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FATE OF SELECTED HIGH EXPLOSIVES IN THE ENVIRONMENT: A LITERATURE REVIEW

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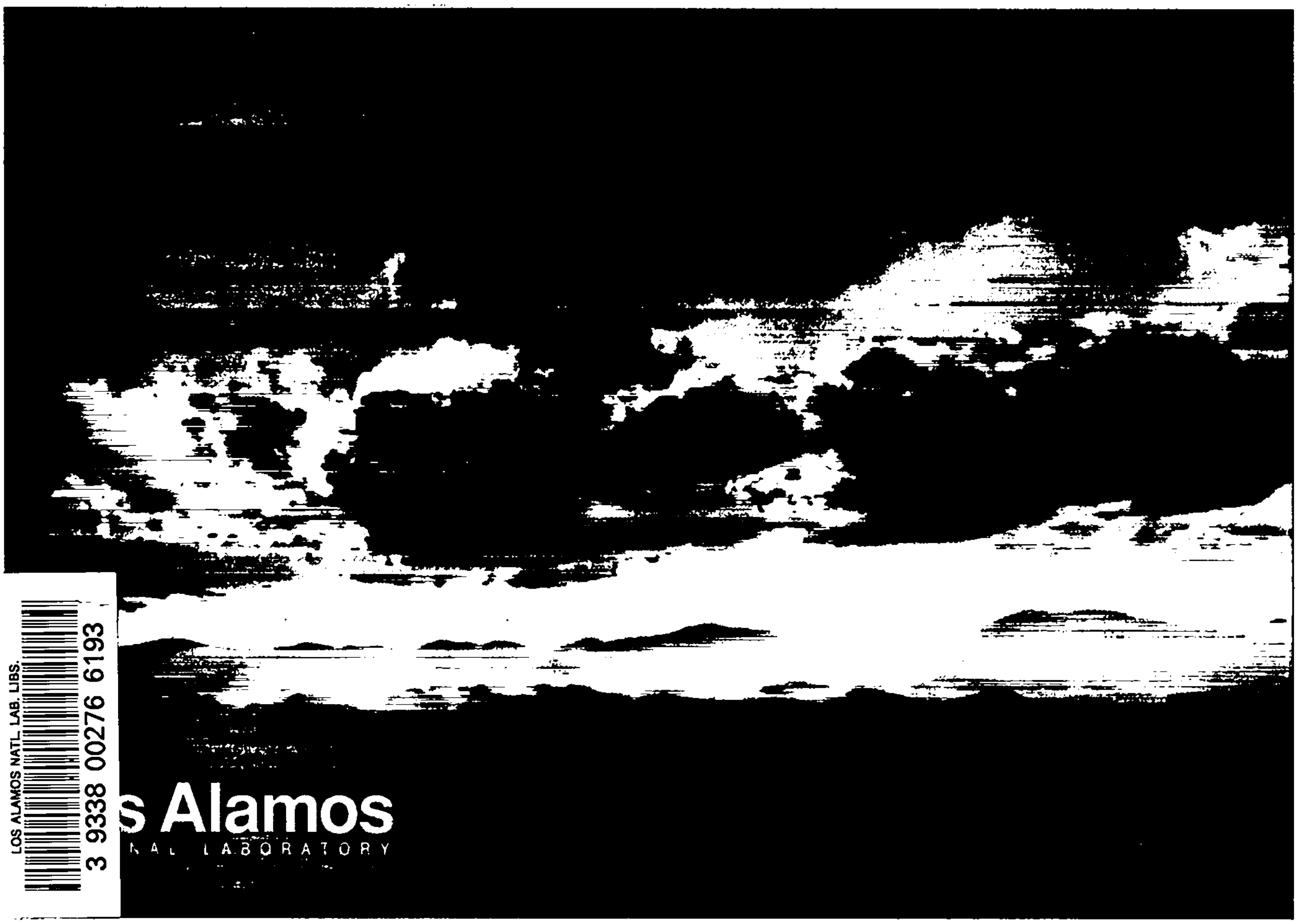
DEPLETED URANIUM INVESTIGATIONS PROGRAM



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FATE OF SELECTED HIGH EXPLOSIVES IN THE ENVIRONMENT: A LITERATURE REVIEW

by

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I. INTRODUCTION

The objective of this document is to report on the current literature of environmental fate of 4 explosives. The particular explosives selected are those in use, or anticipated to be used at Eglin Air Force Base, Florida, the funding agency for this work. They are: TNT, RDX, HMX, and NTO. This report is not intended to be an exhaustive search of the literature, but to present the current status on the subject. The ultimate desire is to be able to use this information in the design of environmental sampling characterization and investigations for high explosives. General properties and history of these explosives will be presented, along with recommended exposure limits, followed by a compilation of their degradation products and brief review of results of some environmental sampling for high explosives in soil and groundwater.

II. GENERAL DISCUSSION OF TNT, RDX, HMX, AND NTO

The following discussion of general properties and exposure effects to humans is summarized from Gibbs and Popolato (1980), Fedoroff and Sheffield (1966), Yinon (1990), and U.S. EPA (1991).

