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ANALYSIS OF THE LONG-TERM FATE OF MUNITIONS CONSTITUENTS FROM UNEXPLODED ORDNANCE AND DISCARDED MILITARY MUNITIONS ON TERRESTRIAL SITES

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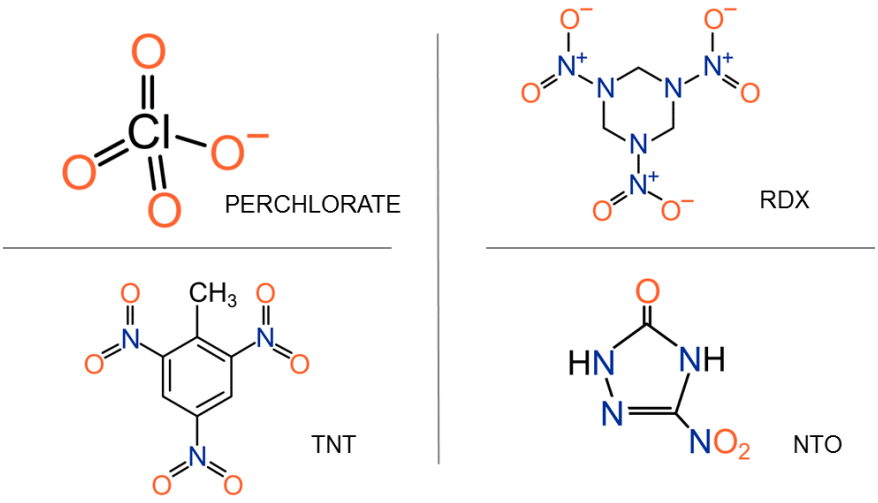

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14. ABSTRACT
The main focus of this report is to provide remedial project managers (RPMs) and corrective action project officers with a summary of information regarding the nature of munitions constituents (MC) with an emphasis on energetic residues and metals at military training ranges and munitions open burn (OB) and open detonation (OD) demolition units. For this document, MC refers to chemicals associated with military explosives and propellants. The report includes background on characteristics of MC including: physical and chemical properties, fate and transport, toxicity and regulatory guidance, summary of laboratory- and field-deployed methods designed to provide cleanup strategies.

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ACRONYMS AND ABBREVIATIONS

ADNT	amino-2,6-dinitrotoluene
AP	aminophenol
ATSDR	Agency for Toxic Substances and Disease Registry
BAFs	bioaccumulation factors
BMD	benchmark dose
BRAC	Base Realignment and Closure
CalEPA	California Environmental Protection Agency
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DANT	diaminonitrotoluene
DBX-1	copper (I) 5-nitrotetrazolate
DMM	discarded military munition
DNAN	2,4-dinitroanisole
DNB	dinitrobenzene
DNT	dinitrotoluene
DNX	1,3-dinitroso-5-nitro-1,3,5- triazine
DoD	Department of Defense
dw	dry weight
Eco-SSL	Ecological Soil Screening Level
EC_x	effect concentration for x% of the exposed population
Eh	reduction potential
EIM	extremely insensitive munition
ESTCP	Environmental Security Technology Certification Program
FUDS	Formerly used defense site
HEAST	Health Effects Assessment Summary Tables
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HTPB	hydroxyl-terminated polybutadiene
IC_x	inhibitory concentration for x% of the exposed population
IM	insensitive munitions
IMX	insensitive munitions eXplosive
IRIS	Integrated Risk Information System
LC_x	lethal concentration for x% of the exposed population
LC-MS/MS	liquid chromatography mass spectrometry

LOAEL	Lowest Observed Adverse Effect Level
LOEC	lowest observed effect concentration
MC	munition constituents
MCL	maximum contaminant level
MEC	munitions and explosives of concern
MF	modifying factor
MNA	N-methyl-p-nitroaniline
MNA	monitored natural attenuation
MNG	mononitroglycerol
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MRS	munitions response site
NB	nitrobenzene
NC	nitrocellulose
NCEA	National Center for Environmental Assessment
NG	nitroglycerin
NOAEL	no observable adverse effect level
NOEC	no observed effect concentration
NQ	nitroguanidine
NT	nitrotoluene
NTO	3-nitro-1,2,4-triazol-5-one
OB/OD	open burn/open detonation
PAX	Picatinny Arsenal Explosive
PETN	pentaerythritol tetranitrate
POD	point of departure
ppb	part per billion
PPRTV	Provisional Peer Reviewed Toxicity Value
PTX	pyrazolo-triazine explosive
RBC	risk-based concentration
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
RfC	reference concentration
RfD	reference dose
RME	Reasonable Maximum Exposure
RPM	remedial project manager
SERDP	Strategic Environmental Research and Development Program
SF	slope factor
TAT	triaminotoluene

TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TNB	trinitrobenzene
TNT	trinitrotoluene
TNX	hexahydro1,3,5-trinitroso-1,3,5-triazine
UF	uncertainty factor
U.S. EPA	United States Environmental Protection Agency
UXO	unexploded ordnance

GLOSSARY OF TERMS[1]

Blow-in-place. Method used to destroy unexploded ordnance/discarded military munitions, by use of additional explosives, in the location the item is encountered.

Caliber. The diameter of a projectile or the diameter of the bore of a gun or launching tube. Caliber is usually expressed in millimeters or inches. In some instances (primarily with naval ordnance), caliber is also used as a measure of the length of a weapon's barrel. For example, the term "5 inch 38 caliber" describes ordnance used in a 5-inch gun with a barrel length that is 38 times the diameter of the bore [4].

Casing. The fabricated outer part of ordnance designed to hold an explosive charge and the mechanism required to detonate this charge.

Deflagration. A rapid chemical reaction occurring at a rate of less than 3,300 feet per second, in which the output of heat is enough to enable the reaction to proceed and be accelerated without input of heat from another source. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, temperature, and reaction rate, and may cause transition into a detonation [5].

Detonation. A violent chemical reaction within a chemical compound or mechanical mixture involving heat and pressure. The result of the chemical reaction is exertion of extremely high pressure on the surrounding medium. The rate of a detonation is supersonic (i.e., greater than 3,300 feet per second) [6].

Discarded military munitions (DMM). Military munitions that have been abandoned without proper disposal or removed from storage in a military magazine or other storage area for disposal. The term does not include unexploded ordnance, military munitions that are being held for future use or planned disposal, or military munitions that have been properly disposed of consistent with applicable environmental laws and regulations (10 U.S.C. 2710 (e)(2)).

Dud-fired. Munitions that failed to function as intended or as designed. They can be armed or not armed as intended, or at some stage in between.

Explosion. A chemical reaction of any chemical compound or mechanical mixture that, when initiated, undergoes a very rapid combustion or decomposition, releasing large volumes of highly heated gases that exert pressure on the surrounding medium. Also, a mechanical reaction in which failure of the container causes sudden release of pressure from within a pressure vessel. Depending on the rate of energy release, an explosion can be categorized as a deflagration, a detonation, or pressure rupture.

Explosive. A substance or mixture of substances, which is capable, by chemical reaction, of producing gas at such a temperature, pressure and rate as to cause damage to the surroundings.

[1] Terms as defined in U.S. EPA. 2005. EPA Handbook on the Management of Munitions Response Actions; Interim Final.

Explosive filler. The energetic compound or mixture inside a munitions item.

Explosive ordnance disposal (EOD). The detection, identification, field evaluation, rendering-safe recovery, and final disposal of unexploded ordnance or munitions. It may also include the rendering-safe and/or disposal of explosive ordnance that has become hazardous by damage or deterioration, when the disposal of such explosive ordnance is beyond the capabilities of the personnel normally assigned the responsibilities for routine disposal. EOD activities are performed by active duty military personnel.

Explosive soil. Explosive soil refers to any mixture of explosives in soil, sand, clay, or other solid media at concentrations such that the mixture itself is reactive or ignitable. The concentration of a particular explosive in soil necessary to present an explosion hazard depends on whether the explosive is classified as "primary" or "secondary." Guidance on whether an explosive is classified as "primary" or "secondary" can be obtained from Chapters 7 and 8 of TM 9-1300-214, Military Explosives [7].

Explosive train. The arrangement of different explosives in munitions according to the most sensitive and least powerful to the least sensitive and most powerful (initiator - booster -burster). A small quantity of an initiating compound or mixture, such as lead azide, is used to detonate a larger quantity of a booster compound, such as tetryl, that results in the main or booster charge of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) composition, trinitrotoluene (TNT), or other compound or mixture detonating.

Formerly used defense site (FUDS). Real property that was formerly owned by, leased by, possessed by, or otherwise under the jurisdiction of the Secretary of Defense or the components, including organizations that predate Department of Defense (DoD) [7].

Fragmentation. The breaking up of the confining material of a chemical compound or mechanical mixture when an explosion occurs. Fragments may be complete items, subassemblies, or pieces thereof, or pieces of equipment or buildings containing the items [6].

Fuze. A device with explosive components designed to initiate a train of fire or detonation in ordnance [6]. A non-explosive device designed to initiate an explosion in ordnance.

Munitions and explosives of concern (MEC). This term, which distinguishes specific categories of military munitions that may pose unique explosives safety risks, means: (1) unexploded ordnance (UXO); (2) discarded military munitions; or (3) munitions constituents (e.g., TNT, RDX) present in high enough concentrations to pose an explosive hazard. Formerly known as ordnance and explosives (OE).

Munitions constituents (MC). Any materials originating from unexploded ordnance, discarded military munitions, or other military munitions, including explosive and nonexplosive materials, and emission, degradation, or breakdown elements of such ordnance or munitions (10 U.S.C. 2710 (e)(4)). MC may be subject to other statutory authorities, including but not limited to the

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (42 U.S.C. 9601 et seq.) and the Resource Conservation and Recovery Act (42 U.S.C. 6901 et seq.).

Open burning. The combustion of any material without (1) control of combustion air, (2) containment of the combustion reaction in an enclosed device, (3) mixing for complete combustion, and (4) control of emission of the gaseous combustion products.

Open detonation. A chemical process used for the treatment of unserviceable, obsolete, and/or waste munitions whereby an explosive donor charge initiates the munitions to be detonated.

Operational range. A range that is under the jurisdiction, custody, or control of the Secretary of Defense and (A) that is used for range activities; or (B) although not currently being used for range activities, is still considered by the Secretary to be a range and has not been put to a new use that is incompatible with range activities.

Practice ordnance. Ordnance manufactured to serve a training purpose. Practice ordnance generally does not carry a full explosive payload. Practice ordnance may still contain explosive components such as spotting charges, bursters, and propulsion charges.

Projectile. An object projected by an applied force and continuing in motion by its own inertia, as mortar, small arms, and artillery projectiles; also applied to rockets and guided missiles.

Propellant. An agent such as an explosive powder or fuel that can be made to provide the necessary energy for propelling ordnance.

Range. Designated land and water areas set aside, managed, and used to research, develop, test and evaluate military munitions and explosives, other ordnance or weapon systems, or to train military personnel in their use and handling. Ranges include firing lines and positions, maneuver areas, firing lanes, test pads, detonation pads, impact areas, and buffer zones with restricted access and exclusionary areas (40 CFR § 266.601). A recent statutory change added air-space areas designated for military use in accordance with regulations and procedures prescribed by the Administrator of the Federal Aviation Administration (10 U.S.C. 101 (e)(3)).

Unexploded ordnance (UXO). This document will use the term “UXO” as defined in the Military Munitions Rule. “UXO means military munitions that have been primed, fuzed, armed, or otherwise prepared for action, and have been fired, dropped, launched, projected, or placed in such a manner as to constitute a hazard to operations, installation, personnel, or material and that remain unexploded either by malfunction, design, or any other cause.” This definition also covers all ordnance-related items (e.g., low-order fragments) existing on a non-operational range. (40 CFR Part 266.201, 62 FR 6654, February 12, 1997) [8].

Warhead. The payload section of a guided missile, rocket, or torpedo.

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EXECUTIVE SUMMARY

The Navy has approximately 325 terrestrial munition response sites (MRSs) where munitions or munitions constituents (MC) from unexploded ordnance (UXO) and discarded military munitions (DMM) are found and require remediation. This document applicable to closed ranges where the Navy is performing remediation in support of changing the land use designation from range to something else. In addition, the document is applicable to operational ranges where the Navy actively manages our ranges through two programs (ORC and RSEPA) to ensure that munitions constituents (MCs) generally do not substantially impact human health or the environment or migrate off-range.

Department of Defense (DoD) policy requires all military ranges to be operated in ways that ensure their long-term viability to meet the national defense mission while protecting the environment and human health. These specific policies require prevention and response to releases of MC to off-range areas. While the fate and transport of the more common MC, such as trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), in the environment are relatively well known, there are many associated degradation products and other compounds (e.g., picric acid) where the fate, transport, and toxicity characteristics are unclear.

Programs such as Strategic Environmental Research and Development Program (SERDP), Environmental Security Technology Certification Program (ESTCP) and Navy Environmental Sustainability Development to Integration (NESDI) have supported comprehensive research efforts that address all aspects of characterization, monitoring and management of sites that are impacted by MC. Moreover, innovative next generation technologies are under development and offer the potential for ranges to be managed in a fully sustainable manner. Although some of the relevant contents related to the characterization of fate, transport and toxicity of MC may be described in the literature, there is no one reference that captures this information in a concise format. Thus, this technical report provides a broad-scale perspective on the current state of knowledge for numerous MC of interest.

The Naval Facilities Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC), using DoD resources, compiled information on physical and chemical properties that directly affect fate and transport of energetic compounds in the environment. Information on sources of aquatic and human toxicity data is also captured. Data gaps that list research, demonstration and technology transfer needs are summarized to help define future needs. The results of this effort are presented herein, known as an Initiation Decision Report (IDR). The IDR-documents a process by which user requirements are gathered, stakeholder networking is pursued, requirements and an assessment of topic of interest is performed. A gap analysis is performed which compares requirements against available technology or state of science to determine shortfalls. Recommendations for research development are then proposed to fill the technology gaps.

This IDR has been prepared to assist Navy decision makers in developing an informed strategy for making targeted investments to enhance the Navy's ability to manage the challenges presented by MC at MRSs and operational ranges. It is difficult to assess the future success of current investments in relation to current and projected Navy problems. However, it was concluded, that

more effort that assist in improving understanding of fate and transport of legacy munitions such as perchlorate, RDX and new insensitive high explosives (IHE) are needed. Advancing knowledge on environmental fate and transport as well as toxicity of these compounds will support the readiness of the Navy Ranges by reducing costs to programs, future regulatory constraints, and improved methods for impact avoidance and range management.

As MCs play a significant role in compliance issue when they mitigate off-range and are transported into water bodies, or transferred to the biota occupying the sites. The following technology gaps have been identified in this IDR and aim to close these gaps:

(1) Development of sampling and analytical techniques for legacy and IHEs

(2) The investigation of fate and transport properties of MC and the prioritization of MCs into those that are most likely to occur on Navy ranges, and their physical and chemical characteristics;

(3) Research and demonstration needs for MC lifecycle stages,

(4) Toxicity to environmental receptors, and

(5) The investigation and additional technologies for the treatment of legacy munitions such as RDX, HMX, perchlorate and DNTs in surface soil;

It is anticipated that as the abovementioned gaps are realized, new areas of concern and technology gaps will be identified that will benefit from this investigative effort.

1.0 OVERVIEW OF MUNITIONS CONSTITUENTS ISSUES

Please note that this effort is limited to land-based ranges.

The U.S. military operates munitions testing and training ranges that cover millions of acres of land and waters throughout the United States and beyond [9]. According to a December 2003 Government Accountability Office report [10], the Department of Defense (DoD) suspects or acknowledges contamination by military munitions of an estimated 15 million acres of land with an estimated cleanup cost from $8 billion to $35 billion.

Nearly half of the potentially contaminated sites are Formerly Used Defense Sites (FUDS) which are sites that have been decommissioned and were transferred out of the DoD prior to 1986. A relatively small number of sites that have been closed since 1988 are managed under the Base Realignment and Closure (BRAC) program. The majority of the remaining sites are located on active military installations. Of the approximately 3,500 sites identified (as of 2007), approximately 1,000 have had planned cleanup actions completed, about 1,000 have response actions under way or planned, about 500 have been determined to likely not require response actions, and the remaining approximately 1,000 sites have not been evaluated.

Sites with known or suspected munitions contamination are referred to as munitions response sites (MRSs). MRSs can include testing and training ranges, open burn/open detonation (OB/OD) areas, and munitions storage and manufacturing facilities. Two types of hazards from these sites could pose a threat to human health and natural ecosystems: 1) explosive hazards from detonation of munitions and explosives of concern (MEC), and 2) contamination of the environment from munitions constituents (MC).

MEC includes unexploded ordnance (UXO) and discarded military munitions (DMM). These munitions items may be an explosive hazard but can also contribute to MC contamination when UXO and/or DMM are damaged, corroded, or otherwise breached causing MC to leach into the surrounding media. The explosive hazard at MRSs is a simple concept and well understood (i.e., munitions more sensitive to detonation have a greater hazard) in the area of munitions response actions if considered a chemical release.

Testing and training ranges typically have a firing point and an impact area. Impact areas include grenade ranges, artillery ranges, rocket and air to ground ranges. OB/OD areas are where munitions are disposed by burning or detonation. Manufacturing facilities are where munitions are loaded and assembled. Each type of range and facility show different and distinctive distribution of MC.

Testing and training ranges (whether operational or closed) contain rather small concentrations of MCs due to consumption of most of the high explosives during the use of properly functioning munitions. The main source of MC on impact areas are MC released from UXO or low-order detonations. Low-order detonations occur when a detonation reaction is not completed as designed or the reaction occurs at subsonic speed [11-13]. Although low-order detonations can release high concentrations of MC, the occurrence rate of low-order detonations is extremely low and, therefore, not considered a significant source of contamination [11]. It should also be pointed out that the volume of the release from a single low order item is low. To be substantive, there must be an accumulation of items in a given area. OB/OD areas can have high concentrations of MC

present when MC is released during the MEC disposal process. Manufacturing sites typically have higher concentrations of MC available due to the amount of MC handled in these facilities. Although, it should be noted that a release should occur and that if there is no release, there may not be an issue.

This report focuses on the MC hazard at MRSs and presents information on physical and chemical properties that directly affect fate and transport of energetic compounds in the environment. Information on sources of aquatic and human toxicity data is also captured. Data gaps that list research, demonstration and technology transfer needs are also summarized to help define future needs.

This report is designed to serve as a useful reference tool for DoD Remedial Project Managers (RPMs), range managers, and engineers/scientists in supporting site characterization and remedy selection efforts at DoD sites contaminated by MC. The information may also be useful for researchers looking for a further understanding of MC contamination issues and key research gaps.

The scope of this report includes the following:

- **Section 1**: Introduction and overview of MC issues including physical and chemical characteristics
- **Section 2**: MC fate and transport considerations
- **Section 3**: Toxicity of MC
- **Section 4**: Gap Analysis
- **Appendix A**: Detailed characterization of 24 selected MC including compounds listed below:
    - Perchlorate
    - Chlorate
    - Trinitrotoluene (TNT)
    - 1,3,5-trinitroperhydro-1,3,5-triazine (RDX)
    - Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
    - 2,4-dinitrotoluene (2,4-DNT)
    - 2,6-dinitrotoluene (2,6-DNT)
    - Nitrotoluenes (NTs)
    - Nitrobenzene (NB)
    - Tetryl
    - Lead Azide
    - Nitroglycerin (NG)
    - Nitroguanidine (NQ)
    - 3-nitro-1,2,4-triazol-5-one (NTO)
    - 2,4-dinitroanisole (DNAN)
    - Tetrazene explosive
    - Lead styphnate
    - Ammonium picrate

- Picric acid
- Pentaerythritol tetranitrate (PETN)
- N-methyl-p-nitroaniline (MNA)
- Nitrocellulose (NC)
- 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)
- Copper(I) 5-nitrotetrazolate (DBX-1)

- **Appendix B**: Tabulated information on parent compounds listed in Appendix A and the parent compound byproducts
- **Appendix C**: Tabulated toxicological data on compounds listed in Appendix A

1.1 MUNITIONS CONSTITUENTS DEFINITION

MC are "any materials originating from UXO, DMM, or other military munitions, including explosive and non-explosive materials and emission, degradation, or breakdown elements of such ordnance or munitions (10 U.S.C. 2710(e)(3))".

MC include explosives, propellants, pyrotechnics, stabilizers, metals (e.g., lead and magnesium) and other compounds originating from military munitions. Examples include nitro amines such as RDX, nitro aromatics such as TNT, nitrate esters such as NG, and perchlorate.

1.2 SOURCES OF MUNITIONS CONSTITUENTS

Several processes are included in munitions-related activities which can lead to MC-contaminated soil and groundwater [14]. These activities and processes include:

- the release of MC during planned munitions training and testing from the deterioration of intact munitions,
- open burning and open detonation of munitions at disposal/burial pits associated with military ranges, and
- the land disposal of process water contaminated with explosives from explosives manufacturing or demilitarization plants [13].

MC typically found at training and testing ranges include heavy metals, particularly lead and mercury, due to their presence as components of primary or initiating explosives such as lead azide and mercury fulminate. These metals are released to the environment after a detonation or possibly by leaching out of damaged or corroded munitions [15]. It should be noted that there be other metals present and that a proper assessment (historical examination of the munitions used, etc) should be carried out in order to determine this.

Concentrations of MC, such as explosives and metals, and bulk explosives have been found at former OB/OD areas at levels that may require a response. OB/OD operations are used to destroy excess, obsolete, or unserviceable munitions and energetic materials. OB operations employ self-sustained combustion, which is ignited by an external source. In OD operations, explosives and munitions are destroyed by a detonation, which is normally initiated by the detonation of an

energetic charge. In the past, OB/OD operations have been conducted on the land surface or in shallow burn pits. More recently, burn trays and blast boxes have been used to help control and contain emissions and other contamination resulting from OB/OD operations. It should be noted that the donor charge (e.g. C4) is a significant contributor to MC loading at OB/OD or venting area locations that are not actively managed by regularly cleaning up small bits of explosives.

Incomplete combustion of munitions and energetic materials can leave uncombusted TNT, RDX, HMX, PETN, and other explosives. These materials can possibly be spread beyond the immediate vicinity of the OB/OD operation by the kick-out generated by these operations and can contribute to potentially adverse human health and ecological effects [14, 16].

Explosives manufacturing and demilitarization plants are also sources of MC. These facilities can be commercial sites or operated on current or former military installations. Some of these facilities have contaminated soils and groundwater. The manufacture, load, assemble, and pack operations as well as demilitarization of munitions create processing waters that in the past were often disposed of in unlined lagoons, leaving MC behind after infiltration and evaporation [13].

1.3 MC CATEGORIES

MC can be divided into five main categories:

- Explosives,
- Propellants,
- Pyrotechnics,
- Metals, and
- Stabilizers

Explosives, propellants, and pyrotechnics are chemical compounds or mixtures of chemical compounds typically referred to as energetic materials [9, 17]. Metals, in addition to energetic chemicals, are found in nearly all military munitions. Stabilizers are chemical ingredients added to propellants at the time of the manufacturing process to decrease the rate of propellant degradation and reduce the probability of autoignition during its expected useful life [9, 18]. Detailed discussion of each MC category is presented in the following subsections.

1.3.1 EXPLOSIVES

Explosives undergo detonation reactions through a release of their chemical energy as a pressure shock wave at supersonic rates. Explosive, propellant, and to some extent, pyrotechnic compounds are often used in formulations in which additional chemical ingredients are added. These ingredients can be: 1) modifiers to improve output performance, 2) stabilizers to desensitize the energetic material, 3) binders for material consistency, or 4) plasticizers to enhance the plasticity or viscosity of a formulation during manufacture. An example of an explosive formulation is Composition C, which is comprised of RDX, plasticizers, binders, and processing oils. As such, the terms “explosive formulations” or “propellant formulations” do not imply that only one type of energetic material is present in the formulation. As an example, several propellant formulations contain NC (a propellant material) and NG (an explosive material).

Explosive compounds are further classified as primary or secondary high explosives [17]. The explosives presented in this report and their classifications as primary or secondary high explosives include the compounds listed in **Figure 1-1** [7, 19-21].

Primary High Explosives	Secondary High Explosives
•Copper(I) 5-nitrotetrazolate (DBX-1) •Lead azide •Lead styphnate •Tetrazene	•Ammonium picrate •2,4-dinitroanisole (DNAN) •Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) •Nitroglycerin (NG) •Nitroguanidine (NQ) •3-nitro-1, 2, 4-triazol-5-one (NTO) •Pentaerythritol tetranitrate (PETN) •Picric acid •1,3,5-trinitroperhydro-1,3,5-triazine (RDX) •1,3,5-triamino-2,4,6-trinitrobenzene (TATB) •Tetryl •1,3,5-trinitrobenzene (TNB) •Trinitrotoluene (TNT)

Figure 1-1. Summary of Primary and Secondary High Explosives [7, 19-21]

Primary high explosives are highly sensitive to detonation via mechanical impact, friction, or electrical spark [19, 22]. This sensitivity presents a significant safety hazard. The use of primary explosives is therefore limited to detonators and primers (i.e., items requiring only small amounts of explosives), to provide the energy needed to initiate detonations of secondary high explosives or deflagrations of propellants [19, 22].

Secondary high explosives are much less sensitive to such ignitions than primary high explosives, and are capable of providing significant energy output. They can be used as booster charges and as the main explosive fill in munitions and ordnance. In general, the environmental fate and transport of secondary high explosives such as TNT, HMX and RDX are well characterized (Appendix A, Sections 3 through 5) because of their prolific use in military and industrial explosive formulations [7, 19, 22]. On the contrary, fate and transport characteristics of NG, NQ and PETN (Appendix A, Sections 10, 11 and 20, respectively) are not as well researched and summarized throughout the literature, creating a substantial knowledge gap. Although tetryl, ammonium picrate, picric acid, and TATB are no longer actively used, these MC may still be stockpiled or present in buried munitions. As such, Appendix A, Sections 15, 18, 19 and 23, respectively, provide a summary of their fate and transport characteristics.

Both primary and secondary explosives are used to trigger a uniform and predictable detonation of the main body of the explosive [23]. As such, this triggering sequence of events, also known as an explosive train, begins with priming of initiating material (primer or fuze), through boosting material and finally to the main charge. This sequence, depicted in **Figure 1-2**, is typically from

low-yielding, but very sensitive material (primary explosive) to a high-yielding, but not sensitive material (high explosive) and culminates in the detonation of the explosive [9, 22].

Figure 1-2. Chain of Events in an Explosive Train

In terms of explosive formulations, compounds used in insensitive munitions (IMs) often include TNT, RDX, HMX, or PETN, with some combination of modifiers, stabilizers, binders, or plasticizers [20, 24]. Several new munitions filler compounds, such as DNAN (2,4-dinitroanisole) and NTO (3-nitro–1,2,4-triazol-5-one), that are less sensitive to shock and high temperatures are currently fielded as replacements to conventional munitions fillers due to their improved stability and safety during storage, transportation and use. Lower shock sensitivity renders IMs harder to detonate and affects the composition of the fuzing systems. Thus, in explosive mixtures with IMs, higher quantities of donor and booster explosive material need to be used for proper detonation to occur [25].

Two of the new explosives, DNAN and NTO, characterized in detail in Appendix A (Sections 12 and 13), have good detonation characteristics and are the main ingredients in a suite of IMs (**Figure 1-3**). While their benefit to the military is clear, the environmental consequences of their use are not. For example, both DNAN and NTO are more soluble than conventional munitions compounds, such as TNT and RDX, suggesting they have the potential for increased mobility in the environment. **Table 1-1** provides a list of several IMs and extremely insensitive munitions (EIM) formulations and their ingredients.

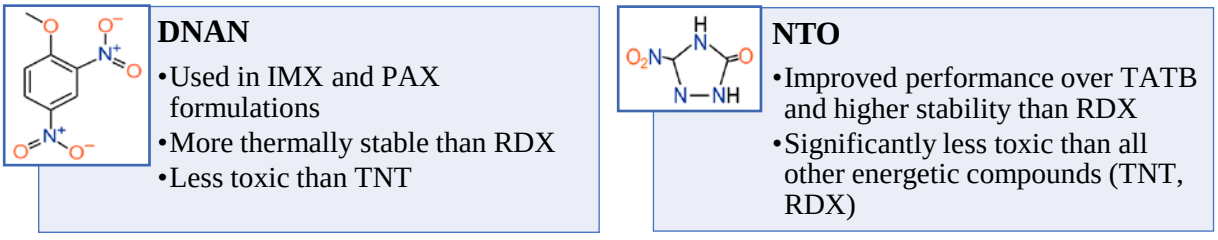

Figure 1-3. Examples of Explosive Used in EIMs

Table 1-1. Typical Explosive Compounds, Uses, and Formulations for Military MC

Compound	Uses	Formulations
Composition B	Artillery, mortars	RDX, TNT, paraffin wax
Cyclotol	Bombs	RDX, TNT (typ.)
Insensitive Munitions eXplosives (IMX)-101	Artillery	DNAN, NQ, NTO
Tritonal	Bombs	TNT, aluminum
Insensitive Munitions eXplosives (IMX)-104	Mortars	NTO, DNAN, RDX
Picatinny Arsenal Explosive (PAX)-21	Mortars	RDX, DNAN, aminophenol
Picatinny Arsenal Explosive (PAX)-48	Artillery, Mortars	DNAN, NTO, HMX
Pentolite	Boosters	PETN, TNT
Semtex 1A	Demolition	PETN, RDX, binder, plasticizer, dye
Semtex 1H	Demolition	PETN, RDX, binder, plasticizer, dye
pyrazolo-triazine explosive (PTX)-2	Antitank rockets	RDX, PETN, TNT
Composition C4	Demolition	RDX, plasticizer, binder, mineral oil
Composition A5	Boosters	RDX, plasticizer
Composition H6	Torpedoes, Depth Charges, Main filler in bombs	RDX, TNT, aluminum powder, stabilizers
Octol	Antitank rockets	PETN, RDX, binder, plasticizer, dye

1.3.2 PROPELLANTS

Propellants are explosive materials formulated and engineered to react at carefully controlled rates, producing a sustained pressure effect over a longer period of time than high explosives [2, 13]. In contrast to the detonation of high explosives, the process of propellant burning is referred to as deflagration, wherein the rate of heat transfer determines the rate of the reaction, which proceeds

at subsonic speeds [26]. Pyrotechnics involve metal-metal oxide driven redox reactions that release a significant amount of heat, but produce less gas than explosives or propellants [7].

