3</sup> /13W	CAR	Shown to be a mutagen to insects <sup>42</sup>	
Asbestos	rat	ipr	280 mg/kg	CAR		
Carbon dioxide	rat	ip1	100 mg/kg	CAR		
	rat	ih1	6pph/24H/(10Dpreg)	TER		
Chromium (III) oxide	rat	ih1	10pph/(7-12Dpreg)	TER		
	rat	ipr	100 mg/kg	CAR		
Cyclonite	rat	itr	100 mg/kg	CAR		
Ethyl nitrate						Potent convulsant in rats at min. oral dose of 10 mg/kg-accumulated in organ tissues. <sup>47</sup>
Formaldehyde	rat	scu	1300mg/kg/65WI	NEO		Induces Heinz body formation in animals (small, rounded inclusions in the blood). Shortens life of blood cells. Dosages of 125 to 250 mg/kg.
Hexamine Hexanal	rat	or1	14g/kg/75WC	NEO		Caused mutations in microorganisms and insects. <sup>42</sup> Caused histologic deviations in liver and kidney tissues of offspring when given to pregnant albino rats in dosages of 1 or 0.012 mg/m <sup>3</sup> . <sup>344</sup>
Methyl ethyl ketone Nitric oxide	rat	ih1	1000 ppm/6-15Dpreg	TER	Caused slight irritation of skin in rabbit.	
Nitrogen dioxide Nitrogen trioxide n-Nitrosodimethylamine	rat rat rat	or1 ih1 ipr	248 mg/kg 37 mg/kg 30 mg/kg	CAR CAR NEO	Caused >90% reduction in the transforming ability of DNA of bacillus <u>Subtilis 746<sup>48</sup></u> <u>Subtilis 746 48</u>	

TABLE 34. (cont.'d)

Substance	Animal	Route	Dosage	Effect	Remarks
	rat	ims	18 mg/kg	NEO	
	rat	par	7 mg/kg/(15-20)preg	NEO	
	rat	ivn	18 mg/kg	NEO	
	mus	orl	370 mg/kg/56WC	CAR	
	mus	ihl	200 µg/m <sup>3</sup> /26WC	CAR	
	mus	ipr	7 mg/kg	NEO	
	mus	scu	4375 µg/kg	CAR	
	mus	unk	13 mg/kg(preg)	TER	
	rbt	orl	202 mg/kg/23WC	CAR	
	ham	orl	21 mg/kg	CAR	
	ham	scu	50 mg/kg/6WI	CAR	
Nitrous Oxide	rat	ihl	50pph/2D/(8-10D)preg	TER	
Ozone	hmn	ihl	100 ppm/1M	SKN	
	man	ihl	1860 pph/75M	CNS	Inhalation of 0.2 ppm for 5 hours increased chromosome aberrations in circulating lymphocytes of hamsters.
	hmn	ihl	100 ppb	IRR	Inhalation of 0.2 ppm for 5 to 7 hrs per day for 3 weeks showed increase in neonatal mortality and slight rupture in nuclear envelope of the myocardial fibers of rats and mice.
	hmn	ihl	1 ppm	PUL	
	hmn	ihl	0.2 ppm/3H	EYE	
	mus	ihl	4.5 ppm/50 HI	NEO	
Phenol	mus	skn	4000 mg/kg/20WI	CAR	See separate discussion
Polycyclic hydrocarbons	rat	orl	50g/kg/I	CAR	
n-propanol	rat	scu	6g/kg/I	CAR	

TABLE 35. DEGREE OF CARCINOGENICITY OF POLYCYCLIC ORGANICS

Substance	Degree of Carcinogenicity*
Benz[a]anthracene	+
7,12-Dimethylbenz[a]anthracene	++++
Dibenz[a,i]anthracene	+
Dibenz[a,h]anthracene	+++
Dibenz[a,c]anthracene	+
Benzo[c]phenanthrene	+++
Dibenzo[a,h]fluorene	<u>+</u>
Dibenzo[a,g]fluorene	+
Dibenzo[a,c]fluorene	<u>+</u>
Benzo[b]fluoranthene	++
Benzo[j]fluoranthene	++
Benz[j]areanthrylene	++
3-Methylcholanthrene	++++
Benzo[a]pyrene	+++
Dibenzo[a,l]pyrene	+
Dibenzo[a,h]pyrene	+++
Dibenzo[a,i]pyrene	+++
Indeno[1,2,3-cd]pyrene	+
Chrysene	<u>+</u>
Dibenzo[b,def]chrysene	++

\*  
+                      Uncertain or weakly carcinogenic  
 +                        Carcinogenic  
 ++,+++ ,++++        Strongly carcinogenic

The TLV's<sup>R</sup> are based on industrial experience and experimental human and animal studies. These are guides to controlling health hazards except for ceiling values which are maximum safe concentrations.

The TLV's<sup>R</sup> are not meant to be used as a basis for either the comparison of relative toxicity or in the evaluation of air pollution hazards, but are frequently used for these purposes. Considering this restriction, the fact that many TLV's<sup>R</sup> are not evaluated on the same basis, and that TLV's<sup>R</sup> apply to workroom conditions, the air pollutants from explosives manufacturing are ranked according to their TLV's<sup>R</sup> in Table 36.<sup>39</sup> This ranking is based on the TWA's and C's.