A. *TNT*

2,4,6-trinitrotoluene, or TNT, is a light yellow or buff crystalline solid which was first crudely prepared in 1863 by Wilbrand; pure TNT was prepared by Hepp in 1880. Manufacturing of TNT began in Germany in 1891, and adopted for use by the German Army in 1902. The U.S. Army began using TNT in 1912, and by 1914 to 1918 TNT became the standard explosive of all armies during World War I. During World War I the production of TNT was limited by the availability of toluene from coal tar. To relieve the shortage, mixtures with ammonium nitrate, or amatols, were used. Some TNT-aluminum (tritonals) were also used during this time. In the 1930's and 1940's, TNT-RDX composites (cyclotols) were developed. By World War II there was widespread use of binary explosive mixtures of TNT with PETN, RDX, Tetryl, and ammonium picrate. The TNT-HMX mixtures were developed by 1952. In 1966, HNS was made from TNT, and in 1978, TATB.

It is the most common military explosive because of its ease in manufacture, its low melting point which makes it suitable for melt-casting or loading operations either as pure TNT or as a composite mixture, low cost from available raw materials, safety in handling due to low sensitivity to impact and friction, fairly high explosive power, chemical and thermal stability, compatibility with other explosives, and a moderate toxicity. All TNT manufacturing in the U.S. use the same chemical process which is treatment of liquid toluene with mixed nitric and sulfuric acids followed by removal of undesired isomers and residual dinitrated toluene.

There are two main variations in the TNT manufacturing processes, the three-stage batch process and the continuous process. TNT can have up to 6 isomers, but only the 2,4,6-(α) isomer is used. The undesired isomers and residual dinitrated species are removed from the reaction mixture by treatment with aqueous sodium sulfite solution or sellite, which reacts with all but the desired 2,4,6-isomer to form water-soluble sulfonate derivatives. The remaining α -TNT is washed and cast molten onto a flaker belt. The spent sellite solution is known as "red water" or "pink water" and constitutes the major waste stream.

The addition of oxygen-rich products to TNT can enhance its explosive capacity. Various materials are added to TNT to form composite explosives. One example is Composition B (Comp B), a mixture of TNT with RDX. Other composite explosives are mixtures with RDX (cyclotols), HMX (octols), ammonium nitrate (amatols), PETN (pentolites), tetryl (tetrytols) and aluminum (tritonals). TNT is known as TNT, Tol, or Trotil in Russia, TNT in the United Kingdom, as Tolite in France, Tri, Trotyl, Tutol, Trinol, and Füllpulver 1902 in Germany and Tritolo in Italy. Chemical properties of TNT are summarized in Table I. TNT may be shipped dry as a Class A explosive.

Table I

Properties of Selected High Explosives

Common Name	Formula	Molecular Weight	Solubility at 20°C Dissolved/100 g	Melting Point (°C)	Ignition Temperature (°C)
TNT	$C_7H_5N_3O_6$	227.13	0.013 g Water 109 g Acetone 55 g Toluene	80.65	300
RDX	$C_3H_6N_6O_6$	222.26	0.005 g Water 6.81 g Acetone 0.020 g Toluene	204.1	229
HMX	$C_4H_8N_8O_8$	296.17	2.4 g Anhydrous Acetone	256-281 (α - δ)	335 (Explosion within 5 sec)
NTO	$C_2H_2N_4O_3$	130	49 g/L Water 18 g/L Acetone 625 g/L DMSO		

Three main modes exist to give an occupational exposure; they are through inhalation, through skin adsorption, and by way of the gastrointestinal tract. Human health effects were determined through examination of exposure data collected through occupational health surveys conducted at U.S. Army Ammunition Plants. Results indicated that atmospheric exposure to

TNT at concentrations ranging from 0.02 to 3.0 mg/m^3 for periods up to 6 months caused abnormalities in the blood, specifically increased white blood cell count and a reduction in hematocrit, hemoglobin, and red blood cells. Exposure can cause a yellow discoloration of the skin, nails, and hair, a bluish discoloration of the mucosa, epigastric pain, tenderness or spasm, an enlarged and palpable liver, and changes in one's electrocardiogram and electroencephalogram. Exposure can also cause an amber to deep red color change in the urine.

An initial atmospheric exposure to TNT may result in mild irritation of the respiratory passageways and skin, and gastrointestinal distress. TNT which is absorbed in sufficient amounts through the skin or lungs can produce signs of cyanosis, aplastic anemia, cataract formation, menstrual disorder, neurological manifestation, and nephrotoxicity. Toxic hepatitis and aplastic anemia are reported to be the principal cause of death after TNT intoxication. The American Conference of Governmental Industrial Hygienists 8-hour time-weighted averaged Threshold Limit Value for exposure is 0.5 mg/m^3. The Occupational Safety and Health Administration Permissible Exposure Limit is 1.5 mg/m^3. The U.S. Navy Bureau of Medicine and Surgery established an interim Maximum Contaminant Level of 0.05 mg/L of TNT in drinking water. The U.S. Environmental Protection Agency recommends health advisory values for drinking water as 0.02 mg/L for 1- and 2-day and longer term periods, and 0.002 mg/L for a lifetime value.