Like explosives, propellants utilize a series of materials in an ignition train (**Figure 1-2**). An electrical or mechanical impulse impinges on the sensitive primer material [23] and ignites the igniter, a pyrotechnic, which in turn ignites the main propellant grain. Propellants can be formulated either as solids or as liquids. Solid propellants are used more frequently in guns, cannons, and smaller rockets [13].

Propellants are designed to provide the energy to deliver (i.e., propel) a projectile to its target at high velocity. For this purpose, propellants typically contain a significant amount of available oxygen within its chemical formula to evolve the gas necessary to facilitate propulsion [27]. Propellant compounds described in this report include NC, NG, and NQ (Appendix A, Sections 10, 11 and 22) and also several perchlorate- or chlorate-based chemicals (e.g., ammonium perchlorate, potassium perchlorate, potassium chlorate) (Appendix A, Sections 1 and 2). It should be noted that NG and NQ are defined as explosive materials (discussed in **Section 1.3**), but these compounds are also categorized for their use in propellant formulations to enhance energy output [28].

Propellant formulations (**Table 1-2**) are further classified as *single-base*, *double-base*, *triple-base*, and *composite*. The type of propellant formulation used depends on the specific needs for delivering the projectile [29]. The propellant selection is determined based on factors such as the pressure-time profile, the flame temperature and its effects on barrel erosion, flash reduction, and energy output.

Table 1-2. Summary of Propellant Classes with Examples [7]

Type	Uses	Examples	Principal Ingredients
Single-base	Small arms, cannons	M1	NC, 2,4-DNT
		M6	NC, 2,4-DNT
		M10	NC, diphenylamine
Double-base	Multiple applications, including small arms	M2	NC, NG, ethyl centralite
		M5	NC, NG, ethyl centralite
		M8	NC, NG, diethyl phthalate
Triple-base	Large caliber guns	M30	NC, NG, NQ, ethyl centralite
		M31	NC, NG, NQ, ethyl centralite
Composite	Rockets and missiles	Class 1.3	Ammonium perchlorate, aluminum, binder (HTPB)

Single-base propellants contain NC as the primary propellant compound. Double-base propellants contain NC and NG, and triple-base propellants include NQ along with NC and NG [27-29]. Composite propellant formulations use ammonium nitrate or ammonium perchlorate as the propellant compound, mixed with a powder metal fuel and a binder. Other offshoots of these propellant classes exist; for example, composite modified double-base propellants combine NG, NC, ammonium perchlorate, and a metal powder to optimize performance.

Similarly, propellant formulations may also contain burn rate modifiers, stabilizers, plasticizers, muzzle flash reducers, and binders to improve performance, safety, and manufacturability [28]. A list of the most common additives used in propellant formulations is provided in **Figure 1-4 [7]**.

Stabilizers	Binders and Plasticizers	Burn Rate Modifiers	Muzzle Flash Reducers
•Diphenylamine •2-nitro-diphenylamine •Diethyl-1,3-diphenylurea (ethyl centralite) •1-methyl-3,3-diphenylurea (akardite)	•Dibutyl phthalate •Diethyl phthalate •Triacetin •Wax •Talc •Titanium oxide •Hydroxyl-terminated polybutadiene (HTPB)	•2,4-DNT •2,6-DNT •Ethyl centralite	•Potassium sulfate •Potassium nitrate

Figure 1-4. Most Common Additive Compounds in Propellant Formulations

1.3.3 PYROTECHNICS

Pyrotechnics are any chemical formulations, not typically classified as explosives or propellants, that are capable of undergoing self-sustained exothermic reactions to produce any combination of heat, light, sound, smoke, and motion [7]. These formulations are used in flares, fireworks, and illuminants for signaling or area marking. The main ingredient in pyrotechnic formulations is often a metal or metal oxide. Other compounds, including propellants, binders, and stabilizers, can be added to enhance pyrotechnic effects or improve chemical stability [29]. For example, a common red star firework formulation consists of strontium carbonate as the red-color generating chemical (i.e., the main effect), potassium chlorate propellant to provide oxygen for the strontium carbonate and some degree of thrust for the firework, red gun powder as a binder, and other ingredients (e.g., dextrin, charcoal, and polyvinyl chloride) as a means to initiate, sustain, or enhance the rate of reaction.

1.3.4 METALS

Metals, in addition to energetic chemicals, are found in nearly all military munitions [8]. Uses of metals in munitions include casings, bullets, projectile cases, projectiles, bomb bodies and fillers. Although metals such as lead, antimony, copper and zinc can be found in trace amounts, lead is often the primary metal contaminant of concern at munitions response program sites [15] due to accumulation after firing rounds. As aluminum, iron and magnesium are not defined as Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) hazardous elemental metals, this document will be limited to lead, antimony, copper and zinc with an emphasis on lead.

For munitions and ordnance, metals can be used in: 1) the device that contains the propellant or explosive (e.g., bullet casing or projectile shell); 2) additives to enhance the energy output of explosive formulations; and 3) chemicals present in propellants and pyrotechnics, or primary explosives [7]. Lead, antimony, copper, iron, aluminum, and zinc are typically used to fabricate projectile bodies, bomb cases, ammunition cartridges, and other military devices. Metals used in explosive and propellant formulations include aluminum and magnesium, which are used to provide an additional, significant amount of energy to a detonation or deflagration reaction (e.g., Tritonal, an explosive formulation comprising TNT and aluminum).

Metals used in propellants and pyrotechnics can serve as the main fuel source or as the oxygen carrier for an exothermic reaction [15, 30]. Metals are also often used in primary explosive compositions because of the highly energetic, relatively unstable bonds formed between the metal and other elements in the composition. Metals described in this report are used in propellants, pyrotechnics, or as primary explosive and are listed in Appendix A, Sections 1 and 2 (potassium chlorate and potassium perchlorate) and Appendix, Sections 16 and 17 (lead azide and lead styphnate).

1.3.5 STABILIZERS

Stabilizers are chemical ingredients added to propellants at the time of the manufacturing process to decrease the rate of propellant degradation and reduce the probability of autoignition during its expected useful life [9, 18]. In propellant chemistry, stabilizers that are employed prevent the acid-catalyzed decomposition of NC, NG and similar nitrate esters [31]. They exert their stabilizing effect by binding the decomposition products such as the free acid and nitrous gasses. At this point, self-heating of the propellant can occur unabated and may reach the point of spontaneous combustion [9, 18]. Many stabilizing compounds display plasticizing (gelatinizing) properties.

Stabilizers are used in propellant and explosive formulations to control the chemical stability and enhance the propellant's properties (hence the name, stabilizer). Typically, these compounds render the formulation less ignition-sensitive (i.e., more resistant to ignition) or prevent hazardous conditions arising from long-term storage of formulations, by scavenging any compounds formed from gradual decomposition of the formulation. Examples of stabilizers described in this document are 2,4-DNT and MNA and are described in Appendix A, Sections 6 and 21.

2.0 MC FATE AND TRANSPORT CONSIDERATIONS

MC fate and transport has become a significant area of research due to the toxicities of several MC or their degradation products. In general, MC can be released to the environment as a result of:

1. Manufacturing processes in which MC are discharged to wastewater;
2. Military range testing in which munitions and ordnance containing MC are used intentionally in training or test and evaluation activities;
3. OB/OD activities in which UXO is intentionally burned or detonated as a removal or disposal operation; and
4. MC leaching out of buried DMM.

Source zones of MC are, in most cases, surface soils at impact areas or firing point areas [14]. However, the geographical location of the range introduces additional unique challenges as geography-dependent variables such as average wind speed, rainfall, snowfall, proximity to groundwater, aridity, and soil alkalinity can influence the dispersion, fate, and transport of the MC [32]. Thus, the mass loading of MC at operational ranges and the impact of the source zone in terms of contamination risk are a function of the time of range operation, use frequency, type of ammunition used and their ranges, dud rate at the range, and geographical location of the range [16]. Also note is that active management also plays a significant role. For example, the source is removed if a range is regularly cleared,

The type of MC discharge route can provide indicators on likely areas of contamination or best practices for controlling MC discharge to the environment. For example, manufacturing processes, as stated previously, are expected to have a higher source of MC available for discharge to the environment. To clarify, this means a potential for large volume release as discussed in the next sentence. Releases of MC from manufacturing processes, should they occur, could be larger in scale and occur over a shorter period of time (i.e., a larger quantity discharged over a short amount of time) than other MC discharge routes [11, 12]. With manufacturing processes, these discharges are also more likely to be waste stream discharges. Information on the quantity of MC discharged and discharge routes can be established and controlled at the manufacturing process [14].

Other routes of MC discharges (range testing, OB/OD activities, and leaching out of UXO) can introduce some variables to the impact on environmental contamination. The amount of MC dispersed onto the soil, the types of MC present, the mobility of each MC in soil, and proximity to groundwater are all factors that influence how quickly MC can reach groundwater. With range testing and OB/OD activities, there is a possibility for unreacted MC mass to be released to the environment [11]. For explosives, this can occur due to the concentrated use of targets on ranges over a long period of time with deposition of small amounts of MC with each detonation, or due to a low-order detonation of an ordnance item, in which the detonation reaction does not proceed to reaction completion or the reaction occurs at subsonic speed [11-13]. In the former case, the cracking of the ordnance shell could allow the reaction to vent and prevent complete detonation of the explosive from occurring. In the latter case, the low-order detonation could be due to a malfunction in the detonation train or material issues with the explosive. In either case, low-order detonations (usually 5% of munitions either duds or low order) producing unreacted MC mass are relatively rare and therefore not considered a significant source of contamination [11].

The leaching of MC out of DMM is likely to release low quantities of unreacted MC mass over a prolonged period of time [33, 34]. Similarly, leaching of MC out of buried DMM could pose an environmental threat as MC is gradually released as a function of corrosion of the metal components and exposure of unreacted MC mass to the environment. It should be noted that this is more common at more acidic east coast ranges and much less common in the arid west that are predominantly alkaline.

Fate and transport of unreacted MC into the environment can be described in terms of physical attenuation, chemical attenuation, and biological attenuation processes. The fate and transport discussion of MC focuses primarily on perchlorate, TNT, DNTs, RDX, HMX, and picric acid to provide an overview of the different fate and transport paths possible for MC.

2.1 PHYSICAL ATTENUATION

Knowledge of the physical attenuation properties of MC is fundamental to understand their fate and transport at a contaminated site. **Figure 2-1** [35] summarizes the primary physical attenuation processes in order of their impact on fate and transport.

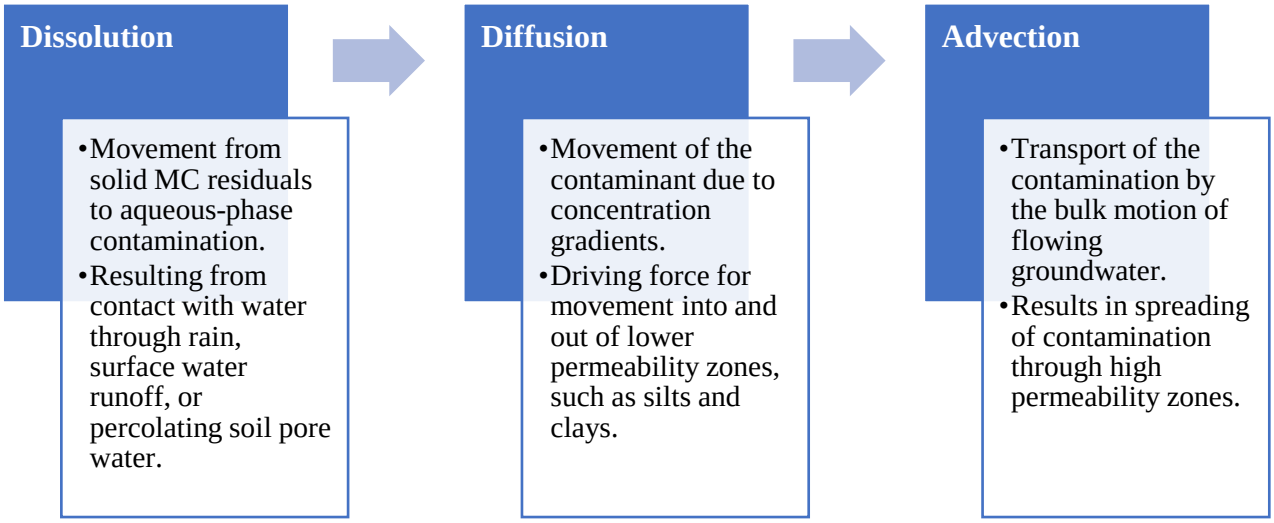

Figure 2-1. Summary of the Physical Attenuation Process for MC [14, 35, 36]

Physical attenuation processes establish the mobility of the MC in the environment and its availability for other attenuation processes [37]. Once dispersed onto soil, a constituent is likely to persist until it comes into contact with water from rainfall, surface water runoff, or percolating soil pore water [38-40]. Dissolution is the first step in introducing MC into the environment. The controlling factors for dissolution are listed in **Table 2-1** along with the factor's impact of dissolution.

Once MC move into the aqueous phase, a variety of factors influence fate and transport. As shown in **Figure 2-1**, two key factors of physical attenuation are diffusion and advection. While these

factors do not directly contribute to MC degradation, they can contribute to MC longevity and dispersion [26, 41].

Table 2-1. Factors that Impact the Dissolution of MC [20, 40, 42-45]

Factor	Impact on Dissolution
pH	Dissolution rates can increase at elevated (> 11) pH. Data for lower pH values (4 to 6) on the dissolution rates of TNT, RDX, and HMX showed no effect.
Temperature	Dissolution rates increase with temperature.
Soil Type	Soil types impact dissolution and sorption. Dissolution is greater in soils with low total organic carbon, surface area, and percent fines, as the MC tend to exhibit less sorption.
Presence of Organic Compounds	Organic matter can affect the dissolution of some organic components of munitions but may have different effect on salts.
Presence of Other Chemicals	Chemicals (e.g., detergents) can enable aqueous transport of some chemicals typically adsorbed to organic material in the soil.
Sorption	Surface attachment of MC particles may serve as long-term sources of contamination because of the unexposed surface area of the particle to water.
Particle Size and Geometry	Influences how quickly the MC can dissolve.
Solubility of Individual MC	Solubility is impacted by reversible sorption, irreversible attenuation and degradation.
Solubility of Multi-component Compounds	For formulations containing more than one MC, solubility of each MC can be limited by diffusion of the constituent from the interior of the compound. The dissolution rate is often determined by how the MC are embedded within a formulation matrix, and how readily water can access the constituents.
Low Order or High Order Denotation	Low order (incomplete) detonation can leave large quantities of explosive residue on the site, whereas high order (complete) detonations typically have smaller point source contamination.
Fractures in Compound	Low order detonations and concentrated use of ranges that lead to accumulation of MC over time can produce fractured energetic fills. These fractured portions provide more access points for water (compared with the unperturbed energetic fill), resulting in faster dissolution.
Water Flow Rate	Dissolution can be enhanced under higher flow rates.

Key indicators for how readily an MC can enter the aqueous phase are solubility and octanol-water partition coefficient (log K_{ow}). In general, compound solubility can be categorized as highly soluble (>100 mg/L), moderately soluble (10 to 100 mg/L), and insoluble (< 10 mg/L) [46]. For

log K_{ow}, values are used to assess if MC tends to be more hydrophilic (log $K_{ow} \approx < 1$) or more hydrophobic ($\approx > 4$). For example, the log K_{ow} value for RDX is 0.87 (as shown in **Table 2-2)**, suggesting that it favors partitioning to the aqueous phase and is highly mobile in groundwater systems. In contrast, 2,6-DNT has a higher log K_{ow} (2.10) and would be less likely to partition in the aqueous phase. As a result, the size of the groundwater plumes is expected to be larger for RDX than 2,6-DNT when all other fate and transport factors are equal [47, 48].

Table 2-2. Water Solubility, Dissolution Rate into Water, and Octanol-Water Partition Coefficient (log K_{ow}) for Selected MCs

MC	Solubility* (mg/L)	Dissolution Rate** ($\mu g\text{-}cm^{-2}\text{-}s^{-1}$)	Log K_{ow}
Perchlorate [49]	2.00e5 (AP^{+}) 1.68e4 (KP^{++})	NA	-5.84 (AP) -7.18 (KP)
Chlorate [26]	7.00e4 (KC^{+*})	NA	NA
TNT [22], 12]	130	0.69	1.86
RDX [44, 50]	47	0.096	0.87
HMX [44, 50]	4.5	0.29	0.54
2,4-DNT [51]	270	NA	1.98
2,6-DNT [51]	180	NA	2.10
NG [13, 47, 52]	173	0.99 (est.)	1.62
NQ [13, 45, 53]	5.00e3	1.20 (est.)	-0.89
Tetrazene [7]	Insoluble	NA	NA
NTs [54]	609 (2-NT) 450 (3-NT) 288 (4-NT)	NA	2.30 (2-NT) 2.42 (3-NT) 2.40 (4-NT)
NB [55]	2100	NA	1.85
NTO [56, 57]	1.28e3 – 2.00e3	NA	0.86
DNAN [19, 58]	213	NA	1.58
Tetryl [59]	75	NA	2.4
Lead Azide [7, 17]	2.3	NA	NA
Lead Styphnate [17, 60, 61]	8	NA	0.006
Ammonium Picrate [17, 62, 63]	1.00e4	NA	0.02
Picric Acid [64, 65]	13.1	NA	1.33
PETN [7, 64, 66]	1.5	NA	1.61
MNA [67]	85	NA	2.10
NC [68]	Insoluble	NA	NA
TATB [17, 64]	32	NA	0.7
DBX-1	NA	NA	NA
*** at 20°C; ** at 30°C** **$^{+}$ Ammonium Perchlorate** **$^{++}$ Potassium Perchlorate** **$^{+*}$ Potassium Chlorate**			

NA – not determined in the literature

In terms of data gaps, **Table 2-2** and data listed in Appendix B show that dissolution rates for approximately 80% of the MC described in this report are not available. These data should be generated to best assess fate and transport properties of these MC. However, these data may be difficult to generate due to several factors that influence the dissolution rate of an MC, including, but not limited to: presence of other compounds, including MC, that could inhibit dissolution; particle size of the MC; and chemical structure of the MC.

While attenuation processes can potentially destroy other contaminants, attenuation of metals relies on immobilization processes that limit their bioavailability [37]. Metals released to soils from MC are generally not bioavailable (they are typically in bulk forms such as bullets or casings); however, weathering and dissolution over time may lead to mobility of contamination to surface water, pore water and groundwater [30]. These processes are generally reversible and dependent on the geochemistry of the affected media. Most notably the pH and oxidation-reduction (redox) potential of the aqueous system (quantified by Eh) can dictate the valence state of the metal contaminants. Mobility is also dependent on properties of the contaminated soil, including soil moisture, degree of weathering and type of organic matter present [15]. In addition, physical attenuation routes for metals include precipitation, co-precipitation and complexation (**Figure 2-2**) [37]. For each metal, certain species dominate under specific geochemical states. Therefore, understanding the geochemistry of the impacted media and the associated mobility of the dominant species is key to assessing physical attenuation mechanisms for metals.

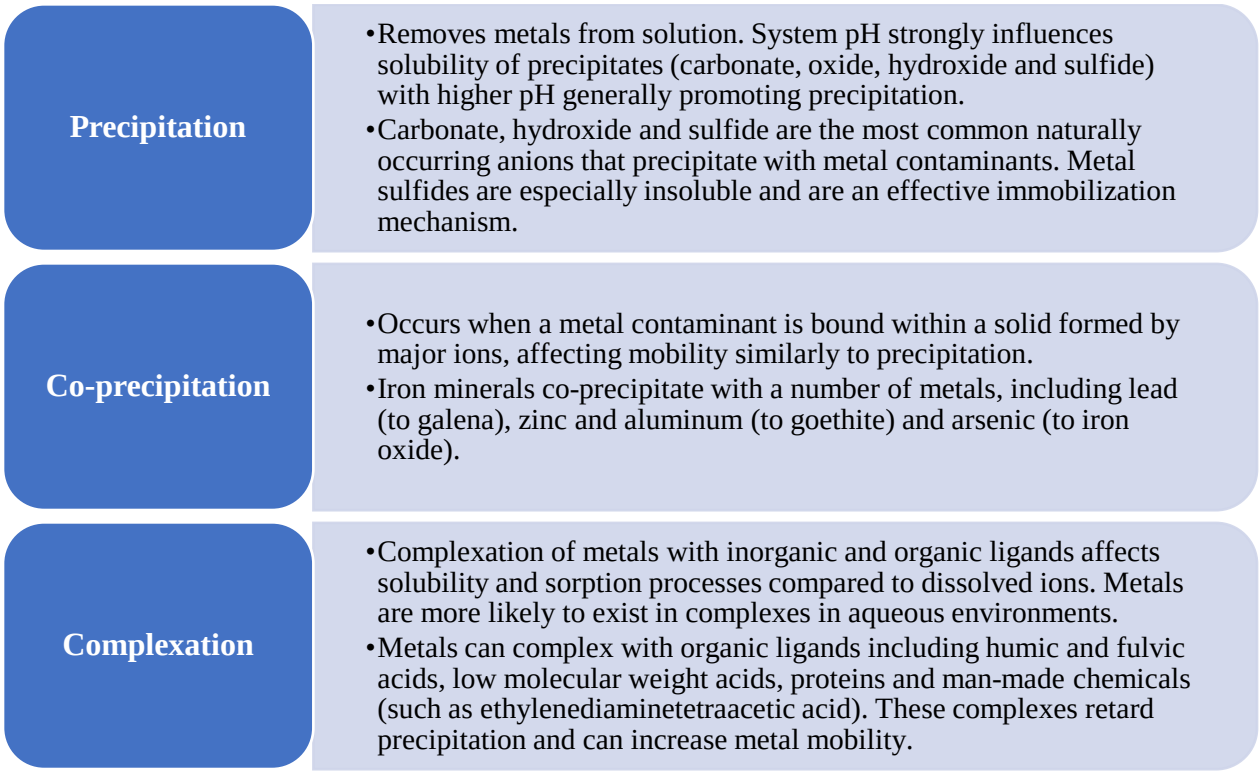

Figure 2-2. Physical Attenuation Processes for Metals (Adapted from [37])

2.2 CHEMICAL ATTENUATION

Chemical attenuation pathways are defined by the chemical transformation or immobility of MC, summarized in **Figure 2-3**. These attenuation processes include sorption, abiotic transformation, photolysis, and hydrolysis.

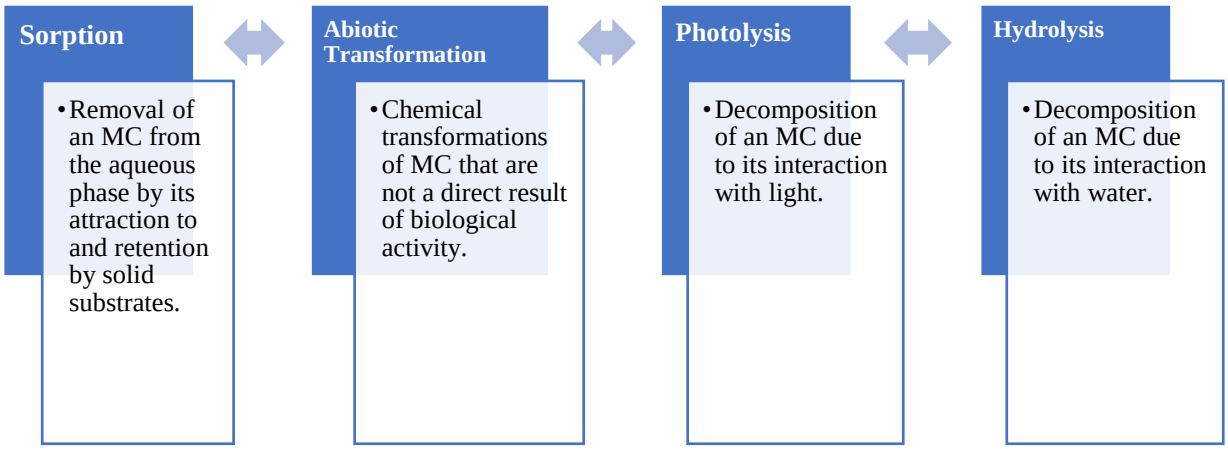

Figure 2-3. Chemical Attenuation Processes for MC

2.2.1 SORPTION PROCESSES

Sorption[2] can be described as either adsorption (sorption only to the surface of the solid substrate) or absorption (sorption within the substrate) [32]. The sorbent (the solid substrate onto which the contaminant is sorbed) has an equilibrium capacity that is affected by a number of parameters, such as pH and temperature. Sorption is generally a reversible process and desorption results in dissolution [26]. This partitioning between aqueous and solid phases is continuous with constant movement to and from sorption sites. The process of sorption is typically described using partition coefficients. The preference for sorption depends on the sorbent type and geochemistry. This preference is defined by the partition coefficient, K_d, which indicates the equilibrium between sorbed and free contaminants [41, 69]. Other partition coefficients exist that comparatively describe soil transport properties, including log K_{ow} and the organic carbon normalized partition coefficient (log K_{oc}). Values for these coefficients are provided in Appendix B and **Table 2-3**. Similar to what was noted in **Table 2-2** for data gaps for MC dissolution rates, **Table 2-3** shows that data for K_d are not reported for 67% of the MC.

[2] Sorption can be considered both a physical and chemical process; hence, it is discussed in both Sections 2.1 (Physical Attenuation Processes) and 2.2 (Chemical Attenuation Processes).

Table 2-3. Partition Coefficients for Selected MCs
(Units are dimensionless unless noted)

MC	K_d	Log K_{OC}	Log K_{ow}
Perchlorate [49]	NA	NA	-5.84 (AP) -7.18 (KP)
Chlorate	NA	NA	NA
TNT [44, 62]	0.04 – 413	37.4	1.86
RDX [50, 62]	0.06 – 8.4	6.26	0.87
HMX [50, 62]	0.12 – 17	1.15	0.54
2,4-DNT [47, 51]	2.34 – 15.3	88.48	1.98
2,6-DNT [47, 51]	0.27 – 2.49	116.0	2.10
NG [47, 62]	0.26 – 1.41	39.2	1.62
NQ [13, 45, 53]	0.14 – 0.61	0.13	-0.89
Tetrazene	NA	NA	NA
NTs [54]	NA	140 (mL/g) (2-NT) NA (3-NT) 138 (4-NT)	2.30 (2-NT) 2.42 (3-NT) 2.40 (4-NT)
NB [55]	NA	1.56	1.85
NTO [56, 57]	NA	0.415 – 125.9 (mL/g)	0.86
DNAN [19, 58]	NA	158.5 – 231.8 (mL/g)	1.58
Tetryl [59]	5.8 (mL/g)	1.69, 2.6, 3.13 – 3.47	2.4
Lead Azide	NA	NA	NA
Lead Styphnate [60]	NA	NA	0.006
Ammonium Picrate [17, 62, 63]	NA	NA	-1.4
Picric Acid [64, 65]	NA	2250 (mL/g)	1.33
PETN **[7, 64, 66]**	NA	2.25 – 3.24	3.71
MNA [67]	NA	NA	2.10
NC	NA	NA	NA
TATB [17, 64]	NA	NA	0.7
DBX-1	NA	NA	NA

NA – not determined in the literature

The example sorption processes for selected MC are further described in Appendix A and below.

TNT: Adsorption of TNT onto soils has been extensively studied and complements data from TNT dissolution studies [36, 39]. With adsorption, the dissolved TNT begins to accumulate at the soil surface, allowing for accumulation and increased bioavailability for biodegradation. The K_{ow} value suggests that TNT has a low sorption onto soils and some degree of mobility in the environment [2, 69]. It has been shown that TNT can be reversibly sorbed in soil systems (diffusion K_d for TNT in surface soils ranges from 2.3 to 11 L/kg) with interactions between the TNT nitro functional groups and soil colloids as the suggested platform forming hydrogen bonding and ion exchange [1, 40].

DNTs: For 2,4-DNT and 2,6-DNT, the log K_{ow} values are close to that of TNT. The log K_{oc} values for 2,4-DNT and 2,6-DNT are both 1.98 and 2.10, indicating that partitioning to organic carbon in soils is limited. Thus, DNTs are expected to be mobile in soils.

Picric Acid (2,4,6-trinitrophenol): Picric acid will result in the solubilization, dissociation (into the picrate anion), and transport of picrate when it comes into contact with water [64]. The picrate anions tend to be highly mobile in soil and do not sorb strongly to soils containing organic content and clay [64]. Despite this anticipated high mobility, the transport of picric acid in soil and its propensity to reach groundwater ultimately depends on the soil type.