TABLE 36. POLLUTANT RANKING BY THRESHOLD LIMIT VALUES BASED ON TIME WEIGHTED AVERAGES<sup>39</sup>

Substance	TLV (mg/m <sup>3</sup> )
Asbestos	5 fibers/cc > 5 $\mu$ m in length human carcinogen
n-nitrosodimethylamine	Suspected human carcinogen
Polycyclic aromatic hydrocarbons	Human carcinogen
Lead fumes and dusts	0.15
Dinitro cresols	0.2 skin
Ozone	0.2
Selenium	0.2
Phosgene	0.4
Barium oxide	0.5
2,4,6-trinitrotoluene	0.5*
Bromine gas	0.7
Copper dusts and mists	1
Sulfuric acid	1
Hydrogen peroxide	1.4
Dinitrotoluene	1.5 skin
Trinitrotoluene (except 2,4,6-)	1.5
Fluorine	2
Hydrofluoric acid	2
Chlorine	3
Formaldehyde	3
Cyanide	5 skin
Nitric acid	5

TABLE 36. (cont'd)

Substance	TLV (mg/m <sup>3</sup> )
Hydrochloric acid	7 C
Tetranitromethane	8
Formic acid	9
Nitrogen dioxide	9
Ammonium sulfamate	10
Boron oxide	10
Hydrogen bromide	10
Hydrogen cyanide	11 skin
Sulfur dioxide	13
Hydrogen sulfide	15
Ammonia	18
Phenol	19 skin
Acetic anhydride	20
Cresol isomers	22
Acetic acid	25
Nitric oxide	30
Nitrotoluene	30 skin
Carbon monoxide	55
Carbon disulfide	60 skin
Butyl alcohol	150 C skin
Acetaldehyde	180
Cyclohexanone	200
Methyl formate	250
Nitromethane	250
Methanol	260 skin
Toluene	375 skin
Propene	500 skin
Methyl ethyl ketone	590
Methyl acetate	610
n-propyl acetate	840
Acetone	2400
Carbon Dioxide	9000

Single Asphixiants

Acetylene  
 Ethane  
 Ethylene  
 Methane  
 Nitrous acid

\*proposed

APPENDIX 3  
TOXICITY DATA

This appendix presents the toxicity data for those emitted substances that have been shown to be either pollutants or pollutant reaction products from explosives manufacturing. The source for this data is the Registry of Toxic Effects. Abbreviations are defined in Table 32.

Acetaldehyde

ihl-hmn	TCLo:134 ppm	TFX:IRR
ipr-rat	LDLo:500 mg/kg	
orl-rat	LD <sub>50</sub> :1930 mg/kg	
ihl-rat	LCLo:4000 ppm/4H	
scu-rat	LD <sub>50</sub> :640 mg/kg	
orl-mus	LD <sub>50</sub> :1232 mg/kg	
scu-mus	LD <sub>50</sub> :560 mg/kg	

Acetic Acid

ihl-hmn	TDLo:816 ppm/3M	TFX:IRR
orl-rat	LD <sub>50</sub> :3310 mg/kg	
orl-mus	LD <sub>50</sub> :4960 mg/kg	
ihl-mus	LC <sub>50</sub> :5620 ppm/1H	
ivn-mus	LD <sub>50</sub> :525 mg/kg	
orl-rbt	LCLo:1200 mg/kg	
skn-rbt	LD <sub>50</sub> :1060 mg/kg	
scu-rbt	LDLo:1200 mg/kg	
rec-rbt	LDLo:600 mg/kg	
Aquatic Toxicity Rating: TLm96:100-10 ppm		

Acetic Anhydride

orl-rat	LD <sub>50</sub> :1780 mg/kg	
ihl-rat	LCLo:1000 ppm/4H	
skn-rbt	LD <sub>50</sub> :4000 mg/kg	
Aquatic Toxicity Rating: TLm96:100-10 ppm		

Acetoacetic Acid Esters (Methylacetoacetate)

orl-rat LD<sub>50</sub>:3000 mg/kg

Acetone

ihl-hmn TCLo:500 ppm TFX:EYE  
ihl-man TCLo:12000 ppm/4H TFX:CNS  
orl-rat LD<sub>50</sub>:9750 mg/kg  
ipr-mus LD<sub>50</sub>:1297 mg/kg  
orl-dog LDLo:8000 mg/kg  
orl-rbt LD<sub>50</sub>:5300 mg/kg  
skn-rbt LD<sub>50</sub>:20 gm/kg  
Aquatic Toxicity Rating: Tm96:over 1000 ppm

Acetylene

No information

Adipic acid

orl-rat LDLo;3600 mg/kg  
ipr-rat LD<sub>50</sub>:275 mg/kg  
orl-mus LD<sub>50</sub>:1900 mg/kg  
ipr-mus LD<sub>50</sub>:275 mg/kg  
ivn-mus LD<sub>50</sub>:680 mg/kg

Allene

No information

Amidosulfate hydrazine

No information

Amidosulfurous acid

No information

Ammonia

ihl-hmn LCLo:10000 ppm/3H  
ihl-hmn TCLo:20 ppm TFX:IRR  
ihl-rat LCLo:2000 ppm/4H  
ihl-mus LC<sub>50</sub>:4837 ppm/1H  
ihl-cat LC<sub>50</sub>:10066 ppm/1H  
ihl-rbt LCLo:10066 ppm/1H  
Aquatic Toxicity Rating: Tm96:10-1 ppm