B. *RDX*

RDX, or hexahydro-1,3,5-trinitro-1,3,5-triazine inherits its name from British activities with the explosive during World War II, when the British code name, Research Department Explosive or Royal Demolition Explosive determined its acronym. It is a colorless, polycrystalline material. RDX is also known as hexahydro-1,3,5-trinitro-s-triazine, cyclotrimethylenetrinitramine, 1,3,5-trinitro-1,3,5-triazocyclohexane, trinitro-trimethylene-triamine, Hexogen, cyclonite, and T4.

RDX was first developed by Henning in Germany in 1899 for medical use. It was not until 1922 when von Herz recognized its potential as an explosive. The method of preparation produced poor yields, thereby rendering its manufacture expensive and unsuitable for large scale production. There was no substantial improvement until World War II, when expanded efforts and change in manufacturing techniques enabled Great Britain to produce up to 180 tons of RDX per week, and Germany to reach a peak production of almost 8 million pounds during the month of June 1945. In addition to its explosive use, RDX has also been used as a rat poison.

Chemical properties are summarized in Table I. RDX has a high chemical stability, nearly that of TNT, - and an explosive power much greater than TNT. It is also more susceptible to shock detonation than TNT. RDX is used as the base charge in detonators, as an ingredient in TNT-based composite explosives such as the cyclotols and Comp B, and as the primary ingredient in plastic-bonded explosives or plastic explosives such as Composition A and Composition C. Although RDX is unsuitable for cast loading, it can be used in fin press loading operations. Cast loading can be accomplished by using a mixture of RDX and TNT, for example 70 percent RDX to 30 percent TNT. RDX is shipped wet as a Class A explosive with not less than 10 percent water content.

Manufacturing of RDX is commonly accomplished by the Woolwich process or the Bachmann method. The Woolwich is a direct nitrolysis process which commonly yields 70 to 75 percent RDX with only a trace of HMX. In the Bachmann process, hexamine is reacted with an ammonium nitrate/nitric acid mixture at 75°C with acetic acid and acetic anhydride. The Bachmann process initially produces about 79 percent RDX with 6 percent HMX, although subsequent aging and recrystallization converts the mixture to a higher RDX content. All handling is in the wet state to decrease the possibility of accidental explosion.

In human health effects investigations of military personnel, dysfunction of the central nervous system were observed, including convulsions and coma. Workers who inhaled RDX dust at unknown levels at an Army ammunition plant for several months became nauseous, unconscious and suffered a loss of reflexes. RDX is known to rapidly spread to body tissues, concentrating in the kidneys, liver, brain, and head. RDX is metabolized by the liver, and its metabolites (uncharacterized) are excreted in urine.

The American Conference of Governmental Industrial Hygienists 8-hour time-weighted average Threshold Limit Value for exposure to RDX is 1.5 mg/m^3. The U.S. Army Medical Bioengineering Research and Development Laboratory recommends an RDX limit of 0.03 mg/L in drinking water. The U.S. Environmental Protection Agency health advisory values for children for 1-day, 4-day, and longer term for drinking water is 0.1 mg/L. Values for adults for long term are 0.4 mg/L and 0.002 mg/L for a lifetime.

C. *HMX*

HMX is an explosive similar to RDX, but with a higher density and much higher melting point. It was initially produced as a by-product of RDX by the Bachmann process. Called cyclotetramethylenetetranitramine, 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine, homocyclonite, or octogen, it is a colorless polycrystalline material. Because of its high density, HMX replaces RDX in explosive applications for which energy and volume are important, such as in castable TNT-based binary explosives, in high-performance plastic-bonded explosives, and in high-performance solid propellants. HMX is an acronym used in Great Britain for High Melting Explosive. HMX is classed as a Class A explosive, and shipped wet with not less than 10 percent water. Properties for HMX are summarized in Table I.

HMX has been found to be poorly adsorbed when ingested by rats. Intravenous doses do not accumulate in body tissues and are partially excreted through urine. Data acquired through an occupational health study of 93 workers at an Army ammunition plant indicated that atmospheric exposure at unknown levels caused no hematologic, hepatic, or renal system abnormalities or auto-immune disease. Patch tests with solid HMX cause skin irritations.

There have been no designated threshold limit value nor short-term exposure limit for HMX. The U.S. EPA Health Advisory Values for drinking water are 5 mg/L for 1- and 4-day, and for longer term for a child, 20 mg/L for long term for an adult, and 0.4 mg/L for a lifetime dose.

D. *NTO*

NTO, or 3-nitro-1,2,4-triazol-5-one, is a new candidate energetic explosive developed by Los Alamos National Laboratory personnel in 1984 (Lee and Coburn, 1985). NTO has the advantages of a calculated detonation velocity and pressure equivalent of RDX, but is less sensitive and more stable than RDX. It is a white polycrystalline compound which is moderately soluble in water. NTO is rather acidic and will react readily with bases such as ammonium hydroxide to form ammonium salts. Chemical properties of NTO are presented in Table I.