RDX: RDX is generally expected to be highly mobile in soil systems [2]. How quickly and widespread the RDX is transported within a given soil matrix is dependent on several factors including, but not limited to: the amount of unreacted RDX dispersed into an environment; the other ingredients present in the energetic formulation that may impede the mobility of RDX; the amount of rainfall or access to water within the dispersed environment; the rates of dissolution and propensity for RDX advection; and the sorption of RDX onto soil. Soil adsorption for RDX is not significant [14, 40, 41] although RDX has been noted to partition to organic content (log $K_{ow} \approx 0.87$) but not sorb significantly to clay soils [70].

HMX: The log K_{ow} value for HMX (0.54) suggests that it favors partitioning into the aqueous phase. However, HMX will only slowly dissolve into water. Once in the aqueous phase, HMX may be transported through vadose zones to groundwater aquifers. Otherwise, HMX will persist in subsurface soil, where aerobic degradation can take place [71]. HMX has been shown to sorb to high clay-content soils (i.e., K_d values of 8.0 L/kg in soil with > 87% clay content and insignificant total organic content versus 2.5 L/kg in soil with 4% clay content and 8.4% total organic content) [71].

Perchlorate: Sorption of perchlorate to soil materials is typically assumed to be negligible. Partitioning coefficients describing sorption of perchlorate to geologic materials are usually found to equal zero [72]; however, there is some evidence of soil organic-perchlorate complexes.

Metals: Abiotic pathways are typically negligible for metals, however, sorption is a significant attenuation pathway. Sorption of metals takes place when either a metal or a complexed ligand is attracted electrically to charged groups in minerals or solid organic materials [37]. Adsorption is much more significant than absorption as an attenuation pathway although absorption of metals is kinetically less reversible than adsorption. Generally, low pH favors sorption of ligands while high pH favors sorption of metal ions. Ion exchange adsorption reactions also occur in the presence of surface-exchanging cations (such as Ca^{2+} and Na^{2+}) and are kinetically dependent on the concentration of surface-exchanging cation sites and on competing species rather than pH. Sorption capacity is also dependent on soil particle size distribution: fine soil particles have greater surface area than coarser material and therefore have a greater capacity for immobilizing metal contaminants [15]. Most importantly, adsorption processes for metals can be reversible if geochemical conditions change [30]. Therefore, the longevity of this attenuation mechanism should be considered when evaluating the applicability of MNA for metals.

2.3 ABIOTIC DEGRADATION, PHOTOLYSIS AND HYDROLYSIS OF MC

Degradation-based processes for chemical attenuation include abiotic degradation, photolysis, and hydrolysis described as follows:

- **Abiotic degradation** of some MC can occur in the presence of ferrous iron (e.g., TNT). A coupled abiotic/biotic degradation appears to produce the fastest rate of complete mineralization for energetics [37, 73] with the exception of perchlorate which degrades rapidly through biogenic processes. This process creates iron-reducing conditions by initially injecting a chemical reductant such as dithionite followed by the injection of a carbon source such as lactate. The chemical reductant dithionite reduces naturally occurring Fe(III) oxides to Fe(II). The Fe(II) is present as sorbed Fe(II), siderite (Fe(II) carbonate) and/or FeS. The Fe(II) produced is sorbed quickly from pH 6.8 and up, low ionic strength water and therefore does not leach from the sediment. The Fe(II) forms a reactive zone that is available for transformation [73, 74].
- Several of the MC can undergo **photolysis** or chemical decomposition driven by certain frequencies of natural light [75-78]. While these reactions are limited to the availability and interaction with natural light, photolysis nonetheless can produce byproducts that can then be transported into groundwater or further reduced. The state of the MC (i.e., solid or in the aqueous phase) will also influence the rate of photolysis; most MC will undergo photolysis with rates higher in the aqueous phase than as a solid [75].
- Some MC may also be degraded via **hydrolysis**, or the breaking of chemical bonds by water. Factors influencing the rate of hydrolysis include pH and temperature [77].

A summary of abiotic, photolytic, and hydrolytic degradation rates, reported as half-lives when available, is provided in Appendix B and **Table 2-4**. It is clear from this table that several data gaps exist for half-life data for several MC, in particular the primary explosives (e.g., lead azide).

Table 2-4. A Summary of Abiotic, Photolytic, and Hydrolytic Degradation Rates for Selected MCs

MC	Abiotic Reduction		Photolysis Half-Life	Hydrolysis Half-Life
	Type	Half-Life		
Perchlorate	NA	NA	NA	NA
Chlorate	NA	NA	NA	NA
TNT	Fe^{2+}	60 hours	30 minutes (fresh water); 200 minutes (pure water) [79]	4 days (pH 11); 1.2 days (pH 11.5); 0.6 days (pH 11.9) [80]
RDX	Fe^{2+}	≈ 20 – 30 hours [2, 81]	0.8 – 2.5 days (aqueous); 76 – 103 days (solid state) [82]	100 hours (pH > 10) [83]
2,6-DNT	NA	NA	12 minutes (fresh water); 0.67 – 1.0 days (pure water) [84]	NA
NG	Fe^{2+} and cast iron [85]	NA	27 days (fresh water); 111 days (moist sand); 126 days (dry sand) [82]	37 days (pH 9) [86] ≈ 1 year (pH 3 - 8) [52]
NQ	Fe^{2+}	30 days (pH 8 – 9) [87]	1 – 2 days (fresh water) [88-90]	NA
Tetrazene	NA	NA	NA	NA
NTs	NA	NA	24 days (2-NT, fresh water) [91]; 6 hours (4-NT, fresh water) [48]	NA
NB	Fe^{2+}	15 hours (high Fe^{2+} soil); 60 hours (moderate Fe^{2+} soil) [92]	Very slow process (aqueous) [76]; 38% degraded over 5 hours (in air) [93]	NA
NTO	Bimetallic iron/nickel or iron/copper suspensions	14 – 33 minutes [94]	8.3 hours – 3 days [24, 42, 95]	NA

NA – not determined in the literature

Table 2-4 (continued). A Summary of Abiotic, Photolytic, and Hydrolytic Degradation Rates for Selected MCs (NA – not determined in the literature)

MC	Abiotic Reduction		Photolysis Half-Life	Hydrolysis Half-Life
	Type	Half-Life		
Tetryl	NA	NA	95.4% degraded in 20 days [59, 77]	2.3% degraded in 20 days; 3.4% degraded in 90 days (20°C) [77]
Lead Azide	NA	NA	Possible [96-98]	Can occur [99]
Lead Styphnate	NA	NA	NA	NA
Ammonium Picrate	NA	NA	Can occur [100]	Dissociates [62, 101]
Picric Acid	NA	NA	NA	NA
PETN	Granular iron 30% granular iron/70% silica	0.26 minutes 1.58 minutes [102]	66% aqueous sample degraded in 21 days [103]	20 days (pH 12, 50°C) [103]
MNA	NA	NA	NA	NA
NC	NA	NA	Negligible [82, 104]	Can occur in alkaline solutions at high temperature (70°C) [105]
TATB	NA	NA	Can occur [106, 107]	Can occur, with alkaline catalyst [108]
DBX-1	NA	NA	NA	NA

N/A – data not available

The example of photolysis, abiotic degradation and hydrolysis for selected MC are further described in Appendix A and below.

TNT

Photolysis: TNT undergoes photolytic conversion in the presence of moisture [109] forming nitrobenzenes, benzaldehydes, azoxydicarboxylic acids, and nitrophenols through oxidation of methyl groups, reduction of nitro groups, and dimer formation [2].

Abiotic Degradation: Abiotic soil degradation of TNT has been well documented. The general pathway for abiotic reduction of TNT involves the reduction of one, two, or all three TNT nitro groups to TNT dimers 2-amino-2,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT). The first two steps include production of 2-hydroxylamino-4,6-dinitrotoluene (4-HA-2,6-DNT) then generating 4-ADNT as shown in **Figure 2-4**. As 4-ADNT is also a common transformation product of TNT, its presence does not indicate a specific transformation mechanism (e.g., abiotic or biotic transformation). This pathway can occur in TNT-contaminated soils and groundwater, in addition to the products formed through reactions such as photolysis.

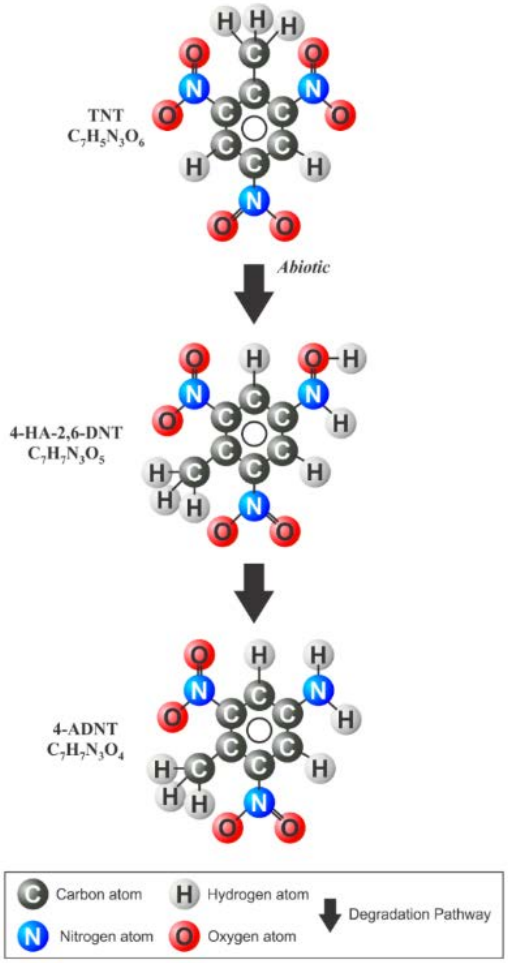

Figure 2-4. First Two Steps of the Abiotic Transformation of TNT [1-3]

Hydrolysis: A number of studies have been conducted on alkaline hydrolysis of TNT in water and highly contaminated soils [110-112] and demonstrate complete degradation of TNT. However, most of these studies only considered the decay of TNT and did not identify final products and intermediate compounds. Among these studies, a few publications proposed that the byproducts in the later stages of TNT hydrolysis could include aromatic ring cleavage species (acetates, formates, oxalates, nitrites) as well as products of polymerization [113].

DNTs

***Photolysis*:** Both 2,4- and 2,6-DNT will readily solubilize in water, where they will undergo photolysis [2, 84, 114]. Photolytic half-lives of 2,4-DNT in fresh water systems range from 2.7 to 9.6 hours; in seawater, this rate is ≈15 hours; and in high-purity laboratory water, this rate is >100 hours [78, 115]. These photolysis rates are slightly slower than those for 2,6-DNT (12 minutes in freshwater; 5 hours in seawater; and 20 hours in high-purity laboratory water).

Abiotic Reduction: Few data are available regarding abiotic reduction of DNTs (either 2,6- or 2,4-DNT). In general, DNTs are resistant to chemical and biological oxidation properties and hydrolysis resulting from their electron withdrawing properties [116].

***Hydrolysis*:** Specific studies on the hydrolysis of DNTs appear to be lacking although predictive models suggest that DNTs are generally resistant to hydrolysis [2, 117]. It is suspected that DNTs are only partially hydrolyzed due to the higher electron density of DNT as compared to TNT which makes attack by nucleophilic bases more difficult [118].

Picric Acid (2,4,6-trinitrophenol)

***Photolysis*:** Picric acid can undergo photolysis and form picramic acid [64, 65]. However, the technical literature also states that picric acid discharged to the environment is not expected to be significantly degraded via photochemical processes [119]. A more complete study on the propensity and factors affecting picric acid photolysis may be warranted.

***Abiotic Reduction*:** Little data were found on other abiotic processes for picric acid. However, in general, nitroaromatic compounds can be reduced via ferrous iron (Fe^{2+}) [65, 120].

***Hydrolysis*:** Picric acid will not undergo hydrolysis, rather the compound will dissociate to yield the picrate anion when dissolved in water. It should be noted that picric acid can also be formed from the hydrolysis of tetryl [64].

RDX

***Photolysis*:** Photolysis data for RDX are available for both solid and aqueous phases of RDX [82]. Aqueous RDX has been shown to undergo photolytic degradation ≈50 to 100 times faster than solid RDX. Half-lives for aqueous RDX were in the range of 0.8 days (in July) to 2.5 days (in October). The half-life for solid phase RDX ranged from 76 days (for moist sand) to 103 days (for dry sand). Variables such as the spectral intensity of the sunlight, latitude, altitude, plant cover, and average amount of cloud cover could have significant impacts on the photolysis rates, indicating that training ranges in northern latitudes (e.g., Canada and Europe) contaminated with RDX may experience lower photolytic degradation of RDX than training ranges in the southern latitude.

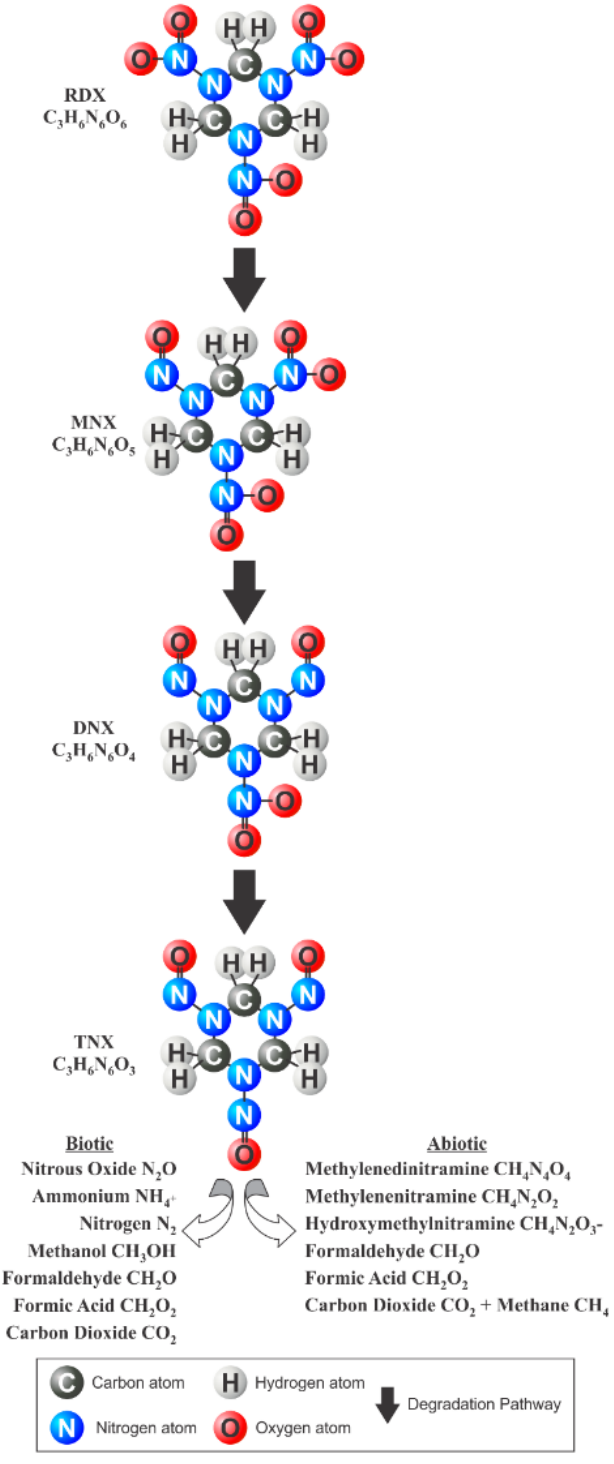

Figure 2-5. Abiotic Reduction of RDX

***Abiotic Reduction*:** Reduction of RDX by iron (Fe^{2+}) in aqueous suspensions of magnetite has been documented [2, 81], producing hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX); hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX); and hexahydro1,3,5-trinitroso-1,3,5-triazine (TNX) in a step-wise reduction process shown in **Figure 2-5**. Negligible reduction of RDX occurred in aqueous suspensions of Fe^{2+} or magnetite alone. Half-life values were in the range of ≈20 to 30 hours, with higher concentrations of Fe^{2+} producing shorter RDX half-lives.

Sample analyses from these same tests with iron (Fe^{2+}) in an aqueous suspension (representative of anoxic sediments where Fe^{2+} is abundant) of magnetite suggest that these MNX, DNX, and TNX "intermediate" products can undergo further transformation in these solutions, resulting in the production of ammonium (NH_4^+), N_2O, and formaldehyde. Additional analysis of Fe^0 has also demonstrated the potential to reduce RDX in both soil and aqueous matrices [2, 81]. NH_4^+ was produced as an end product in these experiments; the levels of the intermediate compounds MNX, DNX, and TNX (**Figure 2-4**) disappeared completely within 96 hours. In a study of RDX degradation in the presence of carbonate and sulfate green rusts, formaldehyde, N_2O, and NH_4^+ were identified as the end products of degradation [74].

***Hydrolysis*:** Amine-based compounds, including nitroamine explosives, can undergo hydrolysis. Hydrolysis of RDX has been reported [83] in alkaline solutions at pH levels greater than 10, forming end products including NO_2^-, formaldehyde, formic acid (CH_2O_2), NH_3, and N_2. The half-life of this process is ≈ 100 hours, slower than aqueous photolysis and biodegradation.

HMX

***Photolysis*:** HMX undergoes photolysis when dispersed or transported (e.g., through advection) into surface waters such as lagoons and rivers [121, 122]. However, photolysis reactions have been shown to occur at very slow rates. Nonetheless, photolysis and biodegradation have been identified as the two major transformation processes of HMX [46]. Because photolysis is identified as one of the main transformation pathways and is a slow process, HMX is expected to persist in the environment. Data on the photolysis rates for HMX in rivers and lagoons [122] suggest that the half-lives for HMX can range from 17 days to 7,900 days. The specific half-life value is highly dependent on the depth of HMX in the surface water; the ability of sunlight to penetrate to these depths; and the turbidity of the water. The photolysis half-life is expected to be longer than the half-life for biodegradation of HMX in water (≈1.76 days) and soil (≈7.39 days).

***Abiotic Reduction*:** Very little data are available on abiotic reactions of HMX in the environment [2]. However, available data do suggest that HMX can be reduced by iron in the form of magnetite and ferrous iron, however, the rates of abiotic reduction for HMX by these processes is significantly less than those for TNT and RDX (ferrous iron removed 98% of TNT and RDX from soil while high concentrations of HMX remained [81]); thus, reduction is likely to be slower than biodegradation of HMX and possibly slower or on the same timescale as HMX photolysis.

***Hydrolysis*:** Little information is available on the hydrolysis of HMX; therefore, hydrolysis is not considered a significant degradation pathway [46]. It is possible for HMX to undergo hydrolysis under alkaline conditions (pH > 10), but at a slow rate with a half-life of ≈288 days [71].

Perchlorate: No clear evidence exists to support occurrence of perchlorate abiotic attenuation, however few studies indicate that anaerobic conditions may favor perchlorate degradation [123].

2.4 BIOLOGICAL ATTENUATION OF MC

Biological attenuation of MC is governed by the biologically-mediated transformation or immobilization of an MC [88, 124]. In addition to biotransformation via microorganisms, these processes include phytoremediation which encompasses transformation and bioaccumulation of MC by plants, and is summarized in **Figure 2-6** [37, 125].

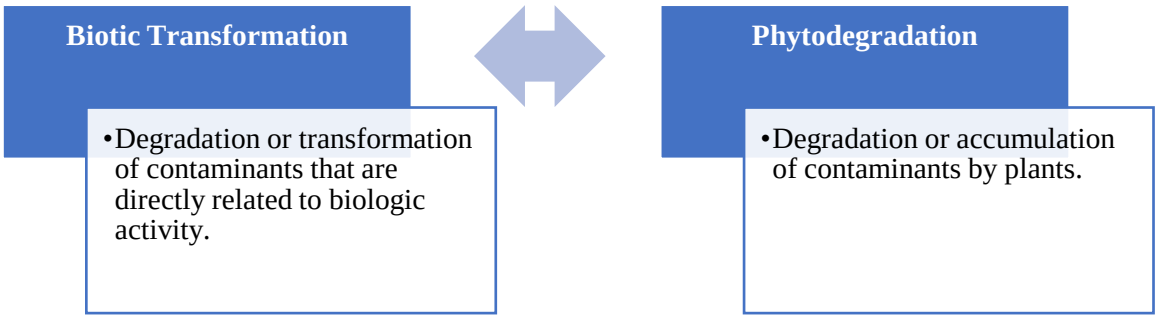

Figure 2-6. Summary of Biological Attenuation Processes for MC

Naturally occurring microorganisms (such as bacteria and fungi) can transform hazardous chemicals to either substances that are less toxic or completely benign. These processes are defined as either biodegradation or biotransformation [120, 126]. Biodegradation can occur through aerobic or anaerobic degradation of organic matter or contaminants, while biotransformation consists of partial transformation and production of intermediates [3, 127]. Contaminant transformation may also occur through direct metabolism, in which energy gain comes directly from the transformation process. Conversely, co-metabolic pathways result from a fortuitous reaction where the microorganisms do not receive energy from the transformation reaction and require a primary energetic substrate to facilitate sustained contaminant biotransformation [3]. Bioremediation may be applied in situ or ex situ to treat both soil and groundwater. Often, site conditions need additional adjustment to enhance a contaminant's degradation rate and to provide an optimal environment to sustain the growth and performance of microbial populations [3].

Degradation of chemical compounds with the use of naturally occurring plants offers an innovative and cost-effective option to address recalcitrant environmental contaminants [128]. The use of plant products, algae or entire plants as a tool to restore or stabilize contaminated sites gives an opportunity to extract, store or degrade a variety of organic and inorganic compounds. The ability to cultivate high plant biomass with a high content of toxic chemicals in a contaminated soil determines successful degradation [129].

Phytodegradation pathways include the following three aspects:

- Phytodegradation: The active uptake and biotransformation of the contaminant.
- Phytoextraction/Phytoaccumulation: The uptake and accumulation, possibly hyperaccumulation, of the contaminant is limited by the uptake and efficiency of plant roots. Phytoextraction targets a variety of heavy metals and organic substrates.
- Rhizodegradation: The degradation or transformation of contaminants within the root zone of the plants.

The selective removal of ions represents a unique plant quality utilized for uptake, regulation and distribution of metals in a soil medium [129]. Absorption dominates as a major rhizosphere uptake mechanism due to the presence of additional protective barriers, which prevent plants from metal toxicity during phytoaccumulation. To date, the DoD has supported several studies as part of the Remediation Management of Distributed Sources of Munitions Constituents on Ranges Program. Those efforts included a large-scale lysimeter study, a bench-top study and an investigation of the effects of explosive-degrading plants on the rhizosphere and soil microbial population [40].

2.4.1 BIODEGRADATION OF EXPLOSIVES

Biological attenuation of nitroaromatic compounds depends on the biodegradation potential of microbial communities present in the environment [120, 126]. The presence of NO_2 electron withdrawing groups on the aromatic ring influences the type of biotransformation mechanisms (i.e., oxidation or reduction) [130, 131]. For example, cyclic nitramine explosives, such as TNT, RDX and HMX, contain multiple nitro groups (R- NO_2) attached onto aromatic or heterocyclic rings that provide protection from an oxidative degradation [126, 131]. The chemical structure of MC suggests that their primary biotransformation process is reductive in nature and is catalyzed by nitroreductases. Catalysis of nitro groups requires a co-substrate and can occur either under aerobic or anaerobic conditions [120]. Furthermore, intermediates of energetics such as TNT can potentially be more toxic than the parent energetic compound. Therefore, monitoring for intermediates should be considered as part of a monitored natural attenuation (MNA) strategy. Depending on the levels of intermediates, enhanced biodegradation (an active remedial strategy) may be needed to obtain complete mineralization [127].

The example biodegradation pathways for selected MC are further described in Appendix A and below.

TNT: Bacterial isolates such as *Pseudomonas, Desulfovibrio sp.*, *Bacillus sp.* and *Staphylococcus sp.* cultured from freshwater or terrestrial environments have been reported to degrade TNT [132-135]. Degradation of TNT occurs in both aerobic and anaerobic conditions and is typically cometabolic in nature. Anaerobic degradation of TNT produces amino-2,6-dinitrotoluene (ADNT) and diaminonitrotoluene DANTs (preferentially 2,4-DANT) [133, 134]. Only under strict anaerobic conditions is TNT transformed to triaminotoluene (TAT). ADNT and DANTs are not degraded by anaerobes and persist in the environment under anaerobic conditions or are oxidized under aerobic conditions.

DNTs: Similarly to TNT, DNTs can be transformed under reducing conditions to mono and/or diamino byproducts [131, 136]. DNTs, with fewer nitro groups, may undergo oxidation under aerobic conditions. The oxidation reactions can either occur: 1) after partial or complete reduction of the nitro groups to hydroxylaminoaromatics, 2) with formation of a hydride Meisenheimer complex, or 3) directly on DNT with release of a nitro group as nitrite and production of a hydroxyl group for ring cleavage [125, 137, 138].

Picric acid (2,4,6-trinitrophenol): Picric acid is also degraded through reduction with formation of Meisenheimer complex as a key intermediate (**Figure 2-7**). In *Rhodococcus (opacus) erythropolis* HL PM-1 [139], *Nocardioides* sp. strain CB 22-2 [140] and *Nocardioides* simplex (formerly *Arthrobacter*) FJ2-1A [141], elimination of nitrite is thought to proceed through this intermediate. The subsequently generated mono- and dinitrophenol can then be oxidated with subsequent ring cleavage.

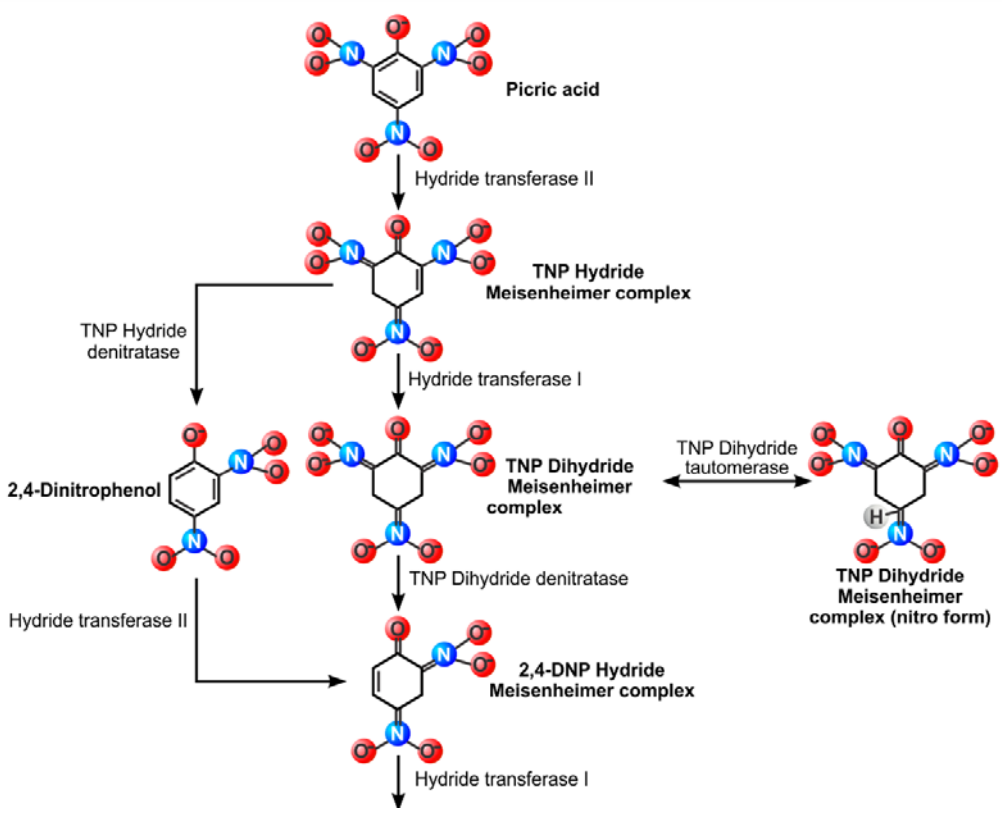

Figure 2-7. First Steps in Biodegradation of Picric Acid by *Nocardioides* sp. strain CB 22-2

RDX: RDX biotransformation reactions occur via co-metabolic processes under anaerobic conditions [142]. RDX is reportedly degraded by anaerobic sludge [143] under nitrate-reducing, sulfidogenic, and/or methanogenic conditions and by specific isolates or by consortia [142]. There is little existing information pertaining to formation of RDX ring cleavage products [144]. As with most other cases, the co-metabolic degradation rate of RDX is much slower than the direct metabolism of the compound [124]. The metabolites may undergo further reduction prior to ring cleavage and transform into toxic hydroxylamino-RDX intermediates, which in another ring

cleavage reaction may yield formaldehyde, methanol, hydrazine, 1,1-dimethylhydrazine and 1,2-dimethylhydrazine.

HMX: While aerobic biodegradation of HMX appears to be negligible, the similarities in structure with RDX make HMX susceptible to anaerobic biotransformation. For example, HMX biotransforms to methane and chloroform under anaerobic conditions when a mixed microbial consortium is present [126]. The biotransformation rate is highest under sulfate-reducing conditions and decreases under electron-accepting conditions in the following order: fermentation, methanogenesis and nitrate-reduction [43].

2.4.2 BIODEGRADATION OF PROPELLANTS

Similarly to explosives, organic propellants are susceptible to biotransformation.