Ammonium amido sulfate and sulfide

No information

Ammonium oxide

No information

Ammonium nitrate

Aquatic toxicity rating: TLm96:over 1000-100 ppm

Ammonium pyrosulfate

No information

Ammonium sulfamate

orl-rat LD<sub>50</sub>:1600 mg/kg  
ipr-rat LD<sub>50</sub>:800 mg/kg  
orl-mus LD<sub>50</sub>:3100 mg/kg

Ammonium sulfate

orl-rat LD<sub>50</sub>:3000 mg/kg

Asbestos

ihl-hmn TCLo:1.2 fibers/cc/19YC TFX:PUL  
ihl-rat TCLo:12 mg/m<sup>3</sup>/13W TFX:CAR  
ipr-rat TDLo:280 mg/kg TFX:CAR  
ipl-rat TDLo:100 mg/kg TFX:CAR

Barium oxide

scu-mus LDLo:20 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

Benzaldehyde

orl-rat LD<sub>50</sub>:1300 mg/kg  
scu-rat LDLo:5000 mg/kg  
orl-gpg LD<sub>50</sub>:1000 mg/kg

Biacetyl

orl-rat LD<sub>50</sub>:1580 mg/kg  
ipr-rat LD<sub>50</sub>:400 mg/kg  
orl-gpg LD<sub>50</sub>:990 mg/kg

Boron Oxide

No information

Bromine (gas)

orl-hmn LDLo:14 mg/kg  
ihl-hmn LCLo:1000 ppm  
ihl-rbt LCLo:180 ppm/7H  
Aquatic Toxicity Rating: TLm96:100-10 ppm

Butene

No information

Butyl alcohol

orl-rat LD<sub>50</sub>:6480 mg/kg  
ihl-rat LCLo:16000 ppm/4H  
ipr-mus LD<sub>50</sub>:771 mg/kg  
orl-rbt LDLo:6000 mg/kg  
Aquatic Toxicity Rating: TLm96:over 1000 ppm

Carbon dioxide

ihl-rat LCLo:657,190 ppm/15M  
ihl-rat TCLo:6 pph/24H/(10D preg) TFX:TER  
ihl-rat TCLo:10 pph/(7-12D preg) TFX:TER

Carbon disulfide

orl-hmn LDLo:14 mg/kg  
ihl-hmn LCLo:4000 ppm/30M  
ihl-hmn TCLo:50 mg/m<sup>3</sup>/7Y TFX:CNS  
ipr-rat LDLo:400 mg/kg  
scu-rat LDLo:300 mg/kg  
Aquatic Toxicity Rating: TLm96:1000-100 ppm

Carbon Monoxide

ihl-man LCLo:4000 ppm/30M  
ihl-man TCLo:650 ppm/45M TFX:CNS  
ihl-rat LC<sub>50</sub>:1807 ppm/4H  
ihl-mus LC<sub>50</sub>:5718 ppm/4H  
ihl-dog LCLo:3841 ppm/46M  
ihl-cat LCLo:8730 ppm/35H  
ihl-gpg LC<sub>50</sub>:2444 ppm/4H

Carbonyl sulfide

ihl-mus LCLo:2900 ppm

Chlorine (gas)

ihl-hmn TCLo:15 ppm TFX:PUL  
ihl-hmn LCLo:430 ppm/30M  
ihl-rat LC<sub>50</sub>:293 ppm/1H  
ihl-mus LC<sub>50</sub>:137 ppm/1H  
ihl-rat LCLo:138 ppm/1H  
Aquatic Toxicity Rating: TLm96:under 1 ppm

Chromium(III)oxide

ipr-rat TDLo:100 mg/kg TFX:CAR  
itr-rat TDLo:100 mg/kg TFX:CAR

Copper(II)oxide

No information

Cresol isomers

Cresol

orl-rat LD<sub>50</sub>:1454 mg/kg  
orl-mus LD<sub>50</sub>:861 mg/kg  
Aquatic Toxicity Rating: TLm96:10-1 ppm

m-Cresol

orl-rat LD<sub>50</sub>:242 mg/kg  
skn-rat LD<sub>50</sub>:620 mg/kg  
unk-rat LD<sub>50</sub>:350 mg/kg  
orl-mus LD<sub>50</sub>:828 mg/kg  
scu-mus LDLo:450 mg/kg  
scu-cat LDLo:180 mg/kg  
orl-rbt LDLo:1400 mg/kg  
skn-rbt LD<sub>50</sub>:2050 mg/kg  
scu-rbt LDLo:500 mg/kg  
ivn-rbt LDLo:280 mg/kg  
ipr-gpg LDLo:150 mg/kg  
scu-frg LDLo:250 mg/kg

o-Cresol

orl-rat LD<sub>50</sub>:121 mg/kg  
skn-rat LD<sub>50</sub>:1100 mg/kg  
orl-mus LD<sub>50</sub>:344 mg/kg  
scu-mus LDLo:410 mg/kg  
scu-cat LDLo:55 mg/kg  
orl-rbt LDLo:940 mg/kg  
skn-rbt LD<sub>50</sub>:1380 mg/kg  
scu-rbt LDLo:450 mg/kg  
ivn-rbt LDLo:180 mg/kg  
ipr-gpg LDLo:360 mg/kg  
scu-frg LDLo:200 mg/kg

p-Cresol

orl-rat LD<sub>50</sub>:207 mg/kg  
skn-rat LD<sub>50</sub>:750 mg/kg  
orl-mus LD<sub>50</sub>:344 mg/kg  
scu-mus LDLo:150 mg/kg  
unk-mus LD<sub>50</sub>:160 mg/kg  
scu-cat LDLo:80 mg/kg  
orl-rbt LDLo:620 mg/kg  
skn-rbt LD<sub>50</sub>:301 mg/kg  
scu-rbt LDLo:300 mg/kg  
ivn-rbt LDLo:180 mg/kg  
ipr-gpg LDLo:100 mg/kg  
scu-frg LDLo:150 mg/kg