Because NTO is a relatively new high explosive, information on its toxicology is forthcoming. Acute oral toxicity, skin sensitization, primary skin irritation and eye instillations were examined in laboratory animals (London, 1988). The acute oral LD50 oral dose for NTO were determined to be greater than 5 g/kg, which is considered only slightly toxic to non-toxic in both rats and mice. Sensitization study in a guinea pig did not show potential sensitizing effects. Skin application investigations on a rabbit demonstrated it was cutaneously nonirritating. NTO was found to be nonirritating in the rabbit eye application.

III. DEGRADATION OF HIGH EXPLOSIVES

A. *Thermal Degradation of High Explosives*

Thermal degradation of high explosives under normal detonation conditions when detonation goes to completion is relatively straightforward. Laboratory examination of HMX detonation in a confinement vessel where products are measured by mass spectrometry under air and vacuum conditions report that the predominant products are nitrogen, oxygen, carbon dioxide, carbon monoxide, and water (Fletcher and Loughran, 1992). Work with other explosives exhibit similar trends. Intermediate products produced during detonation include carbon ion, nitrogen ion, oxygen ion, water, hydrogen cyanide, carbon monoxide, nitrogen gas, nitrous oxide, cyanic acid and carbon dioxide; reaction and quenching between the intermediates occur, so that by the end of the detonation the predominant constituents remaining are water, carbon monoxide, nitrogen gas, and carbon dioxide. A major difference in the degradation products between individual explosives is in their relative amounts (Greiner and others, 1991). Therefore, the major compounds remaining post detonation of TNT, RDX, and HMX are water, carbon dioxide, nitrogen gas and carbon monoxide. Major NTO decomposition products are hydrogen cyanide, nitric oxide, water, CN_2H, cyanamide, cyanic acid, carbon dioxide, and nitrogen dioxide (Östmark and others, 1993).

During 1989 and 1990, a series of open-air detonations with TNT and RDX were conducted by the U.S. Army to compare results from "bang-box" studies in a confined environment to results collected from an aircraft flying though detonation clouds from actual open-air experiments (U.S. Army, 1992). Identified air emissions from detonation of TNT are listed in Table II, which includes inorganic, volatile and semi-volatile compounds. Also included are results of soil sampling. Recovered compounds in the soil above a concentration of 1 ng/g and were detected above background concentrations include TNT, 1,3,5-trinitrobenzene, Benz(a)anthracene, pyrene, and phenol. A similar test was repeated using RDX. Recovered compounds from air emissions and from soil sampling are presented in Table III. Analytes recovered in the soil above background concentrations were pyrene and naphthalene. Measured air emissions were comparable to those of TNT.

Literature on thermal degradation of NTO during open-air detonation was not located.

Table II
Thermal Degradation Products of TNT
(after U.S. Army, 1992)

Analyte	Air Emission	Detected in Soil (ng/g)
carbon dioxide	X	
carbon monoxide	X	
nitrogen oxide	X	
nitrogen dioxide	X	
methane	X	
total nonmethane hydrocarbons	X	
benzene	X	
2,4-dinitrotoluene	X	8.0
2,6-dinitrotoluene	X	2.3
2,4,6-dinitrotoluene	X	360[a]
2-nitronaphthalene	X	1.8
N-nitrosodiphenylamine	X	1.1
1-nitropyrene	X	1.2
naphthalene	X	210
benz(a)anthracene	X	11[a]
benzo(a)pyrene	X	
pyrene	X	53[a]
phenol	X	69[a]
dibenzofuran	X	18
diphenylamine	X	0.79
1,3,5-trinitrobenzene		39[a]

[a] Analyte was detected above background concentration.

Table III
Thermal Degradation Products of RDX
(after U.S. Army, 1992)

Analyte	Detected as Air Emission	Concentration in Soil (ng/g)
carbon dioxide	X	
carbon monoxide	X	
nitrogen oxide	X	
nitrogen dioxide	X	
methane	X	
total nonmethane hydrocarbons	X	
benzene	X	
2,4-dinitrotoluene	X	2.0
2,6-dinitrotoluene	X	0.9
2,4,6-dinitrotoluene	X	0.67
2-nitronaphthalene	X	0.90
1,3,5-trinitrobenzene	X	0.77
2-nitrodiphenylamine	X	0.19
1-nitropyrene	X	0.23
RDX	X	15
naphthalene	X	5.3[a]
benz(a)anthracene	X	2.4
benzo(a)pyrene	X	0.41
pyrene	X	5.3[a]
dibenzofuran	X	0.95
diphenylamine		0.48
N-nitrosodiphenylamine		1.7

[a] Analyte was detected above background concentration.