2,4- and 2,6-DNTs: Studies have shown that both 2,4-DNT and 2,6-DNT can be mineralized through an oxidative pathway with DNTs serving as the sole source of nitrogen, carbon and energy [43, 145]. Biotransformation under anoxic conditions does not result in complete degradation of these contaminants. Rather, the reductive pathway produces corresponding diamontoluenes, which appear recalcitrant to further microbial degradation in an anoxic environment. Overall, DNTs tend to undergo biotransformation and, if not in oxic environments, irreversibly bind to aquifer solids. More detailed discussion of biodegradation of 2,4-DNT and 2,6-DNT is located in Appendix A, Sections 6 and 7, respectively.

NG: NG is biotransformed both aerobically and anaerobically, serving as a sole source of nitrogen to a variety of microorganisms (*P. putida, P. fluorescens, Klebsiella, Rhodococcus, G. candidum, P. chrysosporium*). The biotransformation pathway consists of a step-wise NG denitration [127, 146], with generation of more toxic, soluble, and volatile intermediate products, such as 1,2-dinitroglycerol, 1,3-dinitroglycerol, 1-mononitroglycerol (1-MNG), and 2-mononitroglycerol (2-MNG). Upon complete denitration, the end product is glycerol, which may further mineralize to carbon dioxide [146]. Depending on the microorganisms, complete denitration is not always achieved. Detailed discussion of NG biotransformation is located in Appendix A, Section 10.

NQ: The limited data on biodegradation of NQ indicate that it does not readily biotransform [147], although a few recent studies [147-149] have shown NQ biotransformation in aerobic microcosms after glucose was supplied as a carbon source [148]. When NQ-degrading bacterium *Variovorax* strain VC1 was isolated from soil microcosms containing NQ as the sole nitrogen source, its degradation was still inhibited in the presence of a more favorable source of nitrogen. Mineralization of NQ in aerobic conditions by VC1 produced ammonia, nitrous oxide and carbon dioxide as final products [148]. Detailed discussion of NG biotransformation is located in Appendix A, Section 11.

Perchlorate: Biodegradation of perchlorate has been shown to occur with several soil microorganisms using perchlorate reductase and chlorite dismutase [150-153]. The rate of perchlorate biodegradation depends on the microbial organism, population of microorganisms and environmental conditions in which the degradation reactions occur. For example, in ex situ perchlorate degradation by anaerobic culture of *Dechloromonas* species KJ took up to 70 days for

complete removal when applied in a packed bed reactor [154]. However, when a single culture of an anaerobic enrichment culture was used, perchlorate was degraded in 2 days [150, 155]. Perchlorate-reducing organisms are thought to use a single enzyme (per)chlorate reductase (encoded by *pcr*A gene) to reduce perchlorate (ClO_4^-) to chlorate (ClO_3^-) and chlorate to chlorite (ClO_3^-). Perchlorate reduction produces chlorate (ClO_3^-), which then competes with perchlorate for the Pcr enzyme. As the chlorate concentration increases, it is more likely to be reduced, thus increasing the rate of chlorate reduction and decreasing that of perchlorate. The final products of perchlorate reduction are chloride ion and water as shown in **Figure 2-8** and described in detail in Appendix A, Section 1.

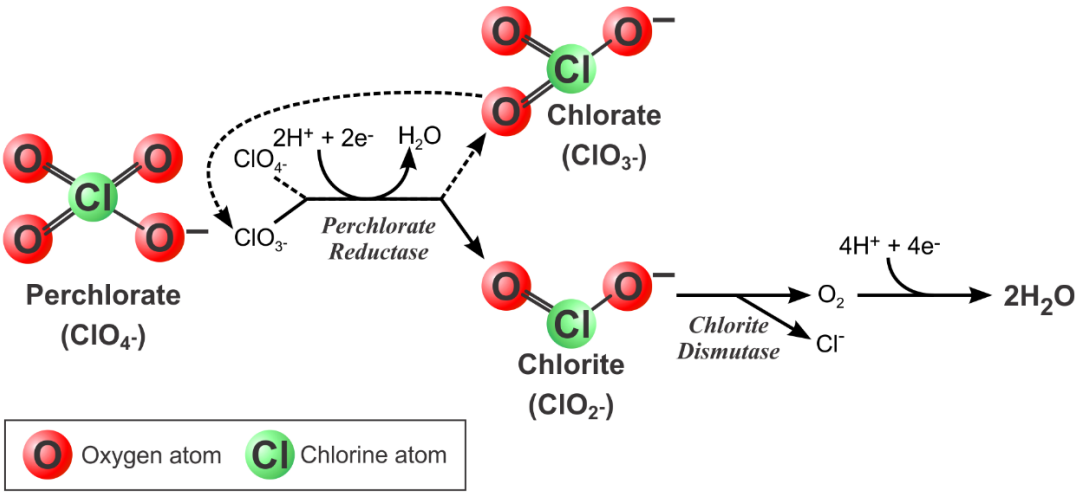

Figure 2-8. Perchlorate Biodegradation Pathway [150, 152, 155]

2.4.3 BIODEGRADATION OF METALS

Geochemistry of a particular site and metal chemistry govern the microbial interactions with the given metal of interest. The biotic cycling of naturally occurring elements, especially iron and manganese, also affects the behavior of many toxic elements [30]. For metals, there are generally two pathways for natural attenuation by biological processes: precipitation and adsorption leading to metal sequestration and changes in geochemical condition due to microbial respiration, including changes in redox potential and pH, leading to reversible changes in solubility [15].

Microbial degradation of organic matter can be coupled to many metabolic pathways, for example sulfate reduction that results in the production of hydrogen sulfide. Metals such as copper form extremely insoluble copper sulfide complexes, such that no complexing ligand can compete with hydrogen sulfide or metal sulfide for copper. Moreover, complexes of lead with sulfide are highly insoluble and stable, enhancing lead properties to co-precipitate with iron particles [15, 30].

Microbially mediated oxidation and reduction reactions can be manipulated for metal remediation. Some microorganisms can oxidize/reduce metal contaminants directly while others produce chemical oxidizing/reducing agents that interact with the metals to trigger a change in oxidation state. Mercury and cadmium have been observed to be oxidized through microbial processes, and arsenic and iron are readily reduced in the presence of appropriate microorganisms [156]. The mobility of metal contaminants is influenced by their oxidation state. Redox reactions can

therefore be used to influence metal mobility [157]. Methylation involves attaching methyl groups to inorganic forms of metal ions to form organometallic compounds. Methylation reactions can be microbially mediated. Organometallic compounds are more volatile than inorganic metals and this process can be used to remove metals through volatilization and subsequent removal from the gas stream. However, organometallics are also more toxic and mobile than other metal forms and may potentially contaminate surrounding surface waters and groundwater [156].

3.0 MC TOXICITY CHARACTERISTICS

MC and known degradation products released to the environment may be harmful to both human and ecological receptors. This section provides an overview of existing and readily available human and ecological toxicity metrics for the MC of interest to assist Navy decision makers in developing an informed strategy for managing MC-contaminated sites. Along with toxicity information, this section provides summaries of the potential adverse health effects associated with exposure to MC and lists United States Environmental Protection Agency (U.S. EPA) risk-based screening levels for the MC.

3.1 HUMAN HEALTH TOXICITY

Toxicity values for many chemicals have been developed by U.S. EPA and other regulatory or public health agencies (for example, Agency for Toxic Substances and Disease Registry [ATSDR], World Health Organization) and have many descriptors and qualifiers: cancer and noncancer, oral and inhalation, and chronic, subchronic, and acute [158]. The toxicity values used to evaluate a particular exposure scenario should be consistent with the calculation being performed (cancer risk versus noncancer risk), the exposure routes of interested (oral, dermal contact, inhalation) and, in the case of noncancer risk, the exposure period being evaluated (chronic, subchronic, or acute exposure) [158].

Toxicity criteria classify adverse effects as carcinogenic or noncarcinogenic (i.e., potential effects other than cancer). For evaluation of potential noncancer effects, U.S. EPA has developed toxicity criteria referred to as oral reference doses (RfDs) and inhalation reference concentrations (RfCs) for effects known or assumed to be produced through a nonlinear mode of action [159]. Carcinogens are agents that induce cancer. Potential carcinogenic effects are expressed as the probability that an individual will develop cancer over a lifetime. For evaluation of potential cancer effects, U.S. EPA has characterized the weight of evidence for human carcinogenicity, and developed toxicity criteria termed oral slope factors (SFs) and oral and inhalation unit risks.

In most cases, toxicity studies with laboratory animals are used to develop toxicity criteria. In addition, epidemiological studies of human populations provide the data used to develop toxicity criteria when available. The dose-response relationships characterized by toxicity values determined from studies of laboratory animals are conducted under controlled conditions designed to minimize responses due to confounding variables, and are conducted at relatively high dose levels to ensure that responses can be observed using as few animals as possible in the experiments. Statistical models and uncertainty factors (UFs) are used to extrapolate the relatively high doses administered to animals to predict potential human responses at dose levels far below those tested in animals.

In-depth summaries of development of noncarcinogenic and carcinogenic toxicity values are provided below. **Table 3-1** and Appendix C summarize the adverse health effects associated with exposure to MC and provide a summary of the toxicity values that currently exist for the MC of interest and U.S. EPA-derived risk-based values that currently exist for the MC.

Table 3-1. Summary of Adverse Health Effects, Toxicity, and Look-up Risk-Based Levels to Protect Health

Munition Constituent	Adverse Health Effects[a]	Cancer Assessment[b]	Toxicity Values[c]										Risk-Based Levels to Protect Health[c]			
			Cancer				Noncancer									
			Oral SF $(mg/kg/day)^{-1}$	Source	Inhalation Unit Risk $(ug/m^3)^{-1}$	Source	Oral RfD (mg/kg/day)	Source	Inhalation RfC (mg/m^3)	Source	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Tap water (ug/L)	key
Perchlorate	Perchlorate affects the ability of the thyroid gland to take up iodine. Iodine is needed to make thyroid hormones that regulate many body functions after they are released into the blood. Perchlorate's inhibition of iodine uptake must be great enough to affect the thyroid before it is considered harmful.	Not likely to be carcinogenic to humans.	ND	ND	N/A	ND	7.0E-4	I	ND	ND	5.5E+01	n	8.2E+02	n	1.4E+01	n
Chlorate	Potassium chlorate causes irritation to the respiratory tract. Symptoms may include coughing and shortness of breath. Ingestion causes irritation to the gastrointestinal tract. Symptoms may include nausea, vomiting and diarrhea.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-trinitrotoluene (TNT)	Workers involved in the production of explosives who were exposed to high concentrations of TNT in workplace air experienced several harmful health effects, including anemia and abnormal liver function. Similar blood and liver effects, as well as spleen enlargement and other harmful effects on the immune system have been observed in animals that ate or breathed 2,4,6-trinitrotoluene. Other effects in humans include skin irritation after prolonged skin contact, and cataract development after long-term (365 days or longer) exposure.	The U.S. EPA has determined that TNT is a possible human carcinogen based on a study in which rats ate TNT for long periods developed tumors of the urinary bladder.	3.0E-02	I	ND	ND	0.0005	I	ND	ND	2.1E+01	c	9.6E+01	c	2.5E+00	c
RDX	Inhalation of dusts containing RDX or swallowing large amounts of RDX may cause temporary seizures, which will stop after the RDX is eliminated from the body. Some people exposed to large amounts of RDX also have alterations in blood pressure and in some components of the blood, but these effects may be secondary to the seizures. Effects associated with long-term, low-level exposure to RDX are not known.	There are no studies reported of cancer in people exposed to RDX. Nonetheless, U.S. EPA has determined that RDX is a possible human carcinogen based on the presence of liver tumors in mice that were exposed to RDX in the food for 1 to 2 years.	1.1E-01	I	ND	ND	3.0E-03	I	ND	ND	6.1E+00	c	2.8E+01	c	7.0E-01	c

Table 3-1. Summary of Adverse Health Effects, Toxicity, and Look-up Risk-Based Levels to Protect Health (continued)

HMX	Information on the adverse health effects of HMX is limited. In one human study, no adverse effects were reported in workers exposed to HMX in air. Studies in rats, mice, and rabbits indicate that HMX may be harmful to the liver and central nervous system if it is swallowed or gets on the skin.	At present, the information needed to determine if HMX causes cancer is insufficient. As such, U.S. EPA has determined that HMX is not classifiable as to its human carcinogenicity.	ND	ND	ND	ND	5.0E-02	I	ND	ND	3.9E+03	n	5.7E+04	n	1.0E+03	n
2,4-DNT	Toxicity to humans has been evaluated in DNT mixture for factory workers, munitions handlers and mining workers. Adverse health effects posed by chronic DNT exposure have been identified in the central nervous system, heart and circulatory system of humans.	Although U.S.EPA has not evaluated pure 2,4-DNT for evidence of human carcinogenic potential, the DNT mixture (containing 2,4-DNT and 2,6-DNT) was classified as a Class B2 (probable human carcinogen based on sufficient evidence of carcinogenicity in animals).	3.1E-01	C	8.9E-05	C	2.0E-03	I	ND	ND	1.7E+00	c	7.4E+00	c	2.4E-01	c
2,6-DNT	See 2,4-DNT	See 2,4-DNT	1.5E+00	P	ND	ND	3.0E-04	X	ND	ND	3.6E-01	c	1.5E+00	c	4.9E-02	c
NG (nitroglycerin)	NG is a commonly prescribed drug and poisoning is relatively uncommon. For industrial exposures (dermal and inhalation): nausea, vomiting, abdominal cramps, headache, confusion, delirium, bradypnea, bradycardia, paralysis, seizures, cyanosis, methemoglobinemia, circulatory collapse and death.	Classified as likely to be carcinogenic to humans because it has tested positive in experimental animals without evidence of carcinogenicity in humans (Source: PPRTV document https://hhpprtv.ornl.gov/issue_papers/Nitroglycerin.pdf).	1.7E-02	P	ND	ND	1.0E-04	P	ND	ND	6.3E+00	n	8.2E+01	n	2.0E+00	n
NQ (Nitroguanidine)	Exposure to chemicals with a strong odor often results in such nonspecific symptoms as headache, dizziness, weakness, and nausea.	CLASSIFICATION: D; not classifiable as to human carcinogenicity.	N/A	ND	N/A	ND	1.0E-01	I	N/A	ND	6.3E+03	n	8.2E+04	n	2.0E+03	n
Tetrazene	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NTs (nitrotoluenes)	Exposure may cause headache, flushing of face; dizziness, dyspnea (difficult breathing), cyanosis, nausea, vomiting, muscular weakness, increased pulse and respiratory rate, irritability and convulsions.	Nitrotoluenes are not classifiable as to their carcinogenicity to humans														
Munition Constituent	**Adverse Health Effects[a]**	**Cancer Assessment[b]**	**Toxicity Values[c]**										**Risk-Based Levels to Protect Health[c]**			
			Cancer						**Noncancer**							

Table 3-1. Summary of Adverse Health Effects, Toxicity, and Look-up Risk-Based Levels to Protect Health (continued)

			Oral SF $(mg/kg/day)^{-1}$	Source	Inhalation Unit Risk $(ug/m^3)^{-1}$	Source	Oral RfD (mg/kg/ day)	Source	Inhalation RfC (mg/m^3)	Source	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Tap water (ug/L)	key
Nitrotoluene, m-	See NT	No human or animal data were available regarding the carcinogenicity of m-nitrotoluene. Available genotoxicity results for m-nitrotoluene were primarily negative.	ND	v	ND	ND	1.0E-04	X	ND	ND	6.3E+00	n	8.2E+01	n	1.7E+00	n
Nitrotoluene, o-	See NT	No human carcinogenicity data were located for o-nitrotoluene, but there was strong evidence for carcinogenicity in rats and mice. The hazard descriptor *likely to be carcinogenic to humans* is applied to *o*-nitrotoluene	2.2E-01	P	ND	ND	9.0E-04	P	ND	ND	3.2E+00	c	1.5E+01	c	3.1E-01	c
Nitrotoluene, p-	See NT	Findings of increased tumor incidences in both male and female rats, as well as in male mice, a second animal species, plus the positive findings in three different organs (clitoral gland, skin, and lung) indicated that p-nitrotoluene is "likely to be carcinogenic to humans". However, p-nitrotoluene was on the low end of the range for this descriptor	1.6E-02	P	ND	ND	4.0E-03	P	ND	- ND	3.4E+01	c	1.4E+02	c	4.3E+00	c
NB (nitrobenzenes)	A small amount of nitrobenzene may cause mild irritation if it contacts the skin or eyes directly. Repeated exposures to a high concentration of nitrobenzene can result in methemoglobinemia, a condition in which the blood's ability to carry oxygen is reduced. Effects such as headache, irritability, dizziness, weakness, and drowsiness may also occur.	Likely to be carcinogenic to humans	ND	ND	4.0E-05	I	2.0E-03	I	9.0E-03	I	5.1E+00	c	2.2E+01	c	1.4E-01	c
NTO (nitrotriazolone)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DNAN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Munition Constituent	**Adverse Health Effects[a]**	**Cancer Assessment[b]**	**Toxicity Values[c]**								**Risk-Based Levels to Protect Health[c]**					
			Cancer				**Noncancer**									

Table 3-1. Summary of Adverse Health Effects, Toxicity, and Look-up Risk-Based Levels to Protect Health (continued)

			Oral SF $(mg/kg/day)^{-1}$	Source	Inhalation Unit Risk $(ug/m^3)^{-1}$	Source	Oral RfD (mg/kg/day)	Source	Inhalation RfC (mg/m^3)	Source	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Tap water (ug/L)	key
Tetryl	Workers at military facilities who breathed tetryl-laden dust complained of coughs, fatigue, headaches, eye irritation, lack of appetite, nosebleeds, nausea, and vomiting. Workers who routinely handled tetryl developed a distinct yellow staining of the hands, neck, and hair. Many workers who had skin contact with tetryl dust or compounds containing tetryl also developed skin rashes.	The carcinogenicity of tetryl in humans and animals has not been studied.	ND	ND	ND	ND	2.0E-03	P	ND	ND	1.6E+02	n	2.3E+03	n	3.9E+01	n
Lead Azide (as Lead)	Long-term use of lead azide and lead styphnate as primary explosives has resulted in lead contamination at artillery and firing ranges and become a major health hazard and environmental problem for both military and civilian personnel. Lead absorbed into the body is distributed to three major compartments: blood, soft tissue, and bone. Evidence shows that lead is a multitargeted toxicant, causing effects in the gastrointestinal tract, hematopoietic system, cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system. Children are more sensitive to lead exposure than are adults.	B2 (Probable human carcinogen - based on sufficient evidence of carcinogenicity in animals)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lead Styphnate (as Lead)	See Lead Azide	See Lead Azide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ammonium Picrate	This chemical can irritate the eyes and skin and is an allergen. Ingestion can cause a bitter taste, nausea, diarrhea, vomiting, abdominal pain, skin eruptions, stupor, and possible death. Breathing high levels can damage the kidneys, liver, and red blood cells.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

	Adverse	Cancer	Toxicity Values[c]	Risk-Based Levels

Table 3-1. Summary of Adverse Health Effects, Toxicity, and Look-up Risk-Based Levels to Protect Health (continued)

Munition Constituent	Health Effects[a]	Assessment[b]	Cancer				Noncancer						to Protect Health[c]			
			Oral SF $(mg/kg/day)^{-1}$	Source	Inhalation Unit Risk $(ug/m^3)^{-1}$	Source	Oral RfD (mg/kg/ day)	Source	Inhalation RfC (mg/m^3)	Source	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Tap water (ug/L)	key
Picric Acid (2,4,6-Trinitrophenol)	Skin irritant and sensitizer. Cumulative liver, kidney, and red blood cell damage; Mutagen; Affected organs: Kidneys, liver, blood, skin, eyes.	ND	ND	ND	ND	ND	9.0E-04	X	ND	ND	5.7E+01	n	7.4E+02	n	1.8E+01	n
PETN (pentaerythritol tetranitrate)	Human systemic effects by ingestion: dermatitis. Effects are similar to those of nitroglycerin, i.e. headache, weakness, and fall in blood pressure. Very low oral toxicity.	ND	4.0E-03	X	ND	ND	2.0E-03	P	ND	ND	1.3E+02	n	5.7E+02	c	1.9E+01	c
MNA	N/A	N/A	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NC (nitrocellulose)	Prolonged exposure can cause nausea, headache, and vomiting.	N/A	N/A	ND	N/A	ND	3.0E+03	P	N/A	ND	1.9E+08	n	2.5E+09	n	6.0E+07	n
TATB (1,3,5-triamino-2,4,6-trinitrobenzene)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DBX-1 (copper(l) 5-nitrotetrazolate)	(As copper) In humans, exposure to high levels of copper in drinking water has resulted in gastrointestinal irritation characterized by recurrent nausea, vomiting, and abdominal pain. Short-term occupational exposure to copper dust or fumes can cause eye and respiratory tract irritation, headaches, vertigo, drowsiness, and a condition known as "metal fume fever.	D (Not classifiable as to human carcinogenicity)	N/A	ND	N/A	ND	4.0E-02	H	ND	ND	3.1E+03	n	4.7E+04	n	8.0E+02	n

(a) Adverse health effects sources include:
1. Hazardous Substances Data Bank at https://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm
2. U.S.EPA's Integrated Risk Information System at https://www.epa.gov/iris
3. Public Health Statements, ToxFaqs, and Toxicity Profiles developed by the Agency for Toxic Substances and Disease Registry at https://www.atsdr.cdc.gov/
4. U.S. Department of Energy (DOE), Office of Environmental Management, Oak Ridge Operations (ORO) Office, Risk Assessment Information System at https://rais.ornl.gov/
5. U.S.EPA's Technical Fact Sheets about Contaminants of Concern at Federal Facilities available at https://www.epa.gov/fedfac/emerging-contaminants-and-federal-facility-contaminants-concern

(b) U.S.EPA Integrated Risk Information System; available at https://www.epa.gov/iris unless otherwise indicated in the table.

(c) Toxicity values provided in Table 3-1 were obtained from the 2017 U.S.EPA Regional Screening Levels (RSL) for Chemical Contaminants at Superfund Sites. (available for download at; https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-june-2017)Original sources of the toxicity values summarized in the 2017 RSL table include the following:
I = IRIS (U.S.EPA's Integrated Risk Information System at https://www.epa.gov/iris)
P = PPRTV (Provisional Peer Reviewed Toxicity Values derived by EPA's Superfund Health Risk Technical Support Center (STSC) for the EPA Superfund program; available at https://hhpprtv.ornl.gov/).
C = Cal EPA (California Environmental Protection Agency (OEHHA) Office of Environmental Health Hazard; available at https://www.arb.ca.gov/toxics/healthval/contable.pdf).
X = Appendix to the chemical specific PPRTV Derivation Support Documents (available at https://hhpprtv.ornl.gov/quickview/pprtv_papers.php).
H = HEAST (EPA Superfund Program's Health Effects Assessment Summary Table; available at https://epa-heast.ornl.gov/).

(d) Risk based levels were obtained from the U.S. EPA RSL Table dated June 2017. Key designations for the RSL incorporate "n" for noncancer effect and "c" for cancer effect.

N/A – not applicable; ND – no data; RfD - reference dose; SF - slope factor

3.1.1 NONCARCINOGENIC TOXICITY

Known noncarcinogenic effects are assumed to have a dose below which no adverse effect occurs or, conversely, above which an adverse effect may be seen. This dose is called the threshold dose. An estimate of the true threshold dose is called a no observed adverse effect level (NOAEL). The lowest dose at which an adverse effect has been observed is called a lowest observed adverse effect level (LOAEL). The NOAEL, or if not available, the LOAEL is used as the point of departure (POD) for extrapolating from experimental data to estimate a threshold level for humans. More recently, toxicity values have been derived using a benchmark dose (BMD) approach to define the POD for an observed adverse outcome, or benchmark response, from experimental observations [160].

The BMD, which corresponds to a lower limit of a one-sided 95% confidence interval on the BMD, is U.S. EPA's preferred approach over using the NOAEL/LOAEL because it is determined using all data from a dose-response curve and is not limited by dose selection [158]. The BMD is selected as the dose level that produces a predetermined change in adverse response; thus, noncancer effects are not expected to occur if the dose is below the threshold [158].

The RfDs and RfCs are developed based on the assumption that thresholds exist for certain toxic effects (e.g., liver or kidney damage). The RfD is expressed in units of milligrams of a chemical per kilogram of body weight per day (mg/kg-day), and the RfC is expressed in units of milligrams of a chemical per cubic meter of air (mg/m^3). In general, the RfDs and RfCs are estimates (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. For evaluation of noncarcinogenic health effects, exposures are characterized as chronic (i.e., longer than 10% of a lifetime). The RfD is developed based on the most sensitive or critical adverse health effect observed in the study population, with the assumption that if the most critical effect is prevented, then all other potential toxic effects are prevented. Specific UFs are applied to the POD or BMD value for this critical effect to account for uncertainties associated with the dose-response relationship [159].

Uncertainties include:

- Use of an animal study to derive a human toxicity value,
- Extrapolation from a LOAEL to a NOAEL,
- Extrapolation from a subchronic (partial lifetime) to a chronic lifetime exposure, and
- Evaluation of sensitive subpopulations.

The resulting RfDs are health protective because of the use of the UFs and modifying factors (MFs), where appropriate. For chemicals with noncarcinogenic effects, an RfD provides reasonable certainty that no noncarcinogenic health effects are expected to occur even if daily exposures were to occur at the RfD level for a lifetime.

3.1.2 CARCINOGENIC TOXICITY

Carcinogenic risk assessment guidelines developed by U.S. EPA [159, 161] are used to assess the carcinogenicity of a chemical. The 1986 classification system was developed according to the weight of evidence from epidemiologic and animal studies and is shown in **Figure 3-1**. The more recent scheme, as shown in **Figure 3-2**, uses a weight of evidence narrative rather than a classification system. While these narrative descriptions represent important advances in carcinogenic risk assessment, the approach has not generally been implemented for all chemicals. Therefore, both classification systems continue to be used to assess carcinogenicity.

For chemicals with known or assumed cancer effects, it is typically presumed in the absence of sufficient evidence that no threshold dose for effects exists (in other words, some incremental level of risk is associated with any dose above zero) [158]. Various models can be used to calculate the SF, but all assume that there is no threshold and use both animal and human data to calculate the SF, with a 95% upper confidence bound on the slope (the actual unit risk is likely lower). To develop the SF, U.S. EPA [162] extrapolates from observed laboratory animal data using mathematical models of dose-response. These models estimate a POD level, usually the 10% response level. The dose at the POD is known as the BMD. Statistical 90% confidence limits around the POD level are developed and the slope of the line from the lower confidence limit on the BMD through the origin is the SF. Hence, the cancer SF is the 95% upper bound on the slope of the dose-response curve in the low dose region. In the new Cancer Guidelines, U.S. EPA recommends gaining an understanding of the mode of action in lieu of the default assumption of linearity. The SF is expressed as the rate of cancer per unit of dose $(mg/kg\text{-}day)^{-1}$ or as an inhalation unit risk factor as the rate of cancer per unit of concentration of inhaled air ($\mu g/m^3$).