1,2-Cyclohexadione

No information

1,3-Cyclohexadione

No information

1,4-Cyclohexadione

No information

Cyclohexanone

ihl-hmn TCLo:75 ppm TFX:IRR  
orl-rat LD<sub>50</sub>:1620 mg/kg  
ihl-rat LCLo:2000 ppm/4H

ipr-mus LD<sub>50</sub>:1350 mg/kg  
orl-mus LDLo:1300 mg/kg  
ivn-dog LDLo:630 mg/kg  
orl-rbt LDLo:1600 mg/kg  
skn-rbt LD<sub>50</sub>:1000 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

Cyclonite - RDX

Cyclopentane

Aquatic Toxicity Rating: TLm96:over 1000 ppm

Cyclopentanone

ipr-mus LD<sub>50</sub>:1960 mg/kg

Dehydroacetic acid

orl-rat LD<sub>50</sub>:500 mg/kg  
scu-rat TDL0:2600 mg/kg/65W  
unk-rat LD<sub>50</sub>:1000 mg/kg  
ipr-mus LD<sub>50</sub>:2000 mg/kg

2,2'-dicarbonyl-3,3',5,5'-tetranitroazobenzene (white compound)

No information

Diketene

orl-rat LD<sub>50</sub>:560 mg/kg  
orl-mus LDLo:800 mg/kg

Dimethyl peroxide

No information

Dinitrogen pentoxide and trioxide

No information

4,6-Dinitro-o-cresol

ihl-hmn TCLo:1 mg/m<sup>3</sup> TFX:CNS  
orl-rat LD<sub>50</sub>:25 mg/kg  
skn-rat LD<sub>50</sub>:200 mg/kg  
ipr-rat LD<sub>50</sub>:28 mg/kg  
orl-mus LD<sub>50</sub>:47 mg/kg  
ipr-mus LD<sub>50</sub>:19 mg/kg  
ihl-cat LCLo:40 mg/m<sup>3</sup>  
skn-gpg LDLo:500 mg/kg  
Aquatic Toxicity Rating: TLm96:10-1 ppm

2,6-Dinitro-p-cresol

ipr-mus LD<sub>50</sub>:24.8 mg/kg

2,4-Dinitrotoluene

orl-rat LD<sub>50</sub>:268 mg/kg  
orl-mus LD<sub>50</sub>:1625 mg/kg  
scu-man LDLo:50 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

2,5-Dinitrotoluene

orl-rat LD<sub>50</sub>:707 mg/kg  
orl-mus LD<sub>50</sub>:1231 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

2,6-Dinitrotoluene

orl-rat LD<sub>50</sub>:177 mg/kg  
orl-mus LD<sub>50</sub>:1000 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

3,4-Dinitrotoluene

orl-rat LD<sub>50</sub>:177 mg/kg  
orl-mus LD<sub>50</sub>:1414 mg/kg  
Aquatic Toxicity Rating: TLm96:100-10 ppm

3,5-Dinitrotoluene

No information

Formic acid

orl-rat LD<sub>50</sub>:1210 mg/kg  
orl-mus LD<sub>50</sub>:1100 mg/kg  
ipr-mus LD<sub>50</sub>:940 mg/kg  
ivn-mus LD<sub>50</sub>:145 mg/kg  
orl-dog LD<sub>50</sub>:4000 mg/kg  
ivn-rbt LD<sub>50</sub>:239 mg/kg

Glyoxal

orl-rat LDLo:100 mg/kg  
ipr-mus LD<sub>50</sub>:200 mg/kg  
orl-gpg LD<sub>50</sub>:760 mg/kg  
Aquatic Toxicity Rating: TLm96:over 1000 ppm

Hexamine

orl-rat LDLo:250 mg/kg  
orl-rat TDLo:14 gm/kg/76WC TFX:NEO

5-Hexenal

No information

Hydrochloric Acid

ihl-hmn LCLo:1300 ppm/30M  
ihl-rat LC<sub>50</sub>:3124 ppm/1H  
ihl-mus LC<sub>50</sub>:2142 ppm/30M  
ipr-mus LD<sub>50</sub>:40 mg/kg  
orl-rbt LD<sub>50</sub>:900 mg/kg

Hydrofluoric Acid

ihl-hmn TCLo:32 ppm TFX:IRR  
ihl-man TCLo:110 ppm/1M TFX:IRR  
ihl-hmn LCLo:50 ppm/30M  
ihl-rat LC<sub>50</sub>:1276 ppm/1H  
ipr-rat LDLo:25 mg/kg  
ihl-mus LC<sub>50</sub>:456 ppm/1H  
ihl-mky LC<sub>50</sub>:1780 ppm/1H  
ihl-rbt LCLo:260 mg/m<sup>3</sup>/7H  
orl-gpg LDLo:80 mg/kg  
ihl-gpg LC<sub>50</sub>:4327 ppm/15M  
scu-gpg LDLo:100 mg/kg  
scu-frg LDLo:112 mg/kg