Results are not as straightforward for open burning due to lower temperatures, greater time periods for reactivity, and greater oxygen. Few actual measurements of combustion products generated exist. As summarized by Carpenter and others (1978), gas sampling was conducted at the Burlington Army Ammunition plant during the burning of 6 g of explosives and then the results were extrapolated to 3.8 tons burned. Burning of HMX (PBX-9404) resulted in generation of primarily oxides of nitrogen, hydrochloric acid, phosphorous pentoxide and carbon monoxide, in order of decreasing weight produced. The burning of TNT primarily produced soot, oxides of nitrogen , carbon monoxide and hydrocarbons, in order of decreasing weight. Carpenter and others (1978) also reports results of experimental burning of high explosives conducted by Mason and Hanger, Silas Mason Co., Inc. on quantities of materials on the order of one gram. They computed emission factors, which are dimensionless numbers that, when multiplied by the weight of explosive detonated or burned, results in the weight of the expected analyte. Based on the computed emission factors, they concluded that burning of TNT would produce primarily soot, followed by oxides of nitrogen, carbon monoxide, fluorocarbons and hydrocarbons, in order of decreasing emission factors. Similarly, burning of HMX (PBX 9404) produced, in order of decreasing emission factors, oxides of nitrogen, hydrochloric acid, carbon monoxide, and phosphorus pentoxide. No information has been located on products produced during burning of RDX or NTO.

B. *Degradation of High Explosives by Other Mechanisms*

1. TNT

Photochemical Degradation

Yinon summarized the findings of photochemical and microbial decomposition of TNT, which shall be reported in an abbreviated form here. When TNT, either in solid or solution form, is exposed to strong sunlight or ultraviolet radiation, it will decompose. Photochemical decomposition will turn an aqueous solution to pink, and then to a rusty-orange after 4 to 6 hours, hence the name "pink water". When a TNT solution at flow rates of 7 to 10 ml/min was exposed to light above 280 nm, decomposition products were identified as 1,3,5-trinitrobenzene (TNB), 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzonitrile, (Burlinson and others, 1973) Table IV. In another experiment, an aqueous solution of TNT was exposed to sunlight for 4 days. Four new compounds were found to be present which were all tetranitroazoxytoluenes, Table IV.

In an experiment where an aqueous solution of TNT was irradiated with UV light, it was found that TNT had photochemically decomposed and the one degradation product which was identified was 4-amino-2,6-dinitrotoluene (4-A), Table IV (Andrews and Osman, 1975). They identified that the degradation was dependent on the exposure time and the distance from the UV light source. Kaplan and others (1975) also studied the photochemical products of TNT degradation by UV light and identified TNB, 4,6-dinitroisoanthranil, 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzonitrile, 2,4,6-trinitrobenzaldoxime, 2,4,6-trinitrobenzyl alcohol, 3,5-dinitrophenol, 2-amino-4,6-dinitrobenzoic acid, 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene, 2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene, 2-carboxy-3,3',5,5'-tetranitroazoxybenzene, 2,4,6-trinitrobenzoic acid, and N-(2,carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide, Table IV.

Table IV
Decomposition Products of TNT
Photochemical Degradation

1,3,5-trinitrobenzene (TNB)
4,6-dinitroanthranil
2,4,6-trinitrobenzaldehyde (TNBAL)
2,4,6-trinitrobenzonitrile
2,2',6,6'-tetranitro-4,4'-azoxytoluene(4,4'-Az)
4,4',6,6'-tetranitro-2,2'-azoxytoluene(2,2'-Az)
2',4-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene
2,4'-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene
4-amino-2,6-dinitrotoluene (4-A)
4,6-dinitroisoanthranil
4,6-dinitroanthranil
2,4,6-trinitrobenzaldehyde
2,4,6-trinitrobenzonitrile
2,4,6-trinitrobenzaldoxime
2,4,6-trinitrobenzyl alcohol (TNBOH)
3,5-dinitrophenol
2-amino-4,6-dinitrobenzoic acid
2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene
2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene
2-carboxy-3,3',5,5'-tetranitroazoxybenzene
2,4,6-trinitrobenzoic acid (TNBA)
N-(2-carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide

Microbial Degradation

Identification of degradation products of TNT as a result of microbial action is associated, for the most part, with laboratory experiments designed to evaluate methods to treat TNT wastes. Won and others (1974) showed three *Pseudomonas*-like organisms metabolically oxidize TNT.

These organisms were designated as isolate "Y", a nitrate reducer, "I", an indole former, and "II". TNT metabolites included 2,2',6,6'-tetranitro-4-azoxytoluene, 2,2',4,4'-tetranitro-6-azoxytoluene, 2-A, and diaminonitrotoluene (not specified). The azoxy compounds degraded to almost complete disappearance within 72 hours after the TNT was depleted.

Traxler (1975) used high concentrations of two *Pseudomonas* isolates, IIPX and S95YUN-5, to remove ^{14}C-labeled TNT from the reaction mixture without the use of a yeast extract supplement. Small amounts of nitrate were observed when the reaction was conducted in a nitrogen-free culture.

Parrish (1977) conducted experiments with 190 cultures of fungi. TNT was transformed by 183 of them; transformation products were identified as 4-A, 4-OHA, and 2,2',6,6',-tetranitro-4,4'-azoxytoluene (4,4'-Az).