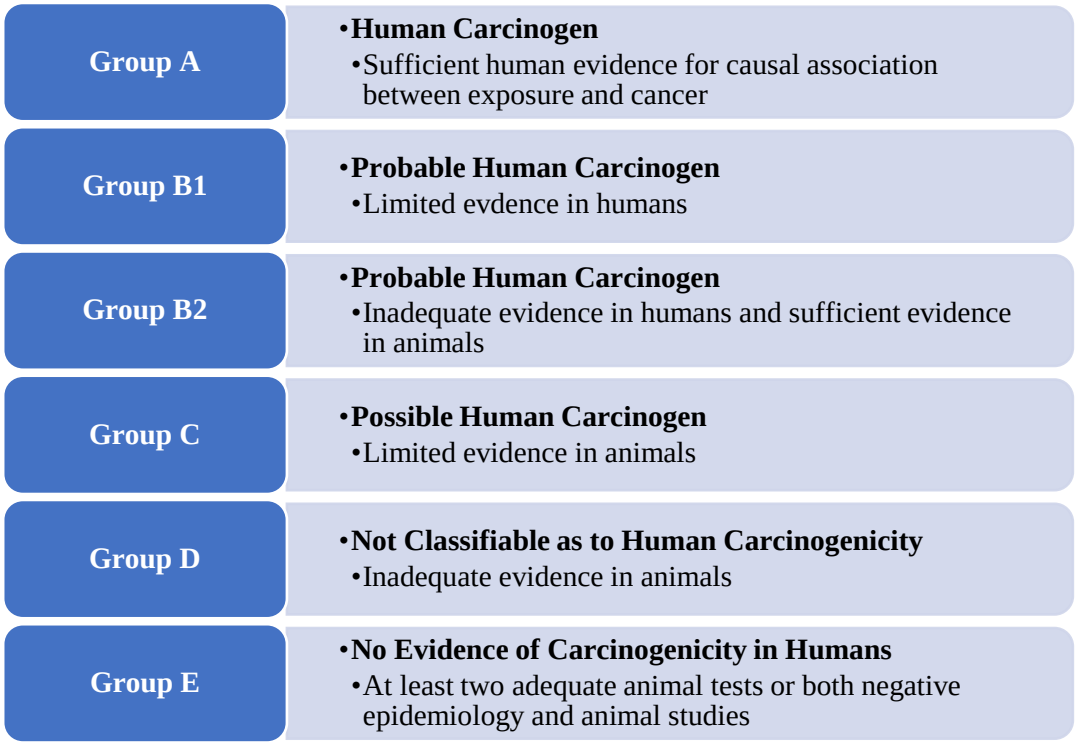

Figure 3-1. U.S. EPA 1986 Carcinogenicity Classification System [161]

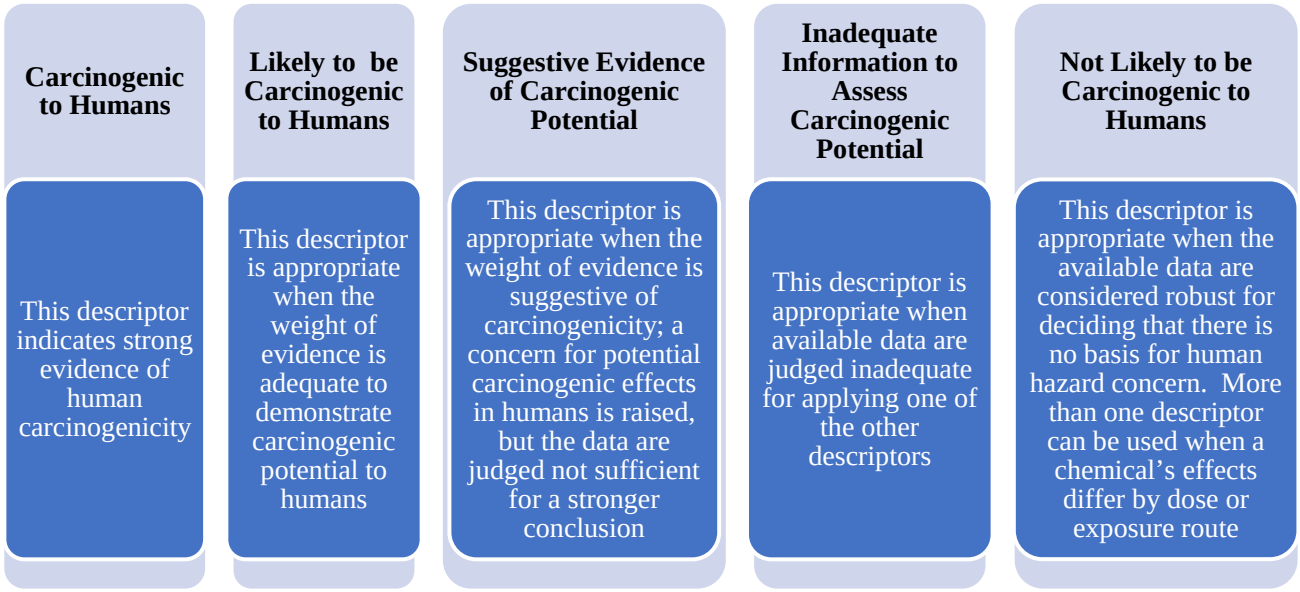

Figure 3-2. U.S. EPA Carcinogenicity Line of Evidence Classification [163]

3.1.3 SOURCES OF TOXICITY

Toxicity data can be obtained from several sources, including various U.S. EPA sources, state databases, the ATSDR, U.S. EPA's National Center for Environmental Assessment (NCEA), Superfund Health Risk Technical Support Center Provisional Peer Reviewed Toxicity Values (PPRTVs), and others. Under the Superfund Program, the primary source of toxicity values for use in human health risk assessments is U.S. EPA's Integrated Risk Information System (IRIS), an online toxicity information database maintained by NCEA. Through IRIS, U.S. EPA evaluates scientific studies and data on human health effects that may result from exposure to substances from releases to the environment.

Selecting toxicity criteria under the Superfund Program follows the Office of Solid Waste and Emergency Response Directive 9285.7-53, which recommends a hierarchy of human health toxicity values for use in risk assessments at Superfund sites. The hierarchy is as follows: (1) U.S. EPA's IRIS; (2) U.S. EPA's PPRTVs (Office of Research and Development, National Center for Environmental Assessment, Superfund Health Risk Technical Support Center); and (3) other sources of information, such as toxicity values from the California Environmental Protection Agency (CalEPA), the ATSDR's minimal risk levels for noncarcinogenic constituents, and U.S. EPA's Health Effects Assessment Summary Tables (HEAST).

Similarly, selecting toxicity values under DoD's emerging contaminant policy [164] follows a hierarchical approach as described below:

a. **Tier 1 – EPA's IRIS**. The toxicity values listed on the IRIS Web site have undergone rigorous peer review and are considered to be validated. The completion of IRIS assessments is a multi-step process including internal peer review, EPA program and

regional office review, Federal interagency review, and external peer review with a public notice and comment period.

b. **Tier 2 – EPA PPRTVs**. The Office of Research and Development/National Center for Environmental Assessment/Superfund Health Risk Technical Support Center develops PPRTVs on a chemical-specific basis when requested by the U.S. EPA's Superfund Program for use in site-specific risk assessments. However, the PPRTVs are developed in a shorter period of time than the IRIS assessments and, although these assessments undergo external peer review, this review may be more limited and does not include U.S. EPA and interagency review as is done with the IRIS assessments. Furthermore, their development typically includes a limited evaluation of information on mode of action, other toxicological end points, and other information that provides a better understanding of the toxicology of these chemicals. Often, the amount of relevant information on the toxicity of these chemicals is less because fewer studies have been conducted and reported. However, the PPRTVs are generally the best quantification of the dose-response scientific data that are available at the time they are developed because the PPRTVs utilize current information and methodologies.

c. **Tier 3 – Other Toxicity Values**. Tier 3 includes additional U.S. EPA and non-EPA sources of toxicity information. Priority should be given to sources of information that use sound science and are the most current, peer reviewed, transparent, and publicly available. Example sources for Tier 3 include the CalEPA Toxicity Criteria Database, the U.S. Department of Human and Health Services minimal risk levels, and the U.S. EPA's HEAST. Values may also be found by using an Internet search engine to search for "toxicity values" for a specific chemical.

3.2 TOXICITY PARAMETERS

Toxicity values are categorized by standard measurements of dose-response relationships or toxicity parameters. Acceptable toxicity parameters include NOAEL, LOAEL, or effect levels for 10 to 20% of the population (EC_{10} and EC_{20}). The effect levels most useful are those at the low end of the dose-response function.

There is no single source that provides toxicological information for all ecological receptors. Potential sources include:
TOXLINE (National Library of Medicine)

- ATSDR toxicity profiles
- BIOIS (Biological Abstracts)
- HSDB (National Library of Medicine)
- ECOTOX database (U.S. EPA)
- Medline (National Library of Medicine)
- Registry of Toxic Effects of Chemical Substances
- Toxicological Benchmarks for Wildlife (Oak Ridge National Laboratory)

3.3 ECOLOGICAL TOXICITY

3.3.1 MC SOIL TOXICITY

Many sites associated with military operations that involve munitions manufacturing, disposal, testing, and training can contain elevated levels of MCs and related compounds in soil. Understanding the impacts of MCs and their byproducts on soil quality, fertility and structure is pivotal to protecting and sustaining the terrestrial ecosystems at these sites. Thus, to achieve these goals an increase in knowledge of the effects of MCs on soil organisms is necessary. The surface soil medium supports three categories of ecological receptors that serve as the base of the terrestrial food web. These receptors include soil invertebrates, plants and the microbial community. The presence of MCs in surface soil has the potential to adversely affect each of these component groups. Soil contamination, which is excess receptor-specific threshold (screening) values, may have consequences with respect to the availability of forage (plants) and prey (invertebrates) for higher trophic levels, as well as decomposition and nutrient cycling processes. In addition, higher trophic levels may be adversely affected by consuming prey items that have accumulated MCs in their tissues.

Selected screening values are presented for invertebrates, plants, and the microbial community ecosystem components in **Table 3-2**. The screening values were obtained from ecotoxicological review articles and other scientific literature. The screening values presented were selected with priority given to those derived following the U.S. EPA's Ecological Soil Screening Level (Eco-SSL) criteria:

1) screening values from Sunahara (2012)[165], which were developed for 2,4-DNT and HMX are based on the robust Eco-SSL approach;
2) lowest available toxicity data for ecologically-relevant endpoints from the comprehensive review [166]; and,
3) for the IM target analytes (i.e., NTO and DNAN), [103, 167, 168]

Table 3-2. Soil Screening Values

Chemical	Organism	Duration	Effect	Value (µM)	Reference
Soil Invertebrates					
Perchlorate	Earthworm	21 days	EC_{50} for cocoon production	1.3	[166]
TNT	Collembola	28 days	EC_{50} for juvenile production	23.5	[166]
RDX	Earthworm	Not reported	EC_{20} for cocoon production	1.2	[166]
HMX	Earthworm, Potworm, Collembola	Various	Eco-SSL for reproduction endpoints	16	[165]
2,4-DNT	Earthworm, Potworm, Collembola	Various	Eco-SSL for reproduction endpoints	18	[165]
2,6-DNT	Potworm	Not reported	EC_{20} for juvenile production	18	[166]
NTO	Earthworm	14 days	Lethality (LC_{20})	1,687	[103]
DNAN	Earthworm	48 hours	EC_{50} for avoidance behavior	31	[167]
Terrestrial Plants					
TNT	Alfalfa	Not reported	EC_{20} for shoot dry mass	4	[166]
RDX	Alfalfa, Japanese millet, Ryegrass	Not reported	Reduced biomass	>9,537	[166]
HMX	Alfalfa, Barnyard grass, Ryegrass	Various	Eco-SSL for growth endpoints	>10,000	[165]
2,4-DNT	Alfalfa, Barnyard grass, Ryegrass	Various	Eco-SSL for growth endpoints	6	[165]
2,6-DNT	Alfalfa	Not reported	EC_{20} for shoot dry mass	0.4	[166]
NTO	Ryegrass	19 days	EC_{50} for growth inhibition	1	[103]
DNAN	Ryegrass	7 days	EC_{50} for seedling emergence	6	[167]
Microbial Community					
TNT	Not reported	Not reported	EC_{20} for metabolic quotient (a sensitive indicator of carbon cycle impairment)	3	[166]
RDX	Indigenous soil microbial community	12 weeks	NOEC -LOEC range for substrate-induced respiration	248 - 1,235	[166]
HMX	Indigenous soil microbial community	Up to 12 weeks	No effects on five microbial indicators, including substrate-induced respiration	>12,500	[166]
2,4-DNT	Not reported	Various	Eco-SSL for litter decomposition, soil respiration, soil enzyme activity	104	[165]
2,6-DNT	Not reported	Not reported	Not reported	NA	Not reported
NTO	Not reported	Not reported	Not reported	NA	Not reported
DNAN	Not reported	~110 hours	IC_{20} for methanogenic inhibition	16 µM*	[168]

EC_x - effect concentration for x% of the exposed population
IC_x – inhibitory concentration for x% of the exposed population
LC_x - lethal concentration for x% of the exposed population

Soil Invertebrates: The majority of ecotoxicological data for soil invertebrates have been generated using earthworms exposed to MCs in artificial soil spiked with MC compounds. Sensitive endpoints for perchlorate and both nitramine and nitroaromatic MCs generally relate to reproductive effects and threshold levels identified as the concentration where significant reductions in the number of earthworm cocoons or juveniles are determined in laboratory studies relative to study controls. The concentration causing a significant decrease in either 50 or 20 percent of the test populations is called the Effect Concentration $(EC)_{50}$ or EC_{20}, respectively. Eco-SSLs were calculated as the geometric mean of the EC_{20} effect levels derived from individual tests that quantified cocoon and juvenile production endpoints [165].

Soil invertebrate screening values for non-IM target analytes range from 1.2 to 23.5 mg/kg (Table 3-2). Available ecotoxicological data suggest that earthworm sensitivity to DNAN is comparable to non-IM analytes with an EC_{50} of 31 mg/kg [167]. Although, it was reported [103] that 14-day exposure to 1,687 mg/kg NTO resulted in death in only 20 percent of the test population, data concerning the threshold effect levels for the more sensitive reproductive or behavioral endpoints were not identified, so it is not clear whether this analyte is generally less toxic that the others.

Terrestrial Plants: The growth endpoint is the primary basis for the available ecotoxicological screening values for plants. In contrast to the soil invertebrate benchmarks, existing information indicates that large variability in the sensitivity of plants to exposure to nitramine and nitroaromatic MCs in soil exist, with the nitramine explosives, RDX and HMX, several orders of magnitude less toxic to plants than nitroaromatic compounds (**Table 3-2**). For instance, screening values for non-IM explosives range from 0.4 (2,4-DNT) to >10,000 (HMX) (**Table 3-2**). Available information for the IM target analytes suggest that plants may be sensitive to exposure to DNAN and NTO in soil, with screening values comparable to the non-IM nitroaromatics.

No ecotoxicity data for perchlorate was identified and available phytotoxicity data are limited to herbaceous species (i.e., grasses). The lack of information on woody plants is a significant data gap given the interest in the use of plants as a phytoremediation option for treating MC-contaminated soil and groundwater.

Microbial Community: Available screening values for assessing the sensitivity of the microbial community to exposure to MC analytes are based on functional rather than structural (e.g., diversity, abundance) aspects and the variability in the nature and ecological significance of reported endpoints makes the assessment of relative sensitivity of this receptor category to different MC analytes challenging. As with plants, the microbial community appears to be more sensitive to nitroaromatic (3 – 104 mg/kg) compared to nitramine (>248 to >12,5000 mg/kg) MC [169].

Ecotoxicological data for microbial community based on exposure to perchlorate, 2,6-DNT, and NTO were not identified, although in the case of 2,6-DNT, the screening value for 2,4-DNT appears to be a reasonable surrogate value [165]. Limited data are available for IM analytes and what is available is not directly comparable to the whole soil-based exposure data for other non-IM analytes.

3.3.2 MC AQUATIC TOXICITY

Ecological toxicity data are composed of effects data relevant to a specific stressor and ecological receptor. Effects elicited by a stressor may range from mortality and reproductive impairment in individuals and populations to disruptions in community and ecosystem function such as primary productivity [170]. In general, effect concentrations protective of sublethal effects (e.g., growth, reproduction) are lower than lethal effect levels and are therefore more appropriate for evaluating long-term (chronic) exposures. Effects data are primarily obtained from controlled laboratory tests although field studies may be useful in understanding biological response to multiple contaminants and structure-activity relationships between related compounds can be used to address toxicological data gaps. A summary of available aquatic toxicity data for the surface water and sediment media is presented in the following sections and available screening criteria and benchmarks for representative MC are presented in this section.

The available ecotoxicological dataset is generally most complete for nitro-substituted phenol, toluene and benzene with less information available for cyclic nitramines (e.g., HMX, RDX) and other explosive categories. Although an area of active research, ecological receptors appear to be less sensitive to recent generation explosives (including CL-20, NTO and DNAN) [167]. MC ecotoxicological data for marine environments is depauperate relative to freshwater habitats and further research on the toxicological mode of action of various MC is necessary to better understand, and ideally predict, differences in relative sensitivity among different taxa. For instance, unicellular algae appear to be particularly sensitive to nitrogen-containing MC due to possible effects of nitrate esters on membrane permeability [171].

Although not included in this review, a robust ecotoxicological dataset also exists for surface soil receptors (e.g., terrestrial plants and invertebrates) and the Strategic Environmental Research and Development Program (SERDP) has supported toxicological studies to address terrestrial ecotoxicological data gaps. In addition, the U.S. Army Center for Health Promotion and Preventive Medicine Wildlife Toxicity Assessment Program has compiled wildlife toxicity assessment reports for a majority of the important environmental contaminants of military concern [52].

Surface Water: Toxicity data for a variety of freshwater and marine species and endpoints is usually derived from laboratory studies in which contaminant-spiked water exposures are designed to bracket the threshold concentration range and to derive toxicity benchmarks [171-173] (see Section 3.2.3). Although most investigations of the aqueous toxicity of explosives and related compounds are usually performed using freshwater organisms, including bacteria, algae, invertebrates, fish and amphibians [62], toxicity data for a variety of energetic compounds have been also generated using marine species (**Figure 3-3**).

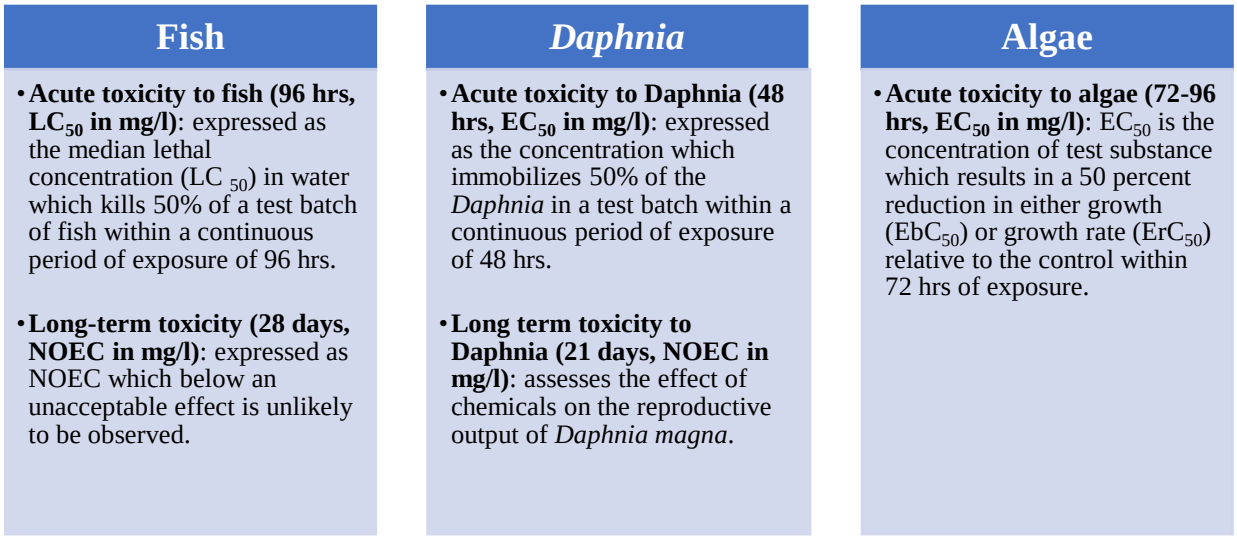

Figure 3-3. Three Trophic Levels Used in Testing of Aquatic Toxicity [57, 174]

The release of explosives into the environment can occur during munitions production, storage, transport and use as well as handling and final dispersal and disposal. As a result, explosive compounds such as TNT, TNB, RDX, HMX or tetryl have been detected in surface water of numerous military installations [175]. Following release to the environment, MC may undergo a variety of abiotic and biotic transformations in aquatic systems including oxidation, photolytic and hydrolytic reactions and, consequently, organisms may be exposed not only to the parent compounds but also their degradation byproducts. Unfortunately, only limited ecotoxicological data are available for these byproducts and information on the biological response to multiple MC exposures is virtually non-existent [32].

Stereochemical considerations are important in understanding the relative toxicity of related MC. For instance, the position of the nitro groups strongly influences the toxicity of nitrobenzene compounds [176]. The toxicity of dinitrobenzenes (DNBs) and TNB to several freshwater test endpoints and species, including invertebrates and fish under specific experimental conditions, ranges from 0.06 to 295 µmoles/L and 1.8 to 12.7 µmoles/L, respectively [171, 172]. In comparison under the same test condition, toxicity of DNBs is one to three orders of magnitude higher than that of NB to freshwater fish (*Poecilia reticulata*). However, the bacterium *Pseudomonas putida* is more sensitive to NB than DNB, suggesting a different mode of toxicity to this microorganism.

As with DNBs, the toxicity of DNTs is isomer dependent. For example, 2,4- and 2,6-DNT differ in toxicity to several tested organisms of freshwater and marine fish with higher sensitivity of these species to 2,6-DNT [174], whereas the marine macroalga *U. fasciata* appears to be more sensitive to 2,4-DNT [172]. Similarly, an increase in the degree of nitration in NTs (e.g., 2,4- and 2,6-DNT) and TNT results in increased toxicity in fish, invertebrates and microalgae. In addition, the TNT degradation byproducts ADNT and DANT (**Table 3-3**) are generally less toxic than the parent compound to freshwater fish *Pimephales promelas* and frog embryos although some degradation

products are more toxic than the parent 2,4-DNT in Microtox (bacterial) and S. *capricornutum* algae growth inhibition tests [167].

Table 3-3. Aquatic Toxicity of Selected Munition Compounds [171, 172, 174]

Test organism	Habitat	Biological Endpoint	Statistical Endpoint	Chemical (µmoles L^{-1})				
				RDX	HMX	NQ	NG	PETN
Fish								
Salmo gairdneri	Fresh water	Survival	96-h LC_{50}	28.8	-	>1,5740	12.3	-
		Fry growth	42-d LOEC	-	-	1,6364	-	-
Arthropods								
Daphnia magna	Fresh water	Survival	48-h LC_{50}	>76.5	-	2,5925	78.5	-
		Reproduction	7-d NOEC, LOEC	13.4, 27.1	-	2498	14.2	-
Algae								
Microcystis aeruginosa	Fresh water	Population	96-h EC_{50}	>144.1	>108.0	-	>44.0	-
		Chlorophyll a reduction	-	-	-	-	>44.0	-
Bacteria								
Vibrio fischeri	Marine	Bio-luminescence	15-min IC_{50}	>181.0	>21.7	-	-	-
			30-min EC_{50}	328.3	>84.4	>19,218	-	46.0

Toxicity data for several marine and freshwater uni- and multicellular organisms [177] exposed to picric acid suggest that it is substantially less toxic than nitrophenols with lower nitration levels. However, as reported for fish and higher invertebrates, the toxicity of nitrophenols to dinitrophenols is correlated with the number of nitro groups. Moreover, hormeosis effects (stimulation at low concentration/inhibition at higher concentrations) have been reported for mono- and dinitrophenols as well as aminophenols (APs) on photosynthesis, respiration and chlorophyll production in the microalga *C. pyrenoidosa* [171]. Cyclic nitramines, such as RDX, appear to be more acutely toxic to freshwater fish (e.g., *P. promelas*, *Salmo gairdneri*, *Lepomis macrochirus*) than HMX which is considered to be non-toxic to aquatic organisms [178].

Studies with NC report no toxicity at concentrations up to 957 µmoles/L when freshwater fish species (*P. promelas*, *L. macrochirus*, *S. gairdneri*, and *I. punctatus*), invertebrates (*D. magna*, *Gammarus fasciatus*, *Asellus militaris*, and *Chironomus tentans*), and microalgae (*M. aeruginosa*, *A. flos-aquae*, and *N. pelliculosa*) were tested [178]. Similarly, NQ toxicity studies showed no acute toxicity to freshwater fish and amphipods. However, rainbow trout exhibited chronic toxicity (LOEC for fry growth of 16,300 µmoles/L).

Sediment: Many sites associated with military operations that involve munitions manufacturing, disposal, testing, and training can contain elevated concentrations of energetic materials and related compounds in sediment. Major explosives detected in sediments at munition plants are: TNT, TNB, RDX, HMX and tetryl as well as their transformation byproducts. In some cases, these

compounds have been detected at exceedingly high concentrations ranging to 711,000 mg/kg [171]. UXO, which is a result of dumping, accidents or wartime activities, is an additional source of an explosive contaminant in marine and freshwater sediments [179]. However, despite their detected presence, knowledge on degradation rate and fate of UXO in sediments is limited as discussed in Section 2. Recent studies of fate of UXO in sediments revealed rapid transformation rates of a variety of nitroaromatic compounds [38]. For example, when TNT was spiked into freshwater or marine sediments for toxicity and bioavailability investigations, ADNTs and diaminonitrotoluenes were detected with transformation continuing during storage or toxicological exposure. The toxicity of TNT, 2-ADNT and 2,4-DANT spiked into sediments was compared using the midge *Chironomus tentans* and lethal toxicity was observed for all of these compounds at similar threshold concentrations (i.e., < 4-fold differences in lowest observed effect concentration (LOEC) values) (**Table 3-4**) [171, 180]. Moreover, the reduced transformation products appear to be less toxic to marine and fresh invertebrates than TNT.

Table 3-4. Aquatic Toxicity of Selected Munition Compounds [181, 182]

Spiked chemical	Test organism	TOC (% dry weight)	NOEC	LOEC	Duration (days)
2,6-DNT	*Ampelisca abdita*	0.10	5	ND	10
2,6-DNT	*Ampelisca abdita*	1.10	0.5	ND	10
Picric acid	*Ampelisca abdita*	0.10	73	162	10
Picric acid	*Ampelisca abdita*	1.10	BLD	BLD	10
Tetryl	*Ampelisca abdita*	0.10	0.5	2	10
Tetryl	*Ampelisca abdita*	1.10	0.1	0.3	10
RDX	*Hyalella azteca*	0.65	102	ND	10
RDX	*Chironomus tentans*	0.65	711	ND	10
HMX	*Hyalella azteca*	0.65	126	ND	10
HMX	*Chironomus tentans*	0.65	146	0.1	10
TNT	*Hyalella azteca*	0.65	<0.1	67	10
TNT	*Chironomus tentans*	0.65	4	37	10
TNB	*Hyalella azteca*	0.65	<0.1	1	10
TNB	*Chironomus tentans*	0.65	8	8	10

ND = not determined due to insufficient mortality, BDL = below detection limit.
NOEC and LOEC are reported as measured sum concentrations of parent and transformation products at experiment initiation. Effects were significant reductions in survival.

2,6-DNT spiked sandy sediments were used to investigate its transformations and toxicity while tracking loss of nitro group from the parent compound [180]. No toxicological response was reported for *Ampelisca abdita* [181] during a 10-day sediment exposure to 2,6-DNT. Since the highest spiked 2,6-DNT concentrations (25 nmol/g tissue) were fairly low in comparison to other nitroaromatic compounds, the effects of this explosive are still under investigation [181, 182]. On the other hand, picric acid treated sediment showed a significant mortality of *A. abdita* in the intermediate concentrations of picric acid which fall below its detection limit [181, 182]. This toxicity was most likely attributed to the unknown degradation products [181, 182]. Similarly, low concentrations of tetryl-spiked sediments caused significant *A. abdita* mortality, but the high concentrations (0.3 nmol/g) of tetryl did not seem to cause any lethal effects. Since tetryl was

phased out from the production process of munitions during the early 1970s, limited research efforts are being conducted to understand its toxicity and transformations.

The cyclic nitramine explosives RDX and HMX show lower solubility and sorption to organic matter compared to TNT, resulting in different fate and transport properties in aquatic systems. In spiked-sediment studies with RDX and HMX, even high concentrations failed to result in significant mortality following 10-day exposures of *L. plumulosus* and *N. arenaceodentata*. Reports of the toxicity of sediments spiked with RDX or HMX transformation products were not found in the available literature [62, 121, 173].

Toxicity data for sediments spiked with nine different explosives and their byproducts exist and provide a snapshot of information on the effects of these chemicals to three freshwater and four marine invertebrate species, including bulk (e.g., *Neanthes arenaceodentata* and *Tubifex tubifex*) and selective (e.g., *Hyalella azteca* and *Chironomus tentans*) deposit feeders. Exposure of invertebrates, such as *C. tentans*, to the MC such as RDX, HMX, TNT and TNB showed promoted growth (i.e., hormesis) and no significant lethality [32, 183]. Similar effects were observed for *H. azteca* exposed to TNB or RDX and for *N. arenaceodentata* exposed to TNT.

3.3.3 MC WILDLIFE TOXICITY

Toxicity reference values (TRVs), which are daily contaminant doses not anticipated to result in unacceptable adverse effects, are available for the three principal categories of terrestrial wildlife including mammals, birds, and reptiles. **Table 3-5** presents both the NOAEL and LOAEL, which are used to bracket the threshold value.

Toxicity to Mammals: Mammalian NOAEL and LOAEL values range from 0.2 to 15.8 mg/kg/day and from 0.3 to 78.8 mg/kg/day, respectively, and, based on the information in Table ECO-3, TNT, 2,4-DNT, and 2,6-DNT appear to be the most toxic and HMX and NTO the least toxic of the target analytes. The TRVs are based on lethality, nervous system, growth and reproductive system endpoint effects.

Toxicity to Birds: Comparable with the mammal TRVs, NOAEL and LOAEL values range from 0.01 to 13 and from 1.3 to 26 respectively. Also, consistent with the mammal TRVs, TNT and 2,4-DNT appear to be the most toxic MC analytes to birds. The avian TRV endpoints include reproductive, growth, immunological system effects, and kidney weight gain (an indication of early onset disease). In addition, DNAN has been documented to cause reversible cataracts and mortality in Japanese quail. No avian TRVs for HMX, 2,6-DNT, and NTO were identified.

Toxicity to Reptiles: NOAEL and LOAEL values for reptiles range from 0.72 to 10.4 and from 3.6 to 51.9 respectively, with RDX the most toxic of the three MC analytes with reptile TRV values. The reptile TRVs are all based on lethality and it is likely that TRVs would be lower if laboratory results for non-lethality endpoints were available. No reptile TRVs were identified for perchlorate, HMX, 2,6-DNT, NTO, and DNAN.