Ethane

No information

Ethylene

Aquatic Toxicity Rating: TLM96:1000-100 ppm

Ethyl Nitrate

Aquatic Toxicity Rating: TLM96:over 1000 ppm

Ethyl nitrite

unk-chd LDLo:200 mg/kg  
Aquatic Toxicity Rating: TLM96:over 1000 ppm

Fluorine

ihl-hmn	TCLo:25 ppm/5M	TFX:EYE
ihl-rat	LC <sub>50</sub> :185 ppm/1H	
ihl-mus	LD <sub>50</sub> :150 ppm/1H	
ihl-rbt	LC <sub>50</sub> :270 ppm/30M	
ihl-gpg	LC <sub>50</sub> :170 ppm/1H	

Formaldehyde

orl-wmn	LDLo:36 mg/kg	
ihl-hmn	TCLo:13.8 ppm	TFX:IRR
orl-rat	LD <sub>50</sub> :800 mg/kg	
ihl-rat	LCLo:250 ppm/4H	
scu-rat	LD <sub>50</sub> :420 mg/kg	
scu-rat	TDL <sub>8</sub> :1300 mg/kg/65 WI	TFX:NEO
ihl-mus	LCLo:900 mg/m <sup>3</sup> /2H	
ipr-mus	LDLo:16 mg/kg	
scu-mus	LD <sub>50</sub> :300 mg/kg	
scu-dog	LDEL:550 mg/kg	
ihl-cat	LCLo:820 mg/m <sup>3</sup> /8H	
skn-rbt	LD <sub>50</sub> :270 mg/kg	
scu-rbt	LDEL:240 mg/kg	
orl-gpg	LD <sub>50</sub> :260 mg/kg	

Aquatic Toxicity Rating: TLM96:100-10 ppm

Hydrogen bromide

ihl-hmn	TCLo:5 ppm	TFX:IRR
ihl-rat	LC <sub>50</sub> :2858 ppm/1H	
ihl-mus	LC <sub>50</sub> :814 ppm/1H	

Hydrogen cyanide

orl-hmn	LDLo:570 µg/kg	
ihl-hmn	LCLo:120 mg/m <sup>3</sup> /1H	
ihl-hmn	LCLo:200 mg/m <sup>3</sup> /10M	
scu-hmn	LDLo:1 mg/kg	
ivn-hmn	LD <sub>50</sub> :1 mg/kg	
ihl-rat	LC <sub>50</sub> :544 ppm/5M	
orl-mus	LD <sub>50</sub> :3700 µg/kg	
ihl-mus	LC <sub>50</sub> :169 ppm/30M	
ipr-mus	LD <sub>50</sub> :2990 µg/kg	
scu-mus	LDLo:3 mg/kg	
ivn-mus	LD <sub>50</sub> :1100 µg/kg	
ims-mus	LD <sub>50</sub> :2700 µg/kg	
orl-dog	LDLo:4 mg/kg	
ihl-dog	LC <sub>50</sub> :300 ppm/3M	
scu-dog	LDLo:1700 µg/kg	
orl-cat	LDLo:2 mg/kg	
ihl-cat	LCLo:2500 mg/m <sup>3</sup>	
scu-cat	LDLo:1100 µg/kg	
ihl-rbt	LCLo:600 mg/m <sup>3</sup> /2M	
ipr-rbt	LD <sub>50</sub> :1570 µg/kg	
scu-rbt	LD <sub>50</sub> :2500 µg/kg	
ivn-rbt	LD <sub>50</sub> :820 µg/kg	
ims-rbt	LD <sub>50</sub> :1100 µg/kg	
scu-gpg	LDLo:100 µg/kg	

Aquatic Toxicity Rating: TLm96:under 1ppm

Hydrogen peroxide

No information

Hydrogen sulfide

ihl-hmn	LCLo:600 ppm/30M
ihl-rat	LC <sub>50</sub> :713 ppm/1H
ihl-mus	LC <sub>50</sub> :673 ppm/1H

Lead oxide (monoxide)

ipr-rat LDLo:430 mg/kg

Methane

Aquatic Toxicity Rating: TLm96:over 1000 ppm

Methanol

orl-hmn LDLo:340 mg/kg  
orl-hmn TDLo:100 mg/kg TFX:EYE  
ihl-hmn TClO:300 ppm TFX:CNS  
orl-rat LD<sub>50</sub>:13 g/kg  
ipr-rat LDLo:1800 mg/kg  
scu-mus LD<sub>50</sub>:9800 mg/kg  
orl-mus LDLo:420 mg/kg  
orl-dog LDLo:6300 mg/kg  
orl-mky LDLo:7000 mg/kg  
ihl-mky LC<sub>50</sub>:1000 ppm  
orl-rbt LDLo:4750 mg/kg  
skn-rbt LD<sub>50</sub>:20 gm/kg  
Aquatic Toxicity Rating: TLm96:over 1000 ppm