Metabolites resulting from aerobic cultivation of *Escherichia coli* with glucose and TNT were identified as monoaminodinitrotoluenes (Naumova and others (1986). McCormick and others (1976) looked at transformation under aerobic and anaerobic conditions using an enzyme preparation from *Veillonella alkalenscens*. They found that reduction depended upon the type of preparation, whether a cell-free extract, resting cells, or growing cells, on the species, and on whether air or H_2 was used. Transformation products were 4-A, 2,4-DA, 4-OHA, 4,4'-Az and 2,4,6-triaminotoluene (TAT). They believed that the presence of azoxy compounds 4,4'-Az and traces of 2,2'-Az were due to nonenzymatic oxidation of the very reactive intermediate 4-OHA.

Hoffsommer and others (1978) looked at microbiological degradation during a 3-year pilot plant study. TNT was biotransformed by activated sludge micro-organisms supplemented with cornsteep water nutrient; transformation products included 4-A, 2-A, 2,4-DA, and 2,6-DA. Osmon and Andrews (1978) studied TNT decomposition in soil and in compost. Decomposition from soil microflora produced 4-A; complete decomposition did not occur. Compost degradation did complete the decomposition process, but the end products could not be identified. Compost decomposition of TNT was also studied by Kaplan and Kaplan (1982). Products identified were 2-A, 4-A, 4,4'-Az, 2,4'-Az, 2,4-DA and 2,6-DA. The TNT was not completely degraded. A review of TNT microbial degradation is also provided in Unkefer and others (1990). A list of microbial decomposition products is found in Table V.

2. RDX

Hydrolysis, Photolysis, and Biodegradation

In investigations on the aqueous alkaline hydrolysis of RDX, products of nitrite, nitrous oxide, ammonia, nitrogen, formaldehyde, and formate anion were obtained (Hoffsommer and others, 1977, Croce and Okamato, 1979). Response to RDX by UV radiation appeared to vary depending upon the presence of ozone (Glover and Hoffsommer, 1979). With ozone, decomposition products included carbon dioxide, nitrate ion, ammonia, carbon monoxide, and formic acid (assumed). Without ozone, the products were nitrite ion, ammonia or ammonia compounds, three organic nitro compounds, formaldehyde, and a predominance of nonextractable carbon compounds, presumed to be formic acid.

Table V
Decomposition Products of TNT
Microbial Decomposition

2,2',6,6'-tetranitro-4-azoxytoluene
2,2',4,4'-tetranitro-6-azoxytoluene
2-amino-4,6-dinitrotoluene (2-A)
diaminonitrotoluene
4-amino-2,6-dinitrotoluene (4-A)
nitrate
4-hydroxylamino-2,6-dinitrotoluene (4-OHA)
2,2',6,6'-tetranitro-4,4'-azoxytoluene (4,4'-Az)
monoaminodinitrotoluene
2,4-diamino-6-nitrotoluene (2,4-DA)
2,4,6-triaminotoluene (TAT)
4,4',6,6'-tetranitro-2,2'-azoxytoluene (2,2'-Az)
2,6-diamino-4-nitrotoluene (2,6-DA)

Hoffsommer and others (1978) in their 3-year pilot plant investigation for treatment of high explosives wastes, looked at degradation of RDX as a companion to TNT. Although TNT was decomposed, RDX remained unconverted. McCormick and others (1981) studied biodegradation of RDX in a mixture of anaerobic sewage sludge. Products formed were hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) after 8 days, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX) and hexahydro-1,3-dinitro-5-nitro-1,3,5-triazine (DNX) after 2 to 3 days, as well as hydrazine, 1,1-dimethyl-2hydrazine, 1,2-dimethylhydrazine, formaldehyde, and methanol, Table VI.

3. HMX

Photolysis, Hydrolysis, and Biodegration

Photolysis transformation products of HMX include nitrogen, nitrous oxide, nitrite ion, nitrate ion, formaldehyde, carbon dioxide and ethyne; microbial transformation products include 1,1-dimethylhydrazine, 1-nitroso-3,5,7-trinitro-1,3,5,7-tetraazocine, 1,3-dinitro-5,7-dinitro-

1,3,5,7-tetraazocine, 1,3,5-trinitro-7-nitro-1,3,5,7-tetraazocine, 1,5-dinitro-3,7-dinitro-1,3,5,7-tetraazocine, and 1,3,5,7-tetranitroso-1,3,5,7-tetraazocine, Table VII (Layton and others, 1987). Photolysis appears to be the major transformation route. Microbial decomposition occurs only with added nutrients and under anaerobic conditions. There has been little research in the area of hydrolysis of HMX.

Table VI
Decomposition Products of RDX
Hydrolysis, Photolysis, and Biodegradation

nitrite
nitrous oxide
ammonia
nitrogen
formaldehyde
formate anion
carbon dioxide
nitrate ion
carbon monoxide
formic acid (?)
formaldehyde
hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)
hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX)
hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX)
hydrazine
1,1-dimethylhydrazine
1,2-dimethylhydrazine
methanol

4. NTO

Literature on photolysis, hydrolysis, and biodegradation of NTO in laboratory or field experiments was not located.