Table 3-5. Wildlife Toxicity Reference Values

Chemical	Test Organism	Duration	Effect	TRV (mg/kg/day)*		Reference
				NOAEL	LOAEL	
Mammals						
Perchlorate	Rabbit	3 months	Nervous system effects	6.4	32	[184]
TNT	Dog	6 months	Decreased weight gain	0.2	0.3	[185]
RDX	Rat	2 years	Decreased growth rates	1.19	2.73	[186]
HMX	Rabbit	Single acute exposure	Lethality	1.0	5.0	[187]
HMX†	Mouse	13 weeks	Lethality	9.0	62.5	[187]
2,4-DNT	Dog	2 years	Loss of hindquarter control, convulsions	0.67	1.4	[188]
2,6-DNT	Rat	1 year	Decrease in body weight	0.7	7.0	[188]
NTO	Rat	90 days	Degeneration and atrophy of the seminiferous tubules	15.8**	78.8**	[189]
DNAN	Rat	90 days	Lethality, reduced body mass in males	4.0***	20***	[190]
Bird						
Perchlorate	Northern Bobwhite	8 weeks	Decreased tibia length	13	26	[184]
TNT	Northern Bobwhite	90 days	Hematological and immune responses	0.07	1.8	[185]
RDX	Northern Bobwhite	14 days, at sensitive life stage	Decreased egg production	3.65	8.14	[186]
HMX	ND	ND	ND	ND	ND	ND
2,4-DNT	Northern Bobwhite	60 days	Increased relative kidney weight	0.01	1.3	[188]
2,6-DNT	ND	ND	ND	ND	ND	ND
NTO	ND	ND	ND	ND	ND	ND
DNAN	Japanese quail	Single acute exposure	Reversible cataracts and lethality	2.4††	12††	[191]

Table 3-5. Wildlife Toxicity Reference Values (Continued)

Chemical	Test Organism	Duration	Effect	TRV (mg/kg/day)*		Reference
				NOAEL	LOAEL	
Reptiles						
Perchlorate	ND	ND	ND	ND	ND	ND
TNT	Western Fence Lizard	Not reported	Lethality	10.4‡	51.9‡	[192]
RDX	Western Fence Lizard	Not reported	Lethality	0.72ǁ	3.6ǁ	[192]
HMX				NA	NA	
2,4-DNT	Western Fence Lizard	Not reported	Lethality	3.8¶	19¶	[192]
2,6-DNT	ND	ND	ND	ND	ND	ND
NTO	ND	ND	ND	ND	ND	ND
DNAN	ND	ND	ND	ND	ND	ND

ND- not determined

* The bird TRV for DNAN and reptile TRVs for TNT, RDX, and 2,4-DNT are based on acute studies (generally a single oral dose) and the associated units are mg/kg rather than daily doses of mg/kg/day.

** TRVs based on a subchronic LOAEL (315 mg.kg/day); an uncertainty factor of 20 applied to estimate NOAEL, and an unceratinty factor of 4 applied to estimate LOAEL

*** TRVs based on a subchronic LOAEL (80 mg.kg/day); an uncertainty factor of 20 applied to estimate NOAEL, and an unceratinty factor of 4 applied to estimate LOAEL

† In addition to the general mammal TRVs presented (1 and 5 mg/kg/day), TRVs (9 and 62.5 mg/kg/day) are also provided more specifically for mammalian ominvores, since toxicity testing with rodents has been well documented.

†† Based on the effects reported at the lowest reported concentration (120 mg/kg) inducing effects; for this acute LOAEL, an uncertainty factor of 50 applied to estimate NOAEL, and an uncertainty factor of 10 applied to estimate LOAEL

‡ Uncertainty factor of 100 applied to the LD_{50} (1,038 mg/kg) to estimate NOAEL and an uncertainty factor of 20 applied to the LD_{50} to estimate LOAEL

ǁ Uncertainty factor of 100 applied to the LD_{50} (72 mg/kg) to estimate NOAEL, and an uncertainty factor of 20 applied to the LD_{50} to estimate LOAEL

¶ Uncertainty factor of 100 applied to the LD_{50} (380 mg/kg) to estimate NOAEL, and an uncertainty factor of 20 applied to the LD_{50} to estimate LOAEL

3.4 BIOACCUMULATION OF MUNITIONS CONSTITUENTS

3.4.1 IN AQUATIC MICROORGANISMS

The presence of explosives and their transformation products in aquatic systems is not well studied and many gaps exist regarding their toxicity. Bioaccumulation and biotransformation potential of these compounds is also not well known, however due to their weakly hydrophobic properties, bioaccumulation of MC is expected to be low. Several studies show that the bioconcentration of explosive compounds is low in a variety of tested aquatic animals and their fish dietary uptake was also low.

Direct uptake from water is expected to be the primary route of exposure of explosives in higher trophic level animals, as dietary uptake of TNT and RDX was substantially less than aqueous uptake. For example, uptake of TNT by fish and invertebrate results in significant bioaccumulation of nonidentified nonextractable and extractable compounds. In contrast, metabolically formed transformation products of TNT appear to be eliminated at much slower rates. Neither the biological half-life nor the chemical nature of nonextractable transformation products of TNT in organisms has been investigated to date. Investigations on the biotransformation of explosives other than TNT in aquatic animals were not found in the available literature and are therefore warranted. Further studies of the fate of explosives in aquatic animals are necessary to reveal the identity of their transformation products present in the tissues of exposed organisms, to further characterize species-specific differences in the bioconcentration of transformation products, and to elucidate the mechanism of toxic action. Information on aquatic toxicity is required to assess hazard and risk of a particular chemical substance to marine and freshwater organisms that live in the water column [193, 194].

3.4.2 TERRESTRIAL BIOACCUMULATION

Bioaccumulation factors (BAFs) for terrestrial settings are presented in **Table 3-6** for the transfer of MCs in soil to lower trophic levels (i.e., plant and earthworm). BAFs generally represent the ratio of MC concentration in tissue (on a dry weight basis) to the MC concentration in soil (on a dry weight basis) and are used in risk assessment exposure modeling. Biomagnification is a term that applied to uptake factors that exceed 1. BAFs were summarized for both terrestrial plants and soil invertebrates (i.e., earthworm).

BAFs for Terrestrial Plants: Plant BAFs were established for both above- and below-ground plant compartments. Based on available information summarized in **Table 3-6**, most plant BAFs exceed 1 (i.e., they biomagnify in terrestrial plant tissue) [103, 165]. Uptake factors for the nitramine MC analytes are the largest with BAFs for RDX and HMX ranging to 27.1 and 77.4 in above-ground parts, respectively. BAFs for perchlorate and nitroaromatic MCs are lower but most values are also greater than 1 although available information suggests that transfer to roots is lower than to above-ground parts. No BAFs for IM target analytes were identified.

BAFs for Terrestrial Invertebrates: In general, available information suggests that MC uptake by earthworms is lower than in terrestrial plants (**Table 3-6**). There is some evidence of biomagnification between the soil – invertebrate compartment with BAFs for perchlorate, RDX,

and DNAN ranging from 2.26 to 12; however, BAFs for nitroaromatic analytes, HMX, and NTO are all less than 1 [169].

Table 3-6. Terrestrial Bioaccumulation Factors

Chemical	BAF soil-to-plant (g soil/g tissue)			BAF soil-to-earthworm (g soil/g tissue)	Reference
	Foliage or Shoot	Root	Reference		
Perchlorate	19.5	NA	[169]	2.26	[169]
TNT	5.87 [b]	0.75[a] 10.6[b]	[a][165] [b][169]	0.0649	[169]
RDX	77.4[a] 40.9[b]	6.4[a] 5.26[b]	[a][165] [b][169]	7.35[a] 4.32[b]	[a] [165] [b] [169]
HMX	27.1[a] 19.6[b]	2.0[a] 0.226[b]	[a] [165] [b] [169]	0.469	[169]
2,4-DNT	7.6	7.3	[165]	Similar to TNT, substantial accumulation did not occur in earthworm relative to soil concentrations	[165]
2,6-DNT	4.21	NA	[169]	NA	NA
NTO	NA	NA	NA	0.2	[103]
DNAN	NA	NA	NA	12	[103]

NA – not available

[a] The Sunahara (2012)[165] BAFs (generally selected as the highest non-labelled BAFs available); the soil-to-invertebrate BAF is the ratio of the tissue uptake rate constant to the tissue elimination rate constant.

[b] BAFs from Tsao and Sample (2005)[169] were based on pooled monocot and dicot data.

3.5 CRITERIA AND SCREENING BENCHMARKS

Although a variety of toxicity data are available for numerous explosives and related compounds, only a few of these chemicals have been used and become abundant in some terrestrial and aquatic systems. Therefore, screening ecological benchmarks are used to identify chemical concentrations in environmental media that are at or below thresholds for effects to ecological receptors. **Table 3-7** and data collected in Appendix C summarize some available aqueous toxicological data for MC including information for the IM compounds DNAN and NTO. Researchers have proposed interim water quality criteria (based on the Final Acute Values and Final Chronic Values, respectively[3]) for TNT. In the case of other MC, with more limited data, the lowest available acute and chronic values are presented in **Table 3-7**.

[3] The derivation of water quality criteria requires a minimum of eight acceptable acute toxicity data for a range of taxonomic groups, at least three chronic test results for fish and invertebrates and results for at least one plant species (Stephen, C.E., D.I. Mount, D.J. Hansen, J.R. Gentile, G.A. Chapman and W.A. Brungs, 1985. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses; USEPA, Office of Research and Development, PB85-227049).

Available acute and chronic values range over three to four orders of magnitude with adverse effects for most compounds observed at molar threshold concentrations in the range of 0.1 to 10 µmoles L^{-1}. Aquatic organisms appear to be particularly sensitive to TNT (and tetryl) whereas the limited available data suggest that the IM compounds exhibit limited or no aquatic toxicity (**Table 3-7**).

Table 3-7. Water Quality Criteria for the Protection of Aquatic Life (Modified from [171])

Chemical	Acute Value (µmoles L^{-1})	Chronic Value (µmoles L^{-1})	Habitat	Reference
2,4,6-TNT	4.99	0.176	Freshwater	[176]
2,4,6-TNT	0.376	0.125	Marine	[172]
2,4,6-TNT	0.616	0.269	Combined	[195]
1,3,5-TNB	0.282	0.052	Freshwater	[176]
1,3-DNB	1.28	0.101	Freshwater	[176]
3,5-DNA	2.51	0.322	Freshwater	[176]
2-A-4,6-DNT	1.78	0.096	Freshwater	[176]
HMX	12.66	1.11	Freshwater	[176]
HMX	2.53	-	Freshwater	[196]
RDX	6.26	0.837	Freshwater	[176]
RDX	1.58	0	Freshwater	[194]
NG	1.8	0.03	Freshwater	[197]
DNAN	186.7	30.3	Freshwater	[198]
NTO	17,149	398	Freshwater	[198]

Table 3-8 summarizes estimated sediment benchmarks for various MC using an equilibrium partitioning approach[4], which relates the sediment concentration to the equivalent interstitial water concentration [199, 200] (i.e., the benthic organism effect level estimated using available chronic water quality criteria values). The sediment benchmarks provided in **Table 3-8** assume an organic-carbon content of 1% and are expressed as molar concentrations.

[4] Sediment organic carbon is assumed to be an important factor in determining the interstitial water exposure concentration at equilibrium and the sediment benchmark is thus typically expressed on an organic carbon-normalized basis. Low and high sediment benchmarks were developed based on a range of available partitioning values (K_{oc}).

Table 3-8. Sediment Quality Benchmarks for the Protection of Benthic Invertebrates

Chemical	Selected Toxicity Value (µg L^{-1})	K_{oc} (L kg^{-1})		Sediment Quality Benchmarks (SQB) (µmoles kg^{-1} dw)	
		Low	High	Low	High
2,4,6-TNT	28.4	37.4	451	11	128
2-ADNT	19	65.9	81	13	15
4-ADNT	30	116	-	35	-
2,4-DANT	19	4.9	-	0.93	-
2,6-DANT	19	4.9	-	0.93	-
2,4-DNT	2,400	88.4	300	2,122	7,200
2,6-DNT	1,800	116	150	2,088	2,700
Picric acid	9,200	37.4	-	3,441	-
Tetryl	15	41.9	406	6.3	61
HMX	330	1.15	130	3.8	429
RDX	186	6.26	42	12	78
NG	186	39.2	180	1,266	5,814
NQ	260,000	0.13	25	338	65,000
PETN	850,000	38.3	179	325,550	1,521,000

As indicated previously, **Table 3-8** illustrates the higher aquatic toxicity (and corresponding lower sediment benchmarks) of some TNT transformation products (i.e., 2,4- and 2,6-DANT). The lower estimated sediment benchmarks for TNT, tetryl, HMX and RDX are in the range of 1 to 10 µmoles kg^{-1} dry weight (dw), whereas comparable values for dinitrotoluenes, picric acid and PETN exceed 1,000 µmoles kg^{-1} dw.

3.6 EXAMPLE REGULATORY GUIDANCE FOR MC

Interactions between environmental contaminants and ecological receptors are crucial for risk assessment, development of management objectives that aid environment protection, and to maintain the health status of human and environmental receptors. Despite a variety of strategies proposed to contain or minimize the environmental release of MC, human and environmental receptors continue to be exposed to these potentially hazardous contaminants. Compared to the vast acreage of Navy bombing ranges, any kind of substantive impact is limited to a micro-fraction of the total acreage. Therefore, determination of effects of these chemical residues and their byproducts in water and soil continues to be a need for environmental and wildlife toxicologists.

With the development of an understanding of the basic chemical properties and toxicological information on a chemical, the next steps require: 1) evaluation of potential effects of the primary degradation products of the parent chemical, and 2) evaluation of other subtle endpoint effects of the chemical [9]. Since these areas of contamination often include wildlife habitat, risk incurred from exposure needs to be evaluated. This is particularly important in a risk management context when balancing the potential for adverse effects from exposure against habitat alterations associated with cleanup operations.

During site investigations, screening criteria, such as U.S. EPA risk-based concentrations (RBCs) and Range and Munitions Use Subcommittee screening values are used to determine what environmental contaminants require additional investigation and possibly a full risk assessment [201]. The RBCs can serve as screening levels or soil cleanup levels for achieving site closure. For example, the RBC for the explosive RDX is 0.61 parts per billion (ppb) or less [201] as listed in Appendix C.

When moving into the remediation phase of a range cleanup, formal remedial action objectives must be selected. These target cleanup concentrations are based on health risks, but they also consider other factors such as technical limitations for detecting the chemical and the economic impacts of remediating to a specific level. The remedial objectives selected can have several sources, including a national standard, such as the maximum contaminant level (MCL) or a standard promulgated by the state where the site is located [9]. For instance, at Camp Edwards, the cleanup goal for RDX is 2.0 ppb, which is the lifetime drinking water health advisory published by the U.S. EPA [202]. For compounds that only recently became visible as an environmental problem, selection of appropriate cleanup goals can be a contentious issue. For compounds, such as emerging contaminants and IM, for which cleanup goals do not exist, some agreement must be reached by the parties involved in the cleanup.

Emerging contaminants demonstrate low acute toxicity but cause significant reproductive effects at very low levels of exposure. In addition, the effects of exposure to aquatic organisms during the early stages of life may not be observed until adulthood. Therefore, traditional toxicity test endpoints may not be sufficiently comprehensive for criteria derivation for these chemicals and the chemicals may also have specific modes of action that may affect only certain types of aquatic animals (e.g., vertebrates such as fish). Therefore, U.S. EPA developed a White Paper Aquatic Life Criteria for Contaminants of Emerging Concern: Part I Challenges and Recommendations [203] detailing the technical issues and recommendations to serve as a basis for modifying existing guidelines. These modifications should enable the Agency to better address emerging contaminants and develop ambient water quality criteria when appropriate for protection of aquatic life that makes the best use of available science.

Some states set similar fixed concentrations as cleanup goals for soil, but especially at large and complex sites, soil cleanup goals are based upon site-specific data and the risk assessments conducted using such data [9]. After determining the anticipated land use and associated exposure scenarios, risk assessors calculate the upper bound of the risk combined with the Reasonable Maximum Exposure (RME) in cancer, other diseases, and/or ecological impacts.

4.0 GAP ANALYSIS

4.1 OVERVIEW

During the last decade, SERDP, Environmental Security Technology Certification Program (ESTCP), NESDI and Environmental Quality Technology Program have funded a significant body of basic and applied research to gain a better understanding of the releases of MC resulting from military training activities on ranges and to develop better sampling methodologies applicable for ranges, as well as technologies to treat or contain MC in soil and groundwater. The results from these efforts are contained in numerous technical reports and papers but have not been integrated into standard or traditional environmental practice. In addition, no standards of practice are universally accepted by the regulatory community for conducting range assessments or instituting potential management strategies.

There is no quantitative measure by which to assess available technologies in relation to user need, or specific requirement. The requirement must be screened against the cost, which includes maintaining regulatory compliance, protection of human health and the environment, and impact to mission readiness. However, a simple assessment may be performed, which looks at the ongoing research and development efforts within DoD in each major category of interest in order to make a determination as to the applicability of the proposed outcome in relation to Navy requirements. Gaps can then be derived to initiate discussion on prioritization of issues with the goal of determining an overall RD&T strategy.

In 2007, SERDP and ESTCP hosted a Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches which provided a summary of the state of science on MC as well as identified a variety of needs that would be addressed through research and technology development projects. Several critical needs that were identified are listed in **Table 4-1.**

Extensive literature search, analysis of SERDP and ESTCP report on Research & Demonstration Needs for Management of Munitions Constituents [204] provide the basis to determine and categorize research needs for MC in this IDR. These needs are grouped into five categories:

1. Sampling and analytical techniques,
2. Fate and transport of MC,
3. Toxicity to environmental receptors, and
4. Treatment options.

Table 4-1. Selected Critical and High Priority Research and Development Needs for MC

Need Category	Critical Priority	High Priority
Characterization	Development of Improved Fate and Transport Parameter Values for MCs	Development of LC-MS/MS Based Analytical Methods for Munition Constituents
	N/A	Development of MC Performance Standards for Quality Assurance/Quality Control at Analytical Laboratories
	N/A	Improved Understanding of and Sampling Methods to Determine Mechanisms Controlling MC Concentrations in Surface Water
Risk, Modeling and Assessment	Improved Understanding of the Role of Valence State in Fate, Transport and Toxicity of Heavy Metals Associated with MC	Development of Fate and Transport Parameters for MC in Varying Soil Types
	Development of Analytical Detection Methods for MCs Using LC-MS/MS	Development of Terrestrial Toxicity-Based Screening Benchmarks
	Development of Toxicity Data for MC and Their Byproducts	Develop Aquatic Toxicity Data Sets for MC to Support Development of Water Quality Criteria
	Improved Understanding of Fate and Transport Properties of MC as Military Grade Mixtures	Evaluation of Potential Releases of MC from Firing Points Located Near Installation Boundaries
	N/A	Compilation of Data on MC Currently Not Included in MIDAS

4.2 SAMPLING AND ANALYTICAL TECHNIQUES

Despite the new research and advancements in the area of IMs, no specific sampling and/or analytical approaches for their detection exist to date. Critical gaps that have been identified need to be addressed in order to protect human and ecological life from adverse effects of MC. The most emerging needs within this area include:

- Development of standardized analytical and extraction methods for IMs and their byproducts.
- Development and integration of multi-incremental sampling on ranges with heterogeneously distributed MC.
- Development of sample extraction and liquid chromatography mass spectrometry (LC-MS/MS) based analytical methods as well as quality assurance/quality control for MC and metabolites in environmental matrices.
- Validation of standard operating procedures for incremental sampling in sediments.

4.3 FATE AND TRANSPORT OF MC

Manufacturing, combat and training events may result in the release of MC into the environment, which in turn causes significant cost to the DoD as well as an ecological threat. Improved knowledge on the fate and transport of these compounds as well as their byproducts can minimize natural resource damage as well as cleanup costs. Thus, fate and transport of legacy compounds and new generation of IMs is an important research area awaiting development.

The most critical and high priority needs for this area of research are listed below:

- Development of evaluation methods for prediction of fate and transport of IMs and their byproducts.
- Development of rate of release of NG, 2,4-DNT and NQ from propellant residues.
- Development of an understanding on fate and transport of MC in the vadose zone with focus on: (1) interactions between the MC and the soil surface, (2) preferential flow paths burrowed out in soil by growing roots, and (3) interactions between the MC and the root surface.
- Measurements of fate and transport properties of legacy and IM compounds including: ionization constants, rate constants for hydrolysis, oxidation, photooxidation, biotic and abiotic reduction, water solubility, Henry's law constant and octanol-water partition coefficients.
- Development of improved fate and transport models to predict exposure and risk of MC in field scenarios.
- Vertical migration of metals, particularly lead on ranges.
- Improved field screening tools for measuring MCs at low detection levels to perform risk assessment.

4.4 TOXICITY TO ENVIRONMENTAL RECEPTORS

The state of science and limitations are usually identified in four correlated areas: hazard identification, toxicity assessment, exposure assessment, and risk characterization. Research needs and specific gaps for MC are listed below.

Hazard Identification. The objective of hazard identification is the determination of a relationship between an environmental contaminant and a demonstrated injury to human health and/or the environment. The definition of injury may be cancer, birth defects or neurological effects in case of human health. Several MC commonly associated with military munitions such as HMX, RDX, DNT and heavy metals are listed as environmental concerns. Gaps related to hazard identification of these compounds are as follows:

- Improvements in tools to gather and organize the abovementioned data on MC chemical releases (e.g., loading rate, exposure types, health effects, fate).
- Generation of data on chemical releases on ranges available to risk assessors and modelers for use in all parts of the risk assessment process.

- Development and verification of fate and transport predictive models for surface water and soil pathways.
- More work is needed on defining a reasonable methodology for establishing and defending realistic, site specific exposure scenarios for both human health and ecological risk assessment.
- Development of a data system that uses a geographic information system to identify and verify where munitions have been disposed in the impact area.
- Improvement in understanding of the role of the valence state in the fate, transport and toxicity of heavy metals associated with MC.

Toxicity Assessment. The assessment of toxicity of a specific compound aids in establishing the quantitative relationship between exposure (or dose) and response to a specific contaminant that caused an adverse health or environmental effect. Although many studies have addressed toxicity of MC to the ecological receptors, a variety of data gaps in toxicity assessment remain to be addressed:

- Development of a structured process to evaluate quality of existing toxicity data.
- Development of an online human health and ecological toxicity database including data quality descriptors and information on benchmark derivation.
- Validation of existing dissolution models for metals.
- Generate toxicological, chemical and physical property data of MC byproducts with specific focus on understanding mobility, toxicity and bioavailability of the MC byproducts relative to the parent compounds.
- Development of terrestrial toxicity-based (chronic and acute) screening benchmarks.
- Generate a complete human health toxicity dataset for the MC of concern. Both chronic and acute human health toxicity for selected MC and their byproducts are needed to aid development of toxicity benchmarks.
- Development of aquatic toxicity data sets for MC to support development of water quality criteria.
- Development of methods to select representative species as indicators of ecological risk at operational ranges.
- Development of toxicity data for MC and their byproducts.

Exposure Assessment. The assessment determines the actual level of exposure and absorption of a toxicant among the population of exposed individuals. Questions that are answered within the exposure assessment pertain to the sources of pollutant (e.g., target areas, firing points, leaking duds etc.), its concentration at the source, its transformation pathways and actual intakes by impacted receptors.

The main gaps in exposure assessment of MC are listed below:

- Generation of basic fate and transport parameters such as vapor pressure, Henry's Law constants and solubility for NG and amines of DNT.
- Determination of dissolution rates, on-site concentrations leading to off-site exposure, spatial distribution of the MC and understanding of pathways to the receptors of legacy and IM compounds.

4.5 TREATMENT OPTIONS

Research and development gaps were identified for treatment options of different media contaminated with MC. Specific knowledge gaps and research needs are listed below:

Wastewater from Manufacturing. Manufacturing facilities are currently utilizing sequential anaerobic/aerobic biological treatment to remove MC and inorganic nitrates with a traditional wastewater treatment plant process. While this process has been effective for treatment of manufacturing wastewaters containing legacy MC such as TNT, RDX, HMX, DNT or NC, no effective strategies exist for removal of new generations of IMs such as NTO or DNAN. The chemical characteristics of the new IMs render conventional removal technologies ineffective due to the high solubility of newer constituents.

Despite development of several new treatment options, none of them was cost effective and robust enough. None of these technologies addressed the issue of treatment of mixed wastes of legacy and IM constituents, thus the development of new technologies remains a significant gap. SERDP and ESTCP determined several specific research needs that included:

- Development of a better understanding of treatment of specific MC and mixtures of MC,
- Determine the impacts of IM waste on treatment of legacy MC wastewaters,
- Develop treatment technologies that treat both legacy and MC compounds,
- Determine if treatment train approaches can be used to treat mixed MC waste.

Contaminated Soils. Research performed to date has advanced the understanding on MC-soil interactions. However, several research needs remain unanswered:

- Determine basis for persistence of RDX in soil,
- Develop applicability of current technologies for treating mixed MC and IMs,
- Develop techniques to maximize sorption/biodegradation at the soil surface and/or minimize transport of more soluble IMs,
- Develop new delivery systems for treatment amendments to range soils,
- Develop standard sampling and analysis protocol for IMs in soil.

Contaminated Groundwater. Due to the possibility of dissolution and contamination of groundwater with MC, an understanding of basic fate and transport phenomena needs to be greatly expanded. Overall research needs for MC in groundwater are as follows:

- Determine fate and transport of legacy and IM compounds in groundwater, including sorption, biotransformation and biodegradation,
- Evaluate currently existing technologies for treatment of legacy and IM compounds in groundwater,
- Develop standard sampling, preservation and analysis protocols for IMs in groundwater.

4.6 SUMMARY AND RECOMMENDATIONS

Initial DoD efforts focused on policy implementation and legislative changes, however, there are numerous ongoing and planned research and development efforts focused on broader range of questions ranging from development of new analytical methods for MC detection and sampling to environmental transport and treatment of exploded ordnance. SERDP/ESTCP and Army-specific programs fund majority of this work while Navy funding has been mostly focused on marine mammal issues, underwater munitions, underwater corrosion and munitions transport.

New technologies currently under development may fulfill Navy objectives from technological, management and implementation perspective but it is unknown how soon these technologies can be readily applied to Navy ranges, or if they will require modifications. Additional limitation is regulatory and public acceptance of innovative programs. Before any investment strategy is put in place, discussions must be conducted to analyze a broad array of needs identified in this IDR. Extensive coordination with other services on current and planned efforts should be an immediate goal to gain maximum leveraging of existing funds, share expertise, avoid duplication of efforts and to identify program areas that are applicable for DoD-wide implementation and are uniquely suited to Navy needs.

Below are six recommended new starts for consideration chosen based on the gap analysis process performed during development of this report.

Apply improved models to predict the chemical properties and fate of new materials in surface soils. Several models exist and can be used to predict fate- determining properties of legacy MCs and IHE. However, most of these models are not suited for prediction of explosive compound behavior in formulations. New efforts, including demonstration with the use of range soils contaminated with MCs, should be proposed to assess actual performance of existing tools. The various models should be validated in terms of application range, precision and transparency for IHE and related MC.

Validate improved methods of amendment delivery to range soils. Impact areas are difficult to treat given the repeated detonations that can cause transport and displacement of amendments out of the treatment area. New techniques that deliver amendments in an effective manner to much larger and often remote areas are needed to be implemented.

Demonstrate and validate treatment technologies for treatment of IHE and legacy MC in mixtures with ionic energetic materials, aluminized formulations, binders/additives, plasticizers and processing agents. Some of the newer generation IHE dissolve quickly and are very soluble in water. These compounds pose greater risk to groundwater than most legacy MC. Surface treatments or amendments that can effectively sequester or retain the IHE compound and promote its degradation are needed. Moreover, demonstration of effective treatment of explosive compounds with degradation of binders, plasticizers and processing agents present in explosive formulations is of an increased interest to the regulators.

Characterize OB emissions at ranges. The characterization of OB emissions should be performed using existing models and should measure organics, inorganics (e.g., Pb, Cr) and particulates for both IHE and legacy MC. These measurements can be used to develop emission factors that will allow DoD facilities to dispose of munitions in compliance with environmental regulations.

Demonstrate improved alternative methods to blow in place on land. Detonation of expended munitions and unexploded ordnances through blow in place will remain a needed operation. With higher insensitivity of new IHE materials reaching higher order detonations using standard blow in place procedures proves to be challenging. An ability to identify type of the munition handled beforehand and safe alternative detonation and removal procedures are needed to prevent further release of MCs, offsite migration and to increase safety of the procedure.

Application of new recycling and recovery methods for metals present on ranges. Recycling and recovery of metals released and deposited on ranges through detonation of MCs could be valuable to the Navy. Metal recovery could prevent human and ecological health risks, and costs associated with leaving metals on site, or with ex situ treatments and disposal of metal-contaminated soil off-site. Range design modification allowing for easier recovery of metals could be tested under this need.

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APPENDIX A

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1. PERCHLORATE

1.1 INTRODUCTION

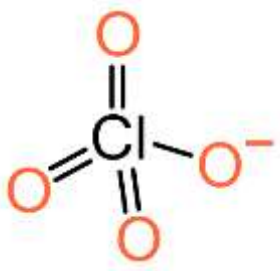

Figure 1-1. Chemical Structure of the Perchlorate Ion

Names: Perchlorate
Abbreviations and Other Names: N/A
CAS No.: 14797-73-0
Chemical Formula: ClO_4^-
Occurrence in Mixtures/Compositions: Ammonium perchlorate, sodium perchlorate, potassium perchlorate
Natural Occurrence: Naturally-occurring perchlorate at its most abundant can be found commingled with deposits of sodium nitrate in the Atacama Desert of northern Chile.
Physical/Chemical Properties: The physical/chemical properties of perchlorate salts are provided in Table 1-1.