Methyl acetate

orl-rat LDLo:4800 mg/kg  
ihl-mus LClO:80 mg/m<sup>3</sup>/31M  
ihl-cat LClO:67 mg/m<sup>3</sup>/56M  
scu-cat LDLo:3000 mg/kg  
orl-rbt LD<sub>50</sub>:3700 mg/kg  
scu-gpg LDLo:3000 mg/kg  
Aquatic Toxicity TLm96:1000-100 ppm

Methyl ethyl ketone

ihl-hmn TClO:300 ppm TFX:PNS  
ihl-wmn TClO:398 ppm TFX:CNS  
ihl-hmn TClO:100 ppm/5M TFX:IRR  
orl-rat LD<sub>50</sub>:3400 mg/kg  
ihl-rat LClO:2000 ppm/4H  
ihl-rat TClO:1000 ppm/(6-15D preg) TFX:TER  
ipr-rat LDLo:2000 mg/kg  
ipr-mus LD<sub>50</sub>:616 mg/kg  
skn-rbt LD<sub>50</sub>:13 gm/kg  
Aquatic Toxicity Rating: TLm96:over 1000 ppm

Methyl formate

ihl-gpg LCLo:10,000 ppm  
orl-rbt LD<sub>50</sub>:1620 mg/kg

Methyl nitrate

No information

Methyl nitrite

ihl-rat LCLo:250 ppm/4H

Nitric acid

Aquatic Toxicity Rating: TLm96:100-10 ppm

Nitric oxide

ihl-mus LCLo:320 ppm  
ihl-rbt LC<sub>50</sub>:315 ppm/15M

Nitrocresol isomers

2-Nitro-p-cresol

orl-rat LD<sub>50</sub>:3360 mg/kg

4-Nitro-m-cresol

ipr-mus LDLo:500 mg/kg

Nitroform

No information

Nitrogen dioxide

ihl-hmn TCLo:64 ppm  
ihl-rat LC<sub>50</sub>:88 ppm/4H  
ihl-mus LCLo:260 ppm/30 M  
ihl-mky LCLo:44 ppm/6H  
ihl-rbt LC<sub>50</sub>:315 ppm/15M

TFX:PUL

Nitrogen trioxide

No information

Nitromethane

orl-rat LD<sub>50</sub>:940 mg/kg  
orl-mus LD<sub>50</sub>:950 mg/kg  
Orl-dog LDLo:125 mg/kg  
scu-dog LDLo:565 mg/kg  
ivn-dog LDLo:800 mg/kg<sub>3</sub>  
ihl-mky LCLo:2446 mg/m<sup>3</sup>  
orl-rbt LDLo:750 mg/kg  
ivn-rbt LDLo:750 mg/kg

Nitrosamines (n-nitrosodimethylamine)

orl-rat LD<sub>50</sub>:26 mg/kg  
orl-rat TDLo:248 mg/kg/31WI TFX:CAR  
ihl-rat LC<sub>50</sub>:78 ppm/4H  
ihl-rat TCLo:37 mg/kg TFX:CAR  
ipr-rat LD<sub>50</sub>:36 mg/kg  
ipr-rat TDLo:30 mg/kg TFX:NEO  
scu-rat LD<sub>50</sub>:45 mg/kg  
ivn-rat TDLo:40 mg/kg  
ims-rat TDLo:18 mg/kg TFX:NEO  
par-rat TDLo:7 mg/kg/(15-21D preg) TFX:NEO  
ivn-rat TDLo:18 mg/kg TFX:NEO  
orl-mus TDLo:370 mg/kg/56WC TFX:CAR  
ihl-mus LC<sub>50</sub>:57 ppm/4H  
ihl-mus TCLo:200 µg/m<sup>3</sup>/26WC TFX:CAR  
ipr-mus LDLo:9 mg/kg  
ipr-mus TDLo:7 mg/kg TFX:NEO  
scu-mus TDLo:4375 µg/kg TFX:CAR  
unk-mus TDLo:13 mg/kg (preg) TFX:TER  
unk-mus LDLo:20 mg/kg  
orl-dog LDLo:20 mg/kg  
ihl-dog LCLo:16 ppm/4H  
orl-rbt TDLo:202 mg/kg/23WC TFX:CAR  
unk-rbt LDLo:10 mg/kg  
unk-gpg LDLo:25 mg/kg  
orl-ham TDLo:21 mg/kg TFX:CAR  
scu-ham LD<sub>50</sub>:28 mg/kg  
scu-ham TDLo:50 mg/kg/6WI TFX:CAR

o-nitrosobenzoic acid

No information

Nitrosomethane

No information

Nitrosotoluene isomers

No information

Nitrotoluenes

$\alpha$ -nitrotoluene

No information

2-nitrotoluene

orl-rat LD<sub>50</sub>:891 mg/kg  
orl-mus LD<sub>50</sub>:2462 mg/kg  
Aquatic Toxicity Trating: TLm96:100-10 ppm

3-nitrotoluene

orl-rat LD<sub>50</sub>:1072 mg/kg  
orl-mus LD<sub>50</sub>:330 mg/kg  
orl-rbt LD<sub>50</sub>:2400 mg/kg  
orl-gpg LD<sub>50</sub>:3600 mg/kg

4-nitrotoluene

orl-rat LD<sub>50</sub>:2144 mg/kg  
orl-mus LD<sub>50</sub>:1231 mg/kg  
ipr-mam LD<sub>50</sub>:940 mg/kg