Table VII
Decomposition Products of HMX Photolysis and Biodegradation

- nitrogen
- nitrous oxide
- nitrite ion
- nitrate ion
- 1,1-dimethylhydrazine
- formaldehyde
- carbon dioxide
- ethyne
- 1-nitroso-3,5,7-trinitro-1,3,5,7-tetraazocine
- 1,3-dinitroso-5,7-dinitro-1,3,5,7-tetraazocine
- 1,5-dinitroso-3,7-dinitro-1,3,5,7-tetraazocine
- 1,3,5,7-tetranitroso-1,3,5,7-tetraazocine
- 1,3,5-trinitroso-7-nitro-1,3,5,7-tetraazocine

IV. ENVIRONMENTAL FATE OF TNT, HMX, RDX, AND NTO

One of the earliest studies on the environmental fate of high explosives was performed by DuBois and Baytos in 1972 at an undisturbed forested location on Los Alamos National Laboratory. Samples of PETN, HMX, RDX, TNT, and eight other high explosives were mixed with native soil, replaced, and analyzed periodically for residual explosives. Some samples were mixed with *Pseudomonas aeruginosa* to determine if bacterial action could improve high explosives degradation rates. These samples generally reflect the effect of being buried in the surface soil layers, not deeper than the top few centimeters. After 4 years of exposure time, over 90 percent of the RDX and HMX remained; about 40 percent of the TNT remained. The *Pseudomonas aeruginosa* did not survive the experiment. Only 10 percent were left after 1 month, and essentially were all depleted by 6 months.

DuBois and Baytos continued their experiments for 16 more years (DuBois and Baytos, 1991). After 20 years, over 70 percent of the HMX and RDX, and only about 10 percent of TNT remained. During 1977, a major forest fire passed through the area, burning all vegetation, including trees and forest litter. They concluded that the fire had no effect on the buried explosives. From these data, estimates of high explosives half-lives were made. The half-life of HMX, RDX, and TNT were determined to be 39 years, 36 years, and 1 year, respectively.

Sampling in soil, sediment, and water for high explosives has been reported by a number of investigators. Sampling associated with ongoing explosives use is reported in Purtymun and others (1982). Environmental sampling was performed at the U.S. Department of Energy's Pantex Plant near Amarillo, Texas in support of preparation of an Environmental Impact Statement. Waste water and sediment samples in two drainage ditches from explosive machining operations were collected and analyzed for, among other explosives, TNT, RDX, and HMX. Concentrations of TNT were below the detection limits of 0.01 ppm in the waste water and sediment samples. RDX was found at a concentration of 5.5 ppm near the point of effluent release in one sample; in all other waste water and sediment samples the RDX concentrations were below detection limits. Concentrations of HMX followed similar trends in the two ditches. HMX was detected in the waste water near the point of effluent release in concentrations ranging from 4.2 to 1.5 ppm, and declined with distance away from the outfalls. Sediment concentrations of HMX near the point of effluent release were measured at about 1900 ppm in both ditches, and declined to about 40 ppm in one ditch and 8 ppm in the other ditch where the ditches discharge into onsite playas.

A separate investigation for hazardous materials was performed at Pantex during 1986 (Becker and others, 1987). Coreholes were completed down to depths ranging from 15 to 30 ft and samples collected for analyses for RDX and TNT. A corehole completed at a former burning ground to a total depth of 15 ft did not encounter any RDX or TNT at the detection limits of 0.03 mg/L. In another sampling at Los Alamos National Laboratory, over 100 surface soil samples (0-5 cm) were collected in a watershed containing four active and one inactive firing sites and analyzed for HMX, RDX, and TNT (Becker, 1988). Sample locations were adjusted to remain outside a 50 ft radius surrounding firing site pads. All samples were below detection limits of 0.98, 1.27, and 1.92 µg/g of RDX, HMX, and TNT, respectively.

In another investigation at an inactive, closed firing site at Los Alamos National Laboratory, although the site was used during the 1940's and 1950's and decommissioned in 1953, small chunks of RDX, and possible HMX were identified on the ground surface, indicative of its longevity in the open environment (Haywood and others, 1995). It is believed that these high explosives are remnant debris from a clean-up shot during an attempt to dispose of explosives found in the areas during the 1970's.

Layton and others (1987) have reported results of several investigations on field measurements of high explosives and their degradation products. In one study, sampling of lagoon waters at the Louisiana Army Ammunition Plant used for disposal of TNT and RDX found degradation products of TNB, 3,5-DNA, amino-DNT isomers, TNBOH, 3,5-dinitrophenol, 2-hydroxy-4,6-dinitrobenzoic acid, 2-amino-4,6-dinitrobenzoic acid, and 2,4-dinitrobenzoic acid. They report of other studies on TNT where TNT, 2,4-DNT, 2,6-DNT, DNB, TNB, 2-amino-4,6-DNT and 4-amino-2,6-DNT have been reported in soils, surface and groundwaters. As well, they report the persistence of RDX in surface and ground waters and soils at ammunition plants and open burning/open detonation areas, degradation products of NO_3^- and CN^- in soils and groundwater, and HMX in soils to depths of 45 cm at open burning sites.