Table 1-1. Physical and Chemical Properties of Potassium Perchlorate and Ammonium Perchlorate [1-3]

Property	Ammonium Perchlorate	Potassium Perchlorate	Units
Color	White	White	None
Odor	None	None	None
Physical state	Orthorhombic crystal	Orthorhombic crystal or crystalline powder	None
Melting temperature	> 200	400 – 525	°C
Vapor pressure (@ 20°C)	Nil	Nil	atm
Specific gravity	1.95	2.53	g/cc
Water solubility (@ 20°C)	200	16.8	g/L
Octanol-water partition coefficient (Log K_{OW})	-5.84	-7.18	None

1.2 FATE

Perchlorate salts have historically been used in military applications in gun propellants, pyrotechnics, smoke recipes, or as additives in explosive detonators [1, 2, 4-8].These formulations are typically comprised of ammonium perchlorate or potassium perchlorate as the perchlorate-containing oxidizer components. The health concerns over perchlorate and perchlorate contamination at military test/training ranges and manufacturing sites have been significant enough to warrant Department of Defense (DoD)-funded research and development of new, perchlorate-free classes of propellants and pyrotechnics, along with investment in perchlorate remediation studies [1, 9, 10]. Efforts have been underway to remediate the existing perchlorate contamination in the environment as well as to reduce or eliminate use of this chemical in future energetic formulations.

The environmental fate of perchlorates has been a concern for years as a result of its high mobility and tendency to accumulate in the environment, as well as its known detrimental health effects, particularly regarding disruption of iodide uptake in the thyroid gland [11]. Perchlorate is chemically stable under environmental conditions and possesses a high degree of solubility in water [12]. Thus, water will dissolve, transport, and subsequently disperse perchlorate across a much wider area, although in a much more diluted form. The frequency of perchlorate contamination must be taken into account to assess if the diluted perchlorate levels remain low or begin to increase with increased frequency of contamination.

1.2.1 Relevant Properties

Perchlorate is the oxidizer of choice in several military energetic formulations, including propellants, pyrotechnics, delays, flares, and smoke-generating chemicals. Its high oxidation level (+7) and ease of decomposition render it as a strong candidate for oxidizing components in fuel-oxidizer propellants or as the sole gas-generating component in energetic propulsion applications. Subsequently, these desirable properties have resulted in perchlorate (typically used in the form of ammonium perchlorate and potassium perchlorate in military ordnance) applications in a broad range of energetic formulations. Latest reports [6] show that perchlorate is utilized in 259 different types of ordnances. Moreover, perchlorate use in military training ranges is both widespread and continuous which results in a potentially high risk of perchlorate contamination.

The chemical structure of perchlorate anion is provided in Figure 1-1 while Table1-1 lists some physical and chemical properties of perchlorate formulations of interest (potassium perchlorate and ammonium perchlorate), including, but not limited to, density, water solubility, and octanol-water partition coefficient. The values listed for these properties help to determine the expected transport and fate of perchlorate in the environment. Unlike many of the military explosives, which are organic compounds, perchlorate salts are inorganic, which affects fate and transport in aqueous matrices.

1.2.2 Photolysis

A minimal amount of data is available on the photolytic degradation of perchlorate. However, photolysis plays a role in some of the reactions involved in the natural production of chlorine in the environment [12].

1.2.3 Other Abiotic Reactions

Abiotic reduction of perchlorate can occur with a negligible rate, especially when compared to the much faster rates of its biological degradation under strict anaerobic and facultative anaerobic conditions [12]. When assessing abiotic reduction of perchlorate [12], including perchlorate transport, dilution, dispersion, and adsorption, the chemical reduction of perchlorate in the subsurface does not occur as a result of the significant amount of energy required to overcome the kinetic barrier and chemically reduce the chlorine atom from its +7 oxidation state. Such levels of energy would not be realized in the environment.

The main perchlorate abiotic attenuation pathway is physical and involves dilution [4]. Dilution helps to alleviate local contamination levels in an environmental matrix. Potassium perchlorate has a solubility product constant (K_{sp}) of 1.05×10^{-2}. Although perchlorate can undergo dissolution

and precipitation, the precipitation reaction is unlikely to occur [9-11]. Water-related environmental conditions (e.g., average rainfall) can influence the propensity for perchlorate dilution versus precipitation.

1.2.4 Biodegradation

Complete biodegradation of perchlorate has been shown to occur with several soil microorganisms and enzymes including perchlorate reductase and chlorite dismutase [1, 10-12]. The rate of perchlorate biodegradation depends on the microbial organism, population of microorganisms and environmental conditions in which the degradation reactions occur. For example, perchlorate degradation by anaerobic culture of *Dechloromonas* species KJ took up to 70 days for complete removal when applied in a packed bed reactor [13], but when single culture of the anaerobic enrichment culture was used, perchlorate was degraded in 2 days[11-14].

Biodegradation reactions reduce the perchlorate anion to chloride via reactions listed in Figure 1-2 [13, 15]. Perchlorate ion is reduced to chlorate (ClO_3^-) by perchlorate reductase and chlorate ion is generated. Next, chlorate is reduced to chlorite (ClO_2^-) in reactions catalyzed by chlorate reductase and followed by dismutation reaction of chlorate to chlorite catalyzed by conserved enzyme chlorite dismutase in which chlorine and oxygen are generated. The dismutation of chlorite to chlorine and oxygen is known to be common to all perchlorate-reducing bacteria[13-15]. The rate limiting step is believed to be perchlorate reduction to chlorate. The last step, a non-energy yielding disproportionation of chlorite to oxygen and chloride, is at least 1000 times faster than the perchlorate and chlorate reduction steps [1, 16]. These processes typically occur under strict anaerobic or/and facultative anaerobic conditions in the presence of a carbon source (lactate or acetate), and with a population of perchlorate-degrading microorganism present [17]. Although oxygen is produced during anaerobic reduction, it is only present in small quantities (based on the amount of chlorite reduced) and is quickly reduced to water. Biodegradation is a critical part of the environmental fate of perchlorate, as abiotic degradation is insignificant and perchlorate does not tend to sorb to soils.

Bacteria capable of reducing perchlorate to chloride and oxygen are found throughout the environment and are phylogenetically diverse with members in the alpha, beta, gamma, and epsilon subclasses of the *Proteobacteria* phylum [15-17]. Such bacteria are completely oxidizing, Gram negative, non-fermenting facultative anaerobes found in hydrocarbon-contaminated, pristine soils, aquatic sediments, and farm animal waste lagoons; mostly utilizing nitrate as an electron acceptor [16-18].

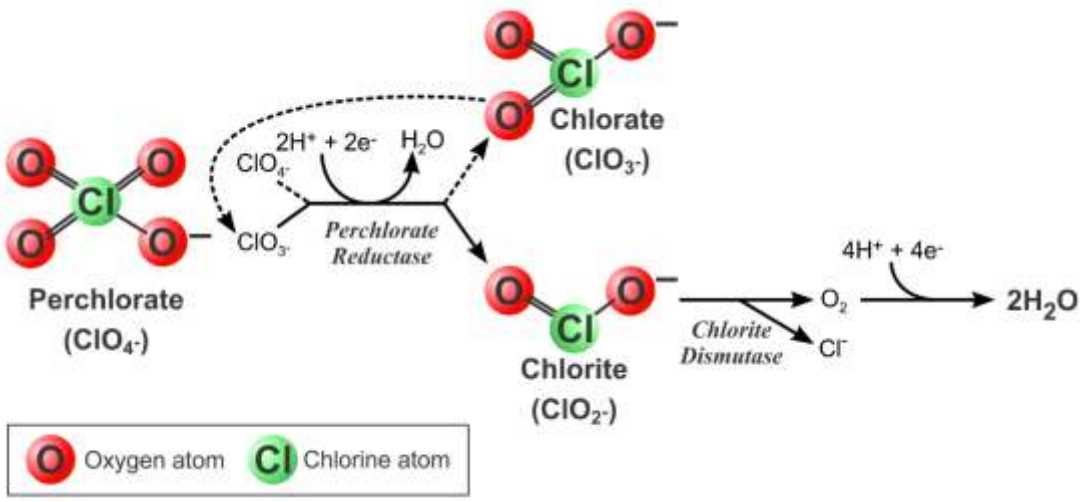

Figure 1-2. Perchlorate Biodegradation Pathway [13, 15]

1.2.5 Hydrolysis

Hydrolysis of perchlorate is not expected to occur, as the perchlorate-containing compounds (e.g., ammonium perchlorate or potassium perchlorate) dissolve in water.

1.2.6 Key Degradation Products

The main degradation pathway for perchlorate is $ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow Cl^- + O_2$. The final degradation products in the complete degradation of perchlorate are oxygen and metal salt containing chloride ion (e.g., potassium chloride [KCl] formed from the complete degradation of potassium perchlorate). In cases of incomplete perchlorate degradation, chlorite may accumulate in the environment and cause an environmental concern. Chlorite (maximum contaminant level [MCL] 1 mg/L) is a known disinfection byproduct produced during degradation of chlorine dioxine.

1.3 TRANSPORT

1.3.1 Transport Process

Perchlorates and perchlorate-containing energetic materials typically exhibit low vapor pressures and poor sorption to soils, but show a high degree of solubility in aqueous matrices [19]. Therefore, dissolution into water, followed by advection and hydrodynamic dispersion are the primary transport processes for perchlorates [19, 20]. Advection refers to the transport of the perchlorate solute within the groundwater, while hydrodynamic dispersion is the movement of solute away from the main path of groundwater due to factors such as flow turbulence or molecular diffusion. These transport processes are nondestructive, meaning that, combined with the low probability of degradation outside of biological or phytotransformation processes, the perchlorate will persist in the environment unless subjected to biological degradation.

1.3.2 Transport in Soil

Perchlorate occurs naturally in soils and in arid environments [3]. Perchlorate-containing compounds do not readily adsorb into minerals or soils but due to their high mobility travel at the same speed as the groundwater supply, and, if in large enough quantities, can stratify in aqueous systems [21]. Perchlorates are also highly soluble in water, with order-of-magnitude higher solubility rates than those of organic energetic materials (e.g., TNT). Furthermore, perchlorates do not partition to soil, as evidenced by the partitioning coefficient data presented in Table 1-1, due to the net negative charge of clay soils. However, perchlorate has been shown to only slightly adsorb to soils in low pH (pH = 5) environments [22] most likely due to a higher positive charge state at low pH and low binding affinity in the aqueous matrices [23]. Once deposited within or on a soil matrix, perchlorate is expected to remain there, relatively unchanged unless subjected to biological degradation processes [3, 22].

1.3.3 Transport in Water

Several studies[22, 24-28] note that perchlorates are water soluble, stable, and highly mobile in aqueous environments. These factors increase the likelihood of transport and persistence of perchlorates in aqueous systems.

The transport of perchlorate in water is typically driven by release of the perchlorate anion when the perchlorate-containing energetic material (e.g., ammonium perchlorate) is dissolved in water with the perchlorate salts exhibiting similar behavior to dense non-aqueous phase liquids (DNAPLs). This can cause perchlorate sinks within the water system until it deposits in a low permeability confining layer where it can accumulate and persist [9].

One of the most significant challenges with perchlorate transport is that it will persist, for upwards of decades, under aerobic conditions [10]. The degradation mechanisms for perchlorate depends on the availability of microorganisms or its uptake by plants species, as other possible degradation pathways (e.g., photolysis) do not occur or occur at very low rates. Unlike many other energetic compounds, perchlorate can be found in groundwater under naturally-occurring conditions up to approximately 1 µg/L [29].

1.4 TOXICITY DATA OF PERCHLORATE

Perchlorate is known to disrupt the uptake of iodine in the thyroid, potentially affecting thyroid function [1]. One of the major concerns is perchlorate impairment of thyroid function in pregnant women, which leads to impaired brain development in fetuses and infants [22][20-22]. Because of the complex anatomy of the thyroid follicle, all of the locations where perchlorate inhibition is exerted remain to be established [30]. One site of this inhibition is the sodium-iodide symporter, a membrane protein located on the basolateral side of the follicular cell, adjacent to the capillaries supplying blood to the thyroid [22, 31]. The thyroid follicle is the functional unit of the thyroid where the organification of iodide may occur, ultimately disrupting formation of the thyroid hormones triiodothyronine (T3) and thyroxine (T4).

The competitive inhibition of iodide uptake is the only direct effect of perchlorate on the thyroid, leading to a reversible chemical-induced iodine deficiency. Alteration of hormones (T4, T3, thyroid-stimulating hormone [TSH]) would be the first observed biological effect of perchlorate

exposure. Following a prolonged increase in TSH, thyroid hyperplasia progressing to thyroid tumors would be expected to occur in rodents [32]. However, the relevance of these tumors has been questioned, since this progression has not been observed in humans. In contrast, human data show that decreased T4 levels, both in pregnant women and neonates, can lead to neuro-developmental deficit, although this has not been confirmed in animals following perchlorate exposure [2, 32]. Therefore, of the two pathways to altered structure and function proposed by a mode-of-action analysis for perchlorate, decreased T4 leading to potential neuro-developmental effects is more relevant to an assessment of human health; this conclusion is also supported by the National Research Council (NRC) [32].

The NRC, on behalf of the DoD, Environmental Protection Agency (EPA), Department of Energy (DOE) and National Aeronautics and Space Administration (NASA), formed a committee in 2003 to assess key scientific issues associated with the health effects of perchlorate. The committee report determined that the development of thyroid tumors as an ultimate result of perchlorate exposure is an unlikely outcome in humans based on two considerations: (1) rats are sensitive to the development of thyroid tumors because their thyroid function is easily disrupted; (2) humans are much less susceptible than rats to disruption of thyroid function and therefore are not likely to develop tumors as a result of perchlorate exposure. Therefore, the NRC committee concluded that the most reasonable pathway of events after changes in thyroid hormone and TSH secretion would be thyroid hypertrophy or hyperplasia, possibly leading to hypothyroidism [8].

1.5 EXAMPLE REGULATORY GUIDELINES FOR PERCHLORATE

As of March 2015, perchlorate has not been regulated by EPA in drinking water. However, in 2011, EPA announced the determination to regulate perchlorate in drinking water which reversed a 2008 preliminary determination stating that perchlorate did not present any meaningful opportunity for health risk reduction for persons served by public water systems. This new determination is based on the same reference dose (RfD) of 0.7 µg/kg/day on which the previous single health reference level (HRL) of 15 µg/L was derived, but accounts for a range of potential alternative HRLs for different life stages such as infants and developing children. The process for establishing a MCL for perchlorate is also taking into account the number of people potentially affected by perchlorate exposure, the amount of perchlorate in drinking water sources, and the cost of removing the contaminant from those sources. U.S. EPA anticipated proposing an MCL for perchlorate by 2013, but this process has been delayed, and it is unknown if, or when, a MCL will be proposed.

Two states already regulate perchlorate in drinking water. The California Department of Public Health set an MCL of 6 µg/L for perchlorate in 2007 based on a Public Health Goal (PHG) of 6 µg/L (established by the Office of Environmental Health Hazard and Assessment [OEHHA] in 2004). In 2015, OEHHA reduced the PHG for perchlorate in drinking water from 6 µg/L to 1 µg/L. In response to the new PHG, California's State Water Resources Control Board's Division of Drinking Water will review the MCL. Massachusetts set an MCL of 2 µg/L in 2006. New Jersey was proposing to establish an MCL of 5 µg/L, but in March 2010, the New Jersey Department of Environmental Protection decided to delay setting the MCL until after a national standard has been set.

1.6 DATA GAPS

Despite several decades of research work several data gaps exist in science pertaining to perchlorate toxicology and fate and transport processes. Studies on subchronic bioassays, two-generation reproductive issues and developmental toxicity to gain more complete understanding of kinetics and mechanisms of long-term exposure to perchlorate need to be completed. Additional questions that still remain unanswered relate to effects of perchlorate on fetal/neonatal mental development and integration of data from existing human and animal studies. Major data gaps are listed below:

A. Fate and Transport

- **Photolysis**: Definitive data on rates/half-lives (even if it is not likely to occur).
- **Abiotic Reaction**: Any data on dilution/precipitation rates as a function of environmental conditions and the type of perchlorate salt. This may improve understanding of transport and persistence.
- **Biodegradation**: Additional data on the availability and rates for naturally-occurring chlorite dismutase.
- **Phytotransformation**: More details on the step-wise reduction reactions of perchlorate, particularly when/if chlorite is formed and its degradation path.
- **Transport**: Data on dilution versus precipitation rates, particularly since dissolved perchlorate ion is a serious health concern.

B. Toxicity

- **Toxicology of Perchlorate**: Studies on subchronic bioassays, two-generation reproductive issues and developmental toxicity need to be developed and completed to understand kinetics of long-term exposure. Additionally, neonatal and fetal studies on perchlorate need to be completed to aid understanding on its effects on human population.

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2. CHLORATE

2.1 INTRODUCTION

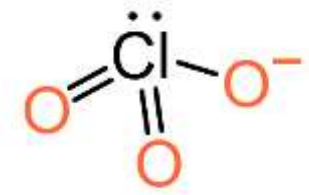

Figure 2-1. Chemical Structure of Chlorate Anion

Names: Chlorate and chlorate-based propellants (potassium chlorate)
Abbreviations and Other Names: Potassium chlorate(V), potcrate
CAS No.: 3811-04-9
Chemical Formula: ClO_3-
Occurrence in Mixtures/Compositions: Various flash powders, colored-smoke formulations, or additives in explosive detonators and primer mixes; also used in several home-made explosive or improvised explosive device (IED) formulations
Natural Occurrence: Chlorates are not formed naturally and have been introduced into the environment in large quantities in the form of disinfectants, bleaching agents, and herbicides.
Physical/Chemical Properties: The physical/chemical properties of perchlorate salts are provided in Table 2-1.

Table 2-1. Physical and Chemical Properties of Potassium Chlorate [6]

Property	Potassium Chlorate	Units
Color	White	
Odor	None	
Physical state	Solid; monoclinic crystal	
Melting temperature	368	^oC
Vapor pressure (@ 20^{o}C)	Negligible	atm
Specific gravity	2.3	None
Water solubility (@ 20^{o}C)	70	g/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{OW})	NA	None

2.2 FATE

Of the chlorate salts, potassium chlorate is the most commonly used in energetic material formulations. Historically, it has been used as the oxidizing agent in primer compositions for small-caliber ammunition, hand grenades, and projectiles [3]. It is also an ingredient in several pyrotechnic formulations, including flash powders and colored-smoke formulations [4]. Due to its sensitivity to ignition, its use is not as widespread as other oxidizing agents, such as those comprised of perchlorate salts (e.g., ammonium perchlorate). Use of chlorate is also limited to smaller charges (e.g., primers) as opposed to rocket motor propellants. However, its ease of ignition, burning speed, and ability to generate white smoke and high-temperature flame upon reaction with a fuel justify its continued use in selected pyrotechnic and primer applications. Data on the fate of potassium chlorate are, in general, lacking. However, some information on the fate can be derived from the fate of energetic materials containing perchlorate salts, because the chlorate salt is often formed during perchlorate degradation processes.

2.2.1 Relevant Properties

The chemical structure of chlorate is shown in Figure 2-1 while Table 2-1 lists selected physical and chemical properties of the chlorate formulation, namely potassium chlorate. Unlike perchlorates, chlorates are not usually formed naturally and thus most chlorate accumulation is a result of man-made contamination processes. Values for the dissolution rate and octanol-water partition coefficient for potassium chlorate were not identified in the surveyed literature. However, it can be numerically estimated with reasonable accuracy.

2.2.2 Photolysis

Similar to perchlorate, no reports of chlorate photosensitivity were found. Thus, photolysis of perchlorates, and by extension chlorates, is not expected to occur [5].

2.2.3 Other Abiotic Reactions

Data on the abiotic reduction of the chlorate anion originates from information on abiotic reduction of perchlorate. However, this is a very broad assumption. The abiotic reduction of perchlorate is reported to be negligible, particularly when compared to other energetic material compounds such as TNT or other degradation processes such as biological degradation of perchlorate [7]. The kinetic barrier for chlorate is lower than perchlorate, meaning that chlorate is chemically reduced more rapidly than perchlorate.

The main abiotic attenuation pathway for perchlorate and, by extension, chlorate is dilution. For perchlorate, dilution helps to alleviate local contamination levels in an environmental matrix and the precipitation reaction is not expected to occur.

2.2.4 Biodegradation

Chlorate does not survive for long periods in the environment and is readily biodegraded by microorganisms under anaerobic conditions. Chlorate degradation rates depend on specific microbial species or microbial communities that perform the degradation reactions. For example, for microbial cultures grown in 20 ^{o}C and 30 ^{o}C, the half-lives of chlorate degradation are 0.1 to 4 days [7]. There is no indication of chlorate bioaccumulation in the environment [10]. As noted, chlorate's biotic degradation pathway follows the same route as perchlorate with two key enzymes involved in its reduction and dismutation. (Per)chlorate reductase catalyzes conversion of chlorate (ClO_3^-) to chlorite (ClO_2^-) followed by the final dismutation of chlorite to chloride (Cl_2) and oxygen catalyzed by chlorite dismutase. The final products of chlorate reduction are chloride ion and water (Figure 2-2).

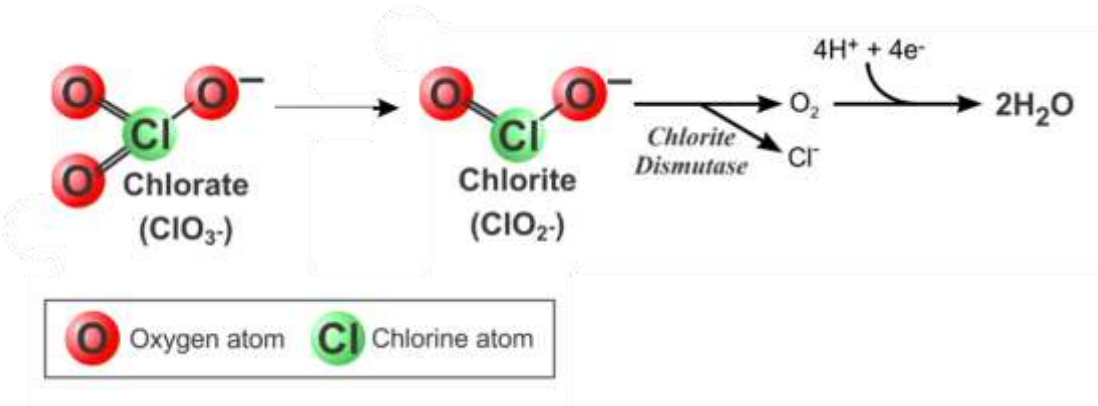

Figure 2-2. (Per)chlorate Biodegradation Pathway [11]

Bacteria capable of reducing (per)chlorate to chloride and oxygen are found throughout the environment and are phylogenetically diverse with members in the alpha, beta, gamma, and epsilon subclasses of the *Proteobacteria* phylum [12]. Such bacteria are complete oxidizers, Gram negative, non-fermenting facultative anaerobes found in hydrocarbon-contaminated, pristine soils, aquatic sediments, and farm animal waste lagoons; most utilize nitrate as an electron acceptor [13].

It is known that oxygen inhibits perchlorate reduction and that chlorite dismutase is not expressed under aerobic growth conditions by most perchlorate reducing microorganisms. However, some studies found that *Pseudomonas* sp. PDA, a chlorate-respiring microorganism, was able to degrade perchlorate and express chlorite dismutase for chlorate catalysis under aerobic conditions [14, 15].

2.2.5 Hydrolysis

Little information exists regarding the hydrolysis of potassium chlorate or the chlorate ion. The perchlorate anion (ClO_4^-) was found to not hydrolyze under typical environmental conditions. Eh (≈ -300mV - +700 mV) and pH (≈ 3.5 – 10) ranges suggest that chlorate ion may show similar properties to perchlorate.

2.2.6 Key Degradation Products

The key degradation products of chlorate are chloride and oxygen, which are produced from the compete degradation of the chlorate anion (Figure 2-2). Moreover, toxic chlorite anion may be generated from phytotransformation processes due to the capability of the nitrate reductase to competitive chlorate degradation [16].

2.3 TRANSPORT

2.3.1 Transport Process

Chlorate is a common perchlorate degradation byproduct. Chlorate anions are water soluble and do not readily sorb to soils, therefore, chlorate dissolution into water, followed by advection and hydrodynamic dispersion, apply for chlorates [17]. The transport of chlorate from its point source of introduction into the environment (i.e., the training or manufacturing site) is expected to be far-reaching once chlorate comes into contact with water.

Because most of the transport information is associated with or derived from studies on perchlorate transport, additional studies that focus primarily on the transport of the chlorate anion are needed.

2.3.2 Transport in Soil

Data for chlorate transport in soil are, in general, lacking. Chlorates are not expected to readily sorb to soils based on similar data provided for perchlorate. Chlorates are highly soluble in water (i.e., 70 g/L for potassium chlorate, 200 g/L for ammonium perchlorate, and 16.8 g/L for potassium perchlorate), more so than other energetic materials such as TNT, RDX, and HMX, which have solubility properties in the mg/L range [18]. It is assumed that, like perchlorates, chlorates do not partition to soil, although a value for the partitioning coefficient provided in Table 2-1 needs to be determined to assess the propensity for chlorate to partition to soil. It is assumed that when deposited onto the soil, chlorates will much more readily dissolve into water systems and are less likely to sorb to soils.

2.3.3 Transport in Water

Chlorates are water soluble, stable, and highly mobile in aqueous environments. Specific data on chlorate transport in water from energetic material synthesis, processing, and use are not available and, therefore, transport data defaults to what has been developed for perchlorates. Perchlorate transport in water is thought to be driven by the rate at which the perchlorate (or chlorate) anion dissolves into water [20], although the specific water dissolution data for potassium chlorate need to be determined, as noted in Table 2-1. Perchlorate, and by extension chlorate, persists in water systems unless degraded by microorganisms or taken up by plant species, as most other possible degradation pathways (e.g., photolysis) are not expected to occur or proceed at very low rates [21].

2.4 TOXICITY DATA OF CHLORATE

Chlorate competes with iodide for transport to the thyroid, although it does not bind as strongly as perchlorate, and it can be metabolized, whereas perchlorate is very stable after ingestion. Reports on high test doses in animals show that high concentrations of chlorate consumption by infants and young children can cause problems to the nervous system and anemia. The same effects could occur in the fetus of a pregnant woman [22].

The chemistry of chlorate indicates that upon ingestion of small quantities from water in the acidic pH, it would be reduced by reaction-reducing agents such as sulfide, nitrite and iodide that are naturally present. These reductive processes are probably slower than those with bromate. Inhalation of chlorate and chlorate salts causes irritation to the respiratory tract [23]. Symptoms may include coughing and shortness of breath. Ingestion causes irritation to the gastrointestinal tract with symptoms such as nausea, vomiting and diarrhea. Chlorate ingestion may also cause abdominal pain, hemolysis, methemoglobinemia, cyanosis, anuria, coma, convulsions, and liver and kidney damage. Death may occur from renal failure, generally in 4 days. The estimated lethal dose for chlorate is from 15 to 30 grams. The toxic dose of potassium chlorate is often reported to be 5 grams, with the lethal adult dose being 15 to 35 grams. Mortality of a child has been reported after ingestion of 1 gram of potassium chlorate [14, 24].

2.5 EXAMPLE REGULATORY GUIDELINES FOR CHLORATE

There is no current MCL for chlorate. The Canadian Guideline of 1 mg/L assumes a relative source contribution (RSC) from drinking water of 80 percent and includes a safety (uncertainty) factor of 1,000 in the calculation from animal toxicology data. California has no MCL but a notification level of 800 µg/L (0.80 mg/L). There is no federal drinking water standard for chlorate ion, but the EPA has set a daily reference dose of 0.03 milligrams per kilogram of body weight (0.03 mg/kg/day). EPA defines a reference dose as "an estimate of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime." When determining what substances merit regulation, EPA considers both health effects and occurrence data. If there is scientifically compelling evidence that shows a large number of U.S. drinking water systems have high amounts of chlorate ion above the current reference concentration of 210 ppb per day, it is possible that EPA may decide to regulate it in the future.

The World Health Organization (WHO) guideline for chlorate is 0.7 mg/L.

2.6 DATA GAPS

Unlike the other MCs researched to date (i.e., TNT, HMX, RDX, and perchlorates), there is no significant body of literature available on chlorate fate and transport pertinent to the use of chlorate as an energetic material. To fill this data gap, there is a need for laboratory-based studies in controlled, surrogate environments as well as field studies to help identify any transport or degradation phenomena that is unique for the chlorate anion (i.e., not derived from the transport or degradation of perchlorates).

The main data gaps identified for chlorate are listed below:

A. Fate and Transport

- **Physical and Chemical Property Data**: Identify the properties for chlorate that are pertinent to transport (i.e., update those values that were derived from perchlorate).
- **Abiotic Reactions**: Identify abiotic reactions that are specific to chlorate; transition away from deriving data from perchlorates.
- **Phytotransformation**: More information is needed on the rates of half-lives of potassium chlorate by plants. This is a known, chlorate-specific degradation path with some laboratory-based data collected.
- **Transport**: Identify laboratory-based or field-based studies particular to the transport and fate of chlorate in the environment. Most of the data provided for chlorate are based on findings for perchlorate. While there are some chemical and physical similarities, some properties (e.g., redox potential) may result in significant differences in fate and transport.

B. Toxicity

- **Determination of MCL**: Chlorate, currently included in the EPA's monitoring of unregulated contaminants and on the contaminant candidate list, could potentially receive a regulatory determination in the near future. U.S. EPA could face its own regulatory challenges, depending on the threshold value used in the development

of a potential chlorate MCL. An MCL of 210 μg/L would significantly increase the nationwide cost of compliance compared with an MCL in the range of WHO's guideline of 700 μg/L or an 80% RSC of 840 μg/L.