Nitrous acid

No information

Nitrous oxide

ihl-rat TCLo:50 pph/2D/(8-10D preg) TFX:TER  
ihl-mus LCLo:1500 ppm  
Aquatic Toxicity Rating: TLm:96 over 1000 ppm

Ozone

ihl-hmn TCLo:100 ppm/1M TFX:SKN  
ihl-mam TCLo:1860 ppb/75M TFX:CNS  
ihl-hmn TCLo:100 ppb TFX:IRR  
ihl-hmn TCLo:1 ppm TFX:PUL  
ihl-hmn TCLo:0.2 ppm/3H TFX:EYE  
ihl-rat LC<sub>50</sub>:4.8 ppm/4H  
ihl-mus LCLo:100 ppm/1H  
ihl-mus TCLo:4.5 ppm/50HI TFX:NEO  
ihl-ham LC<sub>50</sub>:10.5 ppm/4H

4-pentanol

orl-rat LD<sub>50</sub>:3200 mg/kg  
skn-rbt LD<sub>50</sub>:6000 mg/kg  
Aquatic Toxicity Rating: TLm96:1000-100 ppm

1-pentene

No information

Peroxy acetyl nitrate

ihl-mus LC<sub>50</sub>:106 ppm/2H

Peroxy benzoyl nitrate

No information

Phenol

orl-hmn TDLo:14 mg/kg TFX:GIT  
orl-hmn LDLo:140 mg/kg  
orl-rat LD<sub>50</sub>:414 mg/kg  
skn-rat LD<sub>50</sub>:669 mg/kg  
ipr-rat LD<sub>50</sub>:250 mg/kg  
scu-rat LDLo:650 mg/kg  
orl-mus LD<sub>50</sub>:300 mg/kg  
skn-mus TDLo:4000 mg/kg/20WI TFX:CAR  
scu-mus LD<sub>50</sub>:344 mg/kg  
scu-cat LDLo:80 mg/kg  
ivn-cat LDLo:50 mg/kg

orl-rbt LDLo:420 mg/kg  
 skn-rbt LDLo:2000 mg/kg  
 ipr-rbt LDLo:620 mg/kg  
 scu-rbt LDLo:620 mg/kg  
 ivn-rbt LDLo:300 mg/kg  
 ipr-gpg LDLo:300 mg/kg  
 scu-gpg LDLo:450 mg/kg  
 par-frg LDLo:290 mg/kg  
 Aquatic Toxicity Rating: TLm96:100-10 ppm

Phosgene

ihl-hmn LC<sub>50</sub>:3200 mg/m<sup>3</sup>  
 ihl-hmn TCLO:25 ppm/30M TFX:IRR  
 ihl-rat LCLo:50 ppm/30M  
 ihl-mus LC<sub>50</sub>:110 ppm/30M  
 ihl-dog LCLo:79 ppm/30M  
 ihl-mky LC<sub>50</sub>:1087 ppm/1M  
 ihl-cat LC<sub>50</sub>:1482 ppm/1M  
 ihl-rbt LC<sub>50</sub>:3211 ppm/1M  
 ihl-gpg LC<sub>50</sub>:141 ppm/30M  
 ihl-gpg LCLo:31 mg/m<sup>3</sup>/20M

Phosphorous pentoxide

No information

Polycyclic aromatic hydrocarbons

See data in text

n-Propanol

orl-wmn LDLo:5700 mg/kg  
 orl-rat LD<sub>50</sub>:1870 mg/kg  
 orl-rat TDLo:50 gm/kg/1 TFX:CAR  
 ihl-rat LCLo:4000 ppm/4H  
 scu-rat TDLo:6 gm/kg/1 TFX:CAR  
 orl-mus LDLo:140 mg/kg  
 scu-mus LD<sub>50</sub>:3230 mg/kg  
 orl-rbt LDLo:3500 mg/kg  
 skn-rbt LD<sub>50</sub>:5040 mg/kg  
 scu-mam LDLo:5 mg/kg  
 Aquatic Toxicity Rating: TLm96:1000-100 ppm

Propene

Aquatic Toxicity Rating: TLm96:over 1000 ppm

n-Propyl acetate

orl-rat LD<sub>50</sub>:9800 mg/kg  
ihl-rat LCL<sub>0</sub>:8000 ppm/4H  
orl-rbt LD<sub>50</sub>:6630 mg/kg  
Aquatic Toxicity Rating: TLm96:1000-100 ppm

n-Propyl formate

orl-rat LD<sub>50</sub>:3980 mg/kg  
orl-mus LD<sub>50</sub>:3400 mg/kg

Pyruvaldehyde

No information

RDX

orl-rat LD<sub>50</sub>:200 mg/kg  
ipr-rat LDLo:10 mg/kg  
ivn-rat LDLo:18 mg/kg  
orl-mus LD<sub>50</sub>:500 mg/kg  
ivn-mus LD<sub>50</sub>:19 mg/kg  
ivn-dog LDLo:40 mg/kg  
unk-cat LDLo:100 mg/kg  
skn-gpg LDLo:465 mg/kg  
ivn-gpg LD<sub>50</sub>:25 mg/kg