Lebron (1989) reviewed literature on the fate of ordnance in the environment, specific to evaluation of bioremediation technologies to be tested at a former ordnance disposal area at a submarine base. The area of interest was used for burning and detonation of ordnance from 1946 to 1965; main contaminants are TNT and RDX. The maximum observed concentrations were 6000 ppm of TNT and 758 ppm of RDX, with estimation of 99 percent of the TNT and 86 percent of the RDX within the top 10 ft of the soil profile. Also reported was a Navy dump site at Keyport, Washington where mixtures of TNT and TNT/RDX were disposed for 20 years. At this site, percolation through the sandy soil profile has permitted downward migration of these contaminants. High concentrations of trinitrobenzene were also reported, and thought to be a degradation product from the TNT. The Alabama Army Ammunition Plant is another ordnance facility used during World War II where TNT, DNT, tetryl, rifle powder, cannon powder, nitric acid, sodium sulfate, aniline, diphenylamine and dimethylaniline were produced. Explosive production ceased after WWII. Principal contaminants found in the soil profile were TNT, 2,4- and 2,6-DNT, and nitrobenzene, confirming the persistence on the soil surface and into the soil profile.

Assessment of the Umatilla Army Depot Activity in Oregon (Dawson and others, 1982) determined significant TNT and RDX contamination in soils from a TNT sludge pit, where concentrations of TNT were 1800 µg/g and RDX, 340 µg/g. Concentrations at the burn pads were 400 and 100 µg/g for TNT and RDX, respectively. Several aromatic compounds, including nitrobenzene, and semivolatiles were included in the analyses, but not detected. TNT (38 to 180 µg/g) and RDX (43 to 260 µg/g) were found in the subsurface below TNT washout lagoons; concentrations were found to decline from samples collected at 2.5 ft to those at 7.5 ft. Ten mg/L of RDX, 11 mg/L of TNT, and 0.75 mg/L of 2,6-DNT were measured in groundwater at a monitoring well on the east side of the TNT washout lagoons. Repeated measurements 5 months later showed continued explosive contamination in the groundwater, with evidence of contamination in the aquifer spread over several wells in the general vicinity. Depth of water varied from 18 to 93 ft.

Investigations at the Hawthorne Army Ammunition Plant in Nevada were undertaken to determine the extent of explosive contamination and migration in a desert environment (Harris and others, 1989). Two disposal pits in use between the mid-1930's and 1970 accepted waste from loading and demilitarization operations. Samples from the first pit, located on the desert surface away from arroyo drainage, had maximum TNT concentrations of 13,000 ppm, and RDX, HMX, and EXPL-D (ammonium picrate) maximum concentrations of 8000, 1100, and 240 ppm, respectively. Sampling on the periphery of the pit showed no TNT contamination, although RDX at a maximum concentration of 260 ppm was found. Depth samples collected from 6 to 12 inches below the surface showed no detectable amount of explosives. The second pit, located in an arroyo, had considerable contamination of EXPL-D, ranging in concentration from 5 to 800 ppm, and was found at considerable distance from the pit boundaries. Concentrations of EXPL-D were greater at the 12 in depth level (800 ppm) than at the surface (160 ppm), explained by the fact that EXPL-D may be ionized in aqueous media, thereby permitting more rapid transport than the nonionic explosives. HMX and RDX were also found on the surface and at depth. The main conclusion was that explosives deposited in underground pits in desert environments remain contained with very little decomposition occurring over many years. Only explosives on or near the surface have been biotransformed, hydrolyzed, or photolyzed to any noticeable extent, and only ionic compounds, or those transported by surface water can be mobilized for any significant distance.

Although there were numerous investigations reported for TNT, RDX, and HMX, no literature on the environmental fate of NTO could be located. This is not unexpected as NTO is a relatively new high explosive and has not enjoyed much open-air usage.

V. DISCUSSION

TNT has the greatest number of degradation products of the explosives examined here. It is uncertain whether this is due to TNT actually producing the greatest amount of products during its decomposition process, or if it is due to the fact the TNT is the oldest of the four explosives, used most extensively by itself and in marriage with other explosives, and has been studied most intensively.

With regard to all explosives reported, TNT, HMX, RDX, and NTO, the listed decomposition products have been produced, for the most part, as a result of laboratory investigations. It is uncertain whether all these products will be present in an environmental setting as a result of effluents, waste disposal activities, detonation, and open burning. Few environmental investigations examined decomposition products of the primary explosive, and none of these looked at the primary explosive and intentionally tested for all possible decomposition products. Factors expected to affect decomposition product presence include length of time exposed, the amount of exposure to sunlight, temperature variation, presence or absence of anaerobic conditions, ambient moisture conditions, ambient soil characteristics such as pH, electolytic conditions, and composition, as well as the quantity, type and variability of microbes.

The literature did document the following conclusions. TNT degrades the most rapidly, followed by RDX and HMX. No information on degradation rates or fate of NTO in the environment was found. In semi-arid and arid environments, high explosives have the ability to persist for long periods of time, on the order of decades, especially when buried beneath the surface soil layer. In environments of greater rainfall, or where there is an additional water supply from, as an example, an effluent discharge or a washout lagoon, high explosives are able to mobilize and transport through the soil profile into shallow and relatively deep groundwater, where both the primary parent explosive and decomposition products have been documented.

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