Selenium dioxide

scu-rbt LD<sub>50</sub>:4 mg/kg

Soot

No information

Sulfamic acid

orl-rat LD<sub>50</sub>:1600 g/kg  
ipr-rat LDLo:100 mg/kg

Sulfoacetic anhydride

No information

Sulfur dioxide

ihl-hmn	TCLo:3 ppm/5D	TFX:PUL
ihl-man	TCLo:4 ppm/1M	TFX:PUL
ihl-rat	LCLo:611 ppm/5H	
ihl-mus	LCLo:764 ppm/20M	
ihl-gpg	LCLo:5000 ppm/5M	

Sulfuric acid

orl-rat LD<sub>50</sub>:2140 mg/kg

Mist

ihl-hmn	TCLo:3 mg/m <sup>3</sup> /24 W	TFX:MTH
ihl-hmn	TCLo:350 µg/m <sup>3</sup> /3M	TFX:PUL
ihl-rat	LCLo:178 ppm/7H	
ihl-mus	LCLo:140 ppm/210M	
ihl-gpg	LCLo:48 ppm/H	

Sulfur trioxide

Aquatic Toxicity Rating: TLm96:100-10 ppm

Tetranitromethane

ihl-rat	LCLo:33 ppm/6H
ihl-man	LDLo:500 mg/kg

Toluene

ihl-hmn	TCLo:200 ppm	TFX:CNS
ihl-man	TCLo:100 ppm	TFX:PSY
orl-rat	LD <sub>50</sub> :5000 mg/kg	
ihl-rat	LCLo:4000 ppm/4H	
ipr-rat	LDLo:800 mg/kg	
scu-rat	LDLo:5000 mg/kg	
ipr-rat	LD <sub>50</sub> :1640 mg/kg	
ihl-mus	LC <sub>50</sub> :5300 ppm	
skn-rbt	LD <sub>50</sub> :14 gm/kg	
Aquatic Toxicity Rating: TLm96:100-10 ppm		

Trinitrobenzaldehyde

No information

Trinitrobenzene

orl-rat LD<sub>50</sub>:505 mg/kg  
orl-mus LD<sub>50</sub>:572 mg/kg

Trinitrobenzoic acid

No information

2,4,6-Trinitro-m-cresol

ipr-mus LDLo:31 mg/kg  
ipr-mus LD<sub>50</sub>:168 mg/kg

Trinitromethane

No information

Trinitromethylnitrite

No information

Trinitrosomethane

No information

2,4,6-Trinitrotoluene

orl-rat LDLo:700 mg/kg  
orl-cat LDLo:1850 mg/kg  
scu-cat LDLo:200 mg/kg  
orl-rbt LDLo:500 mg/kg  
scu-rbt LDLo:500 mg/kg

2,3,4-; 2,3,5-; 2,4,5-Trinitrotoluene

No information

SUBMIT IN TRIPLICATE

RESEARCH TRIANGLE INSTITUTE  
DUPLICATING ORDER

No. \_\_\_\_\_

Requested By: Bearse / Allen

Project No. 5410

Center / Division RED

Date 9/19/78

Proof Date \_\_\_\_\_

Job Complete Date \_\_\_\_\_

Short Title or Job Description Business Cards

Number of Pages \_\_\_\_\_

Number of Copies Each Page \_\_\_\_\_

PRINTING

- Print One Side Only
- Print Both Sides
- Photographs
- Halftones
- Albanene (reproducible copy)
- NCR - 2 pt. - 3 pt. - 4 pt. - 5 pt.
- No Reduction
- Reduction 92% \_\_\_\_\_ Other \_\_\_\_\_
- Other \_\_\_\_\_

COVERS:  None  Index  Proposal  Window  
 Other \_\_\_\_\_

BINDERY:

- Gather Only
- One Staple Upper Left-Hand Corner
- Saddle Stitch
- Three Staples and Black Tape
- Plastic Spiral Binding
- Perfect Bound
- Padding
- Wrapping

Return One Complete Copy for Review and Approval:  Yes  No

SPECIAL INSTRUCTIONS:

DO NOT WRITE IN THIS SPACE

Date Received \_\_\_\_\_

PRINTING Date Proof Returned \_\_\_\_\_

Both Sides \_\_\_\_\_

Fronts \_\_\_\_\_

Photo Both Sides \_\_\_\_\_

Photo Front \_\_\_\_\_

Albanene \_\_\_\_\_

Colored Paper \_\_\_\_\_

MAKEUP

Red. PU., Pasteups \_\_\_\_\_

Re-Runs \_\_\_\_\_

Comp., Lay-Outs \_\_\_\_\_

LS Half, \_\_\_\_\_ SS Half. \_\_\_\_\_

COVERS

Ind., Prop., Win. \_\_\_\_\_

Perfect Bind, Wrap Around \_\_\_\_\_

Other \_\_\_\_\_

BINDERY

Proof \_\_\_\_\_

Gather only \_\_\_\_\_

G&S LH, 3S; Saddle \_\_\_\_\_

Tape \_\_\_\_\_

Pad & Chip \_\_\_\_\_

Pad NCR \_\_\_\_\_

Drill \_\_\_\_\_

Mech. Bind \_\_\_\_\_

Perfect Bind \_\_\_\_\_

Inserting \_\_\_\_\_

Folding, Fold Outs \_\_\_\_\_

Disa., Re-Bind \_\_\_\_\_

Slip Sheet \_\_\_\_\_

Wrap \_\_\_\_\_

TOTAL

DO NOT WRITE IN THIS SPACE

Approved: Ben H. Cuyler

(Admin. Confirmation)

RTI-39A-2-73