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3. 2,4,6-TRINITROTOLUENE (TNT)

3.1 INTRODUCTION

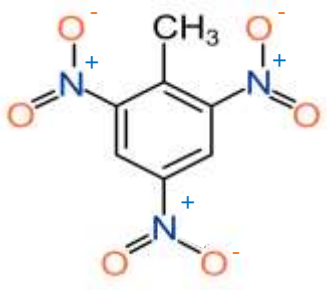

Figure 3-1. Chemical Structure of TNT

Names: 2,4,6-trinitrotoluene
Abbreviations and Other Names: TNT, 2,4,6-Trinitrotoluene, Trilite, Tolite, Trinol, Trotyl, Tritolo, Tritolol, Triton, Tritone, Trotol, Trinitrotoluol, 2,4,6-Trinitromethylbenzene
CAS No.: 118-96-7
Chemical Formula: $C_7H_5N_3O_6$
Occurrence in Mixtures/Compositions: Composition B, IMX 101, Cyclotol
Natural Occurrence: TNT does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of TNT are provided in Table 3-1.

Table 3-1. Physical and Chemical Properties of TNT [8-10]

Property	Value	Units
Color	Yellow	None
Odor	Strong almond scent	None
Physical state	Flakes, needles, or column-shaped crystals; several crystalline structures including orthorhombic and monoclinic	None
Melting temperature	80 – 82	^oC
Vapor pressure (at 20°C)	7.2×10^{-9}	atm
Specific gravity	1.654 (solid), 1.47 (molten)	g/cc
Water solubility (at 20°C)	130	mg/L
Dissolution rate in water (@ 30°C)	0.69	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Organic solvent solubility in:		
Acetone (at 20°C)	8.61×10^5	mg/L
Benzene(at 20°C)	5.89×10^5	mg/L
Toluene(at 20°C)	4.77×10^5	mg/L
Octanol-water partition coefficient (Log K_{ow})	1.86	None

3.2 FATE

The environmental fate of TNT has been studied fairly extensively throughout the years due to its ubiquitous use in most military explosive formulations. Furthermore, its use at training ranges and for disposal activities has provided opportunities to conduct field studies on long-term accumulation, biotransformation, degradation pathways, and chemical processes relevant to the fate of TNT in the environment [4]. As a result, better understanding of not only the pathways and end products for TNT degradation, but also the toxicity and health effects that can be attributed to

TNT contamination in the environment has been gained. This understanding of the environmental fate of TNT can provide a platform to assess remediation opportunities and determine the best paths forward to mitigate the harmful consequences of TNT contamination.

3.2.1 Relevant Properties

TNT contamination is considered a global issue due to its extensive use by militaries throughout the world. Impurities such as 2,4-dinitrotoluene (DNT) are almost always present in TNT formulations at approximately 8% by mass of the finished TNT product [5], resulting in a yellow powder with a pungent, almond odor. When melted and then cast, TNT forms a brittle solid with a distinct yellow color, however, the color of a TNT-containing formulation may vary with the composition, producing, for example, off-white, grey, or red formulations [6].

Six isomers of TNT are known. The alpha isomer (2,4,6-TNT) is the military standard for TNT [7]; other isomers are typically present as impurities at approximately 3% by mass of the finished TNT product. TNT contains a benzene ring skeleton, with three nitro groups and a methyl group occupying the four hydrogen bonding sites on the benzene ring. The chemical structure of TNT is shown in Figure 3-1 and properties of TNT including vapor pressure, density, and solubility are described in Table 3-1.

Properties and data related to the mobility and persistence of TNT in environmental matrices include water solubility, octanol-water portioning coefficient (K_{ow}), qualitative or quantitative (i.e., rates) for hydrolysis, photolysis, and biotransformation-based pathways. These data are summarized from previous relevant studies to provide a summary of TNT processes in the environment (i.e., from dispersion into an environment to its fate and degradation products).

3.2.2 Photolysis

TNT undergoes photolytic conversion in the presence of moisture [11] forming nitrobenzenes, benzaldehydes, azoxydicarboxylic acids, and nitrophenols through oxidation of methyl groups, reduction of nitro groups, and dimer formation [12]. The half-life of photolysis was measured to be in the range of ≈ 30 minutes for natural water to ≈ 200 minutes for pure water [13]. Specific compounds formed as a result of the photolysis of TNT include: 3,3’5,5’-tetranitroazobenzene-2,2’dicarboxylic acid, 2,4,6-TNBA, 1,3,5-trinitrobenzene, 4,6-dinitroanthranil, 2,4,6-trinitrobenzaledehyde, 2,4,6-trinitrobenzonitrile, 2-A,4,6-DNBA, 4-A-2,6-DNA and other azo- and azoxy- derivatives [12, 14, 15].

Aqueous photolysis is a very rapid degradation process for TNT with half-life values of 60 days in surface water, 60 to 120 days in soil, and 240 to 540 days in sediment. The rate of TNT photolysis in pure water increases with increasing pH [16], tripling in value as the pH increases from 4 to a pH of 8. On the contrary, the photolysis in natural waters is not as significantly dependent on the pH but governed by the amount of humic substances present. While photolysis in water is fairly well characterized, data on the degradation products for strictly solid-phase photochemical degradation of TNT is incomplete [17]. Solid TNT undergoes photolysis to form water-soluble products such as 2-amino-4,6-dinitrobenzoic acid (2-A-4,6-DBA). This photodegradation product was first identified in the pink water lagoons at Louisiana Army Ammunition Plant [13, 18], which may account for 60% or more of the dissolved product of TNT

[17]. This means that studies completed without accounting for this photodegradation product (prior to 2010) and closed out due to non-detections of explosive may give a false impression of the state of the groundwater. Current analytical methods strive to detect the TNT and those degradation products which are physically smaller than the TNT molecule, and, as a result, do not detect the 2-amino-4,6-dinitrobenzoic acid, which is nearly twice the size of the TNT. This idea that degradation products of energetics are necessarily always smaller than the original molecule needs adjusting in the technical community.

Some information regarding the rates of solid-phase photolysis, expressed in TNT sample half-life, is available [19]. Solid-phase TNT in direct sunlight had half-life values in the range of 14 to 48 hours from the exposure time [19].

3.2.3 Abiotic Reactions

Abiotic soil degradation of TNT is well documented. Factors that affect abiotic reduction of TNT include matrix pH, organic content, and ion content of the soil (specifically Fe^{2+} and Mn^{2+}) [12, 20, 21]. The presence of Fe^{2+} appears to be the most important factor, with results in half-life values of ≈ 60 hours (2.5 days), placing it in between the rates of photolysis (≈ 30 – 200 minutes) and biotransformation (≈ 7.18 days in water, ≈ 119 days in soil).

The general pathway for abiotic reduction of TNT involves the reduction of one, two, or all three TNT nitro groups to TNT dimers 2-amino-2,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT). The first two steps include production of 2-hydroxylamino-4,6-dinitrotoluene (4-HA-2,6-DNT) and generation of 4-ADNT as shown in Figure 3-2. 4-ADNT is also a typical biotransformation product, thus its presence does not indicate a specific transformation mechanism (e.g., abiotic or biotic transformation). This pathway can occur in TNT-contaminated soils and groundwater, in addition to the products formed through reactions such as photolysis.

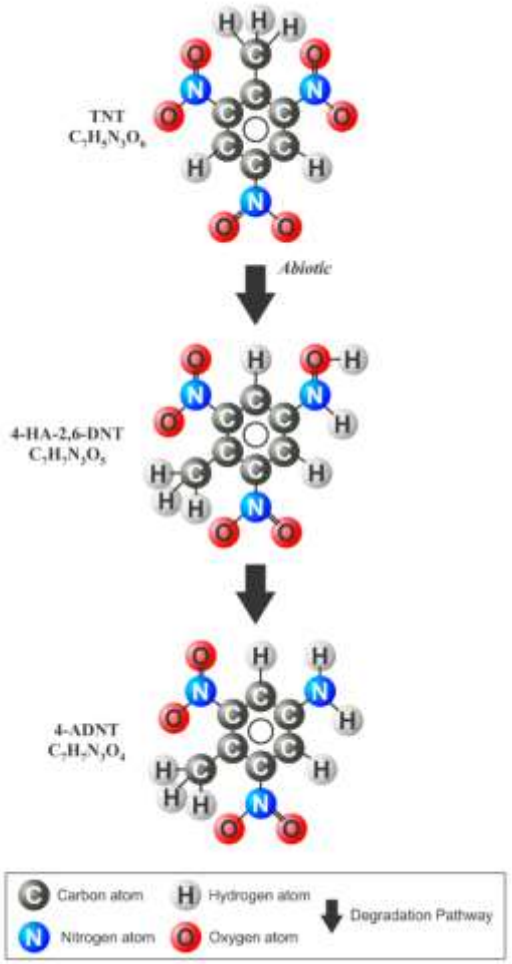

Figure 3-2. First Two Steps of the Abiotic Transformation of TNT [1-4]

3.2.4 Biodegradation

Several studies conducted under aerobic and anaerobic conditions show the biodegradation of TNT [12, 22-26]. The degradation rate of TNT depends on microbial species involved and ranges from several hours when microbial cells were adapted to the TNT and grown in the batch reactor [27] to up to 4 days for some *Pseudomonas sp.* [28]. Bacteria and fungi have demonstrated the capacity to degrade TNT to the amino derivatives 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT, and, in

anaerobic conditions, triaminotoluene (TAT). TAT can then be further reduced to less toxic azo/azoxy/hydrazo/phenolic/acetyl derivatives. Fungi have the capability to mineralize TNT, forming carbon dioxide, methane, and other nitrates in the process [29]. The rate of fungal degradation of TNT varies and depends on fungal culture and cultivation conditions. For example, *P. chrysosporium* species mineralized TNT in aerobic conditions within 20 days of inoculation [30]. When TNT was added into a nutrient-rich medium at the beginning of the incubation, some fungal strains completely removed TNT during several days of incubation and showed higher removal rates than those of *Phanerochaete chrysosporium*. *Irpex lacteus* strain degraded TNT within 12 hours of inoculation onto the N-depleted medium [31].

TNT biodegradation has been reported for a wide variety of bacterial isolates such as *Pseudomonas sp.*, *Desulfovibrio sp.*, *Bacillus sp*. and *Staphylococcus sp*. cultured from freshwater or terrestrial environments. Biotransformation of TNT can take place under aerobic or anaerobic conditions and is typically cometabolic in nature. A common finding is that the nitro groups of the TNT are reduced to anilines (aromatic R-NH_2). Figure 3-3 illustrates this reductive process where TNT is biotransformed in a stepwise manner:

- One of the nitro groups (shown in red and blue) is reduced through biotic reaction to a hydroxylamime (-NHOH) group. Note the two additional hydrogens on either 2-hydroxylamino-4, 6-dinitrotoluene (2-HADNT) or 4-hydroxylamino-4, 6-dinitrotoluene (4-HADNT).
- Next (following the 2-HADNT pathway), the recently formed hydroxylamine group is further reduced to generate 2-amino-2,6-dinitrotoluene (2-ADNT). Both 2-ADNT and 4-ADNT are the most common intermediates of TNT biotransformation and can be generated in oxic or anoxic conditions.
- Under strict anoxic conditions, enzymes can continue the reductive process and remove the remainder of two nitro groups. First, 2,6-diamino-6-nitrotoluene (2,6-DANT) is produced.
- Finally, the last nitro group can be reduced to form 2,4,6-triaminotoluene (TAT), which is highly reactive and can polymerize or irreversibly bind to the organic soil matrix. TAT can then be further reduced to azo/azoxy/hydrazo/phenolic/acetyl derivatives.

TNT has been utilized by heterotrophic bacteria as a sole nitrogen or carbon source via nitrobenzene with both carbon and nitrogen incorporated into macromolecules. Additionally, white-rot fungi and litter-degrading fungus (e.g., *Phanerochaete chrysosporium*) [32] have been observed to completely biodegrade TNT.

3.2.5 Phytotransformation

Plants, such as alfalfa and broad beans, have been shown to perform phytotransformation of TNT [33] through a series of metabolical reactions catalyzed by nitroreductases (reduction of nitro groups into nitroso, hydroxylamino, or amino groups), cytochrome P450 mono-oxygenases and peroxidases (catabolic oxidation) and glutathione S-transferases (conjugation of activated TNT derivatives) [34]. Results from plant studies using poplar trees and bush beans suggest that TNT can be taken up by plants and transformed to two main metabolites: 2-ADNT and 2,6-DANT.

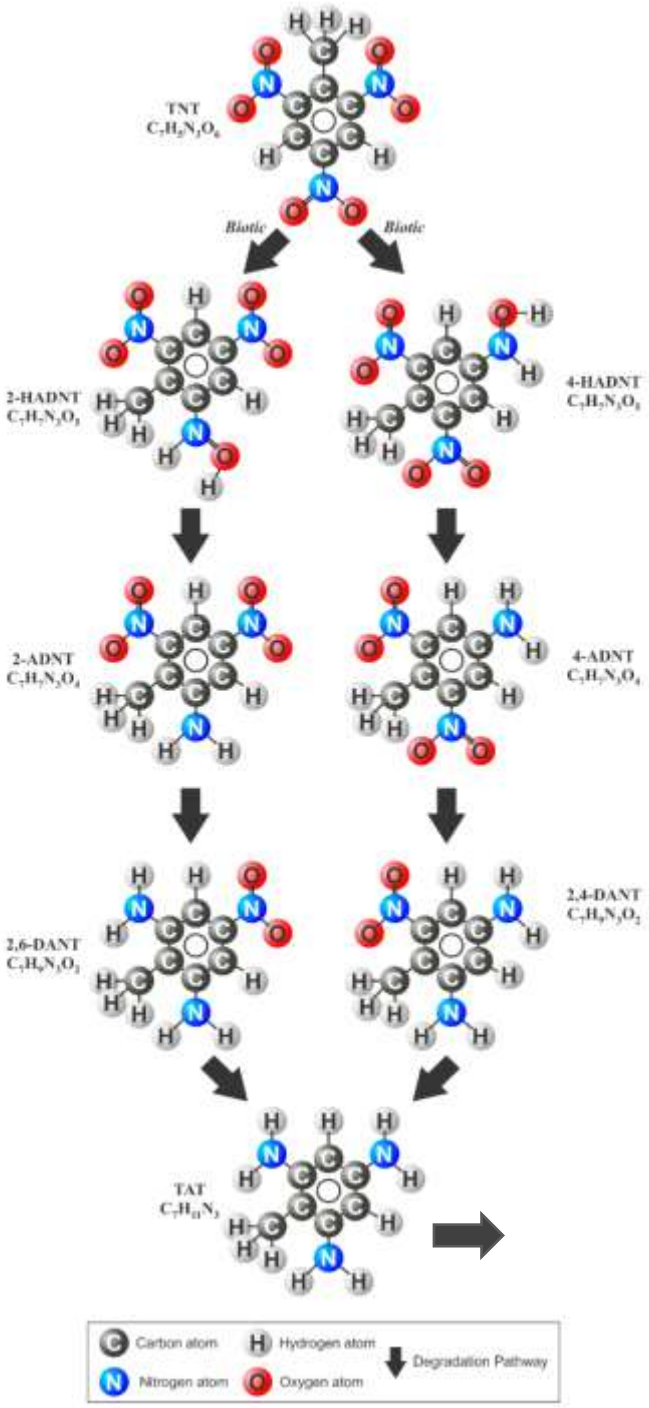

Figure 3-3. Initial Steps of TNT Biodegradation [26, 35-37]

3.2.6 Hydrolysis

A number of studies have been conducted on TNT alkaline hydrolysis in water and highly contaminated soils [38-40]. However, most of these studies only consider the decay of TNT and do not identify intermediate and/ or final compounds. A few publications suggest that the

degradation products in the later stages of TNT hydrolysis could include aromatic ring cleavage species (acetates, formates, oxalates, nitrites) as well as products of polymerization [41].

Experimental data on hydrolysis of nitro-compounds in non-aqueous solutions suggest that this chemical pathway appears to be strongly influenced by the medium in which the reaction takes place. The rate of hydrolysis is also pH-dependent when reactions occur in aqueous environments [42]. However, several reports show TNT hydrolysis in alkaline solutions (very basic) with pH levels greater than 10 [25]. Half-life values for TNT include 4 days (pH 11), 1.2 days (pH 11.5), and 0.6 days (pH 11.9), suggesting that the rate of hydrolytic degradation may increase as alkalinity increases [43]. Overall, these rates of TNT hydrolysis are slower than those reported for photolytic degradation and similar to the rates of abiotic reduction.

3.2.7 Key Degradation Products

When dispersed into the environment TNT can be subjected to degradation via photolysis, abiotic reduction, biological transformation, and phytotransformation. All of these degradation mechanisms should be taken into consideration when assessing the overall fate of TNT in the environment. Therefore, it is paramount to know the "end points" of TNT degradation. In addition to the data on biotransformation of TNT, there is a handful of information on TNT degradation byproducts [36, 37]. TNB, TNBA, DNT, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT were found in detectable levels along with TNT, suggesting that TNT was degraded by photolysis, resulting in TNB and TNBA formation, and microbial degradation, resulting in the formation of 2- and 4-ADNT. DNT was most likely present in TNT as an impurity.

Another study reported the degradation of radio-labelled TNT in bush bean plants in a laboratory setting. Radio-labelled 2- and 4-ADNT metabolites were detected in the leaf, stem, and root tissues [44]. Finally, studies performed on human and animal models have reported that the most common TNT degradation compounds found in urine samples were 2- and 4-ADNT [19]. Thus, the formation of 2- and 4-ADNT from TNT degradation appears to be the rate-limiting step in total TNT degradation [26].

The fate and transport of the amino-based compounds (i.e., 2-ADNT, 4-ADNT, 2,4-DANT, 2,6-DANT, and TAT) continue to be a topic of interest [26, 35]. In general, TNT fate, transport and toxicity data are incomplete, and several knowledge gaps exist. The best characterized TNT degradation byproduct may be 4-ADNT [26] with some physical and chemical data summarized in Table 3-1.

3.3 TRANSPORT

3.3.1 Transport Processes

The transport of TNT in the environment has been studied extensively, mostly because of its use in several different types of ammunition by militaries around the world. The distribution of TNT in the environment is especially high at military test ranges and explosive manufacturing sites with nearly 17 U.S. Army installations with TNT concentrations of up to and in excess of 10,000 µg/gm soil [15]. TNT can be directly deposited in soils from military range testing, open burn/open ordnance disposal operations or leaching from unexploded ordnance that has been embedded in

the ground. Wastewater containing TNT and its byproducts can also infiltrate water systems as a result of TNT synthesis or ordnance casting operations.

3.3.2 Transport in Soil

When deposited into soil systems, TNT is likely mobile in the environment due to its chemical and thermal stability which complicates its biodegradation and remediation efforts [12]. Dissolution into water and adsorption into soils heavily influence TNT transport in the environment and its low volatility renders transport via volatilization unlikely to occur.

TNT dissolution is key to the transport and fate as well as degradation and dispersion in soils mostly due to the mass transfer from the solid to liquid phase as a rate-limiting step [17, 45]. TNT exhibits low solubility in water with a solubility rate higher than the military explosives such as cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX). Once deposited onto soil, its transport mechanism is dictated not only by the solubility or dissolution rates, but also by the amount of precipitation or water available for TNT and the morphological properties (i.e., size and geometry) of TNT particles [46].

TNT transport also corresponds to the type of formulation in which it is used. TNT is often mixed with other explosive materials (e.g., RDX) or binders, waxes, and plasticizers, which can restrict or inhibit TNT dissolution [12, 17, 47-49]. For most explosive formulations, TNT percentages are typically in the range of 25 to 50% of the net explosive formulation mass. For example, Composition B consists of 36% TNT, 63% RDX, and 1% wax; AFX-621 is comprised of 30% TNT, 42% NTO, 24% HMX, and 4% aluminum powder; and some Pentolite formulations contain 50% TNT and 50% PETN. Few formulations may contain 10% or less or 90% or higher percentages (e.g., some Pentolite formulations contain 90% TNT with 10% PETN). The rate of diffusion in such instances may be analogous to molecular diffusion through a porous medium and highly dependent on particle size and packing density.

Adsorption and dissolution of TNT into soils has been extensively studied [47, 50]. With adsorption, the dissolved TNT begins to accumulate at the surface of soil, allowing for accumulation or increased bioavailability for biodegradation. The TNT K_{ow} value suggests low sorption into soils and a significant degree of mobility in the environment [12, 51]. However, it has been shown that TNT can be reversibly sorbed in soil systems (diffusion [K_d] for TNT in surface soils to range from 2.3 to 11 L/kg) with interactions between the TNT nitro functional groups and soil colloids as the suggested platform to form hydrogen bonding and ion exchange.

Soil clay minerals seem to significantly influence sorption of TNT with factors such as clay type, availability of cation exchange sites on the clay surface, and the ionic strength and composition of the water within the clay matrix affecting adsorption rates. Moreover, the rate of adsorption from water to sediments and soils is dependent upon specific cations present [25]. Soils with clay contents rich in K^+ or NH_4^+ ions adsorb up to four orders of magnitude higher (i.e., up to 21,500 L/kg with K^+ or NH_4^+) than clays containing Ca^{2+}, Na^+, Mg^{2+}, or Al^{3+} ions (i.e., $\approx$ 1.7 L/kg). If soil absorption is ion-dependent, TNT may also more readily absorb into soil matrices from saline systems (high in K^+ and Na^+) than into fresh water systems (high in Ca^{2+} ions). The organic carbon fraction in soil plays a significant role in sorption. K_d values for TNT, RDX, and DNT depend on

quantity of organic carbon in soil and result in stronger adsorption of TNT and DNT in comparison to RDX [12].

A number of functional groups influence sorption capability of TNT degradation byproducts. As an example, the sorption of TNT degradation product 2,4-DANT is greater than 4-ADNT [52-54]. This places an importance on understanding the ultimate fate of TNT in terms of its degradation products, the degradation "end points" and their interactions within the environment.

3.3.3 Transport in Water

TNT may undergo photolytic reactions in water, often times competing against transport processes. Change of water color to pink ("pink water") is a known indicator of TNT photolysis. The fate and transport of TNT photodegradation byproducts is not well understood and only a handful of studies exploring TNT photodegradation exist. For example, Pichtel [12] states that previous studies have shown that 45 to 50% of the TNT decomposition products were dissolved into and recovered from water (i.e., the decomposition products discussed in the TNT photolysis section), while the remaining amount of products were considered to be insoluble. The insoluble materials were suspected to contain oligomers of azo and azoxy compounds but were not identified.

3.4 TOXICITY OF TNT

TNT is absorbed through the gastrointestinal tract, skin, and lungs and distributed primarily to the liver, kidneys, lungs, and fat; it is excreted mainly via the urine and bile [35]. TNT metabolism occurs by nitroreduction to amino and hydroxylamino derivatives and by oxidation to benzyl alcohol and benzoic acid derivatives [35, 55, 56].

In animals, signs of acute toxicity to TNT include ataxia, tremors, and mild convulsions. Oral LD50 values of 660 to 1320 mg/kg have been reported for rats [57]. The primary target organs for TNT toxicity in experimental animals following subchronic and chronic oral exposures are: (1) liver (hepatocytomegaly and cirrhosis), (2) blood (hemolytic anemia with secondary alterations in the spleen), and (3) testes (degeneration of the germinal epithelium lining the seminiferous tubules). Chronic oral toxicity studies on rats have also demonstrated TNT-induced anemia and hepatotoxicity, as well as adverse effects on the kidney (hypertrophy and nephropathy) and sternal bone marrow fibrosis [58].

The reference dose (RfD) for chronic oral exposures, 0.0005 mg/kg/day, is based on a lowest-observed-adverse-effect level (LOAEL) of 0.5 mg/kg/day for liver effects in dogs [59] and the subchronic oral RfD was found to be the same as the chronic RfD [60].

Information on the inhalation toxicity of TNT is derived mainly from occupational exposure studies, which indicate that the major effects of chronic exposure to TNT are anemia (decreases in Hgb, Hct, and RBC count), liver dysfunction (increases in serum lactic dehydrogenase, glutamic oxaloacetic transaminase, and bilirubin), and cataracts (equatorial lens opacities). Other reported effects of TNT exposure include dermatitis, leukocytosis, neurological disorders, and nephrotoxicity [61]. An inhalation reference concentration (RfC) for TNT has not been derived to date and limited information is available on the reproductive or developmental toxicity of TNT to

animals or humans following inhalation exposures. Information from occupational exposure studies suggests that TNT may cause menstrual disorders and male impotency [62, 63].

3.5 EXAMPLE REGULATORY GUIDELINES FOR TNT

In 1993, EPA assigned TNT an oral RfD of 5×10^{-4} mg per kg per day (mg/kg/day) [64]. Moreover, the Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.0005 mg/kg/day for intermediate oral exposure (15 to 364 days) [65]. EPA assigned an oral slope factor for carcinogenic risk of 3×10^{-2} mg/kg/day, and the drinking water unit risk is 9.0×10^{-7} micrograms per liter (μg/L) [60, 66].

EPA risk assessments indicate that the drinking water concentration representing a 1×10^{-6} cancer risk level for TNT is 1.0 μg/L [64].With that in mind, EPA established drinking water health advisories for TNT, which are drinking water specific risk level concentrations for cancer (10^{-4} cancer risk) and concentrations of drinking water contaminants at which non-cancer adverse health effects are not anticipated to occur over specific exposure durations [66]. The lifetime health advisory guidance level (mg/L) for TNT in drinking water is 0.002 milligrams per liter and the health advisory for a cancer risk of 10^{-4} is 0.1 mg/L.

For TNT in tap water the risk-based screening level is 2.2 μg/L [60] and residential soil screening level (SSL) is 19 milligrams per kilogram (mg/kg) and an industrial SSL of 79 mg/kg. The soil-to-groundwater risk-based SSL is 1.3×10^{-2} mg/kg [60]. EPA has not established an ambient air level standard or screening level for TNT [60].

Since TNT is an explosive, flammable and toxic chemical, EPA has designated it as a hazardous waste once it becomes a solid waste, and EPA regulations for disposal must be followed [66]. Moreover, the Occupational Safety and Health Administration (OSHA) set a general industry permissible exposure limit of 1.5 milligrams per cubic meter (mg/m^3) as the time-weighted average (TWA) over an 8-hour workday for airborne exposure to TNT [67]. The National Institute for Occupational Safety and Health (NIOSH) established a recommended exposure limit of 0.5 mg/m^3 as the TWA over a 10-hour workday for airborne exposure to TNT [68].

TNT in bulk and in cased munitions is a United Nations Hazard Division 1.1 Explosive (not a flammable solid), and an EPA Resource Conservation and Recovery Act (RCRA) D003 (reactive) waste for military munitions containing TNT [67]. Numerous states have established regulations on explosives for air quality control, solid waste disposal, storage, manufacture and use [65].

3.6 DATA GAPS

Literature reviews revealed several data gaps associated with fate and degradation of TNT. Specific gaps found were also associated with physical and chemical properties of TNT and its degradation products, their propensities to accumulate in the environment and their potential toxic effects. The list below details selected gaps.

A. Fate and Transport

- **TNT Degradation Products:** A complementary set of data is needed on the TNT degradation products, including, but not limited to, 2-A-4,6-DBA, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT. Specific data on the fate, transport, and toxicity of these compounds are, at best, incomplete, or, at worst, completely lacking. Additionally, laboratory standards do not exist to look for all of the DNT isomers and 2-A-4,6-DBA. It is known that these derivatives could accumulate and persist in the environment due to the lack of available degradation pathways. Addressing this data gap could especially be critical to environmental fate studies and toxicity analyses because, in some instances, TNT levels may be below the regulatory limits (thus not raising cause for concern); however, levels of the degradation products, with yet-to-be-determined toxicity and possibly poor transport properties, may be high.

B. Toxicity. Despite considerable attention to assess ecotoxicity of TNT degradation byproducts, only a few studies were designed to specifically meet the EPA criteria for derivation of toxicity benchmarks acceptable for Eco-SSL development. Future research should include determinations of synergistic ecotoxicological effects of frequently used combinations of energetic materials. Additional research efforts should also focus on assessment of effective biological accessibility of such mixtures and resulting transformation products over time, since these may have the greatest long-term effects on the ecosystem and environment.

- Only acute toxicity data for TNT and byproducts are available for mammals and for salamanders. No data are available for birds, reptiles, or other species of amphibians. Long-term (i.e., subchronic to chronic) oral toxicity testing is needed for all vertebrates, and acute data are needed for birds and other species of mammals (non-rodent). In addition, metabolic data that provide evidence of bioavailability of both compounds is needed.

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4. OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX)

4.1 INTRODUCTION

Figure 4-1. Chemical Structure of HMX

Names: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
Abbreviations and Other Names: octogen, High Melting eXplosive, Her Majesty's eXplosive, High-velocity Military eXplosive, or High-Molecular-weight RDX
CAS No.: 2691-41-0
Chemical Formula: $C_4H_8N_8O_8$
Occurrence in Mixtures/Compositions: Primarily used in Octol and several polymer-bonded explosive mixtures (e.g., LX-14 and PBXN-102)
Natural Occurrence: HMX is a man-made chemical; thus, there is no information on its natural occurrence in water or soil matrices.
Physical/Chemical Properties: The physical/chemical properties of HMX are listed in Table 4-1.

Table 4-1. Physical and Chemical Properties of HMX [1, 2]

Property	Value	Units
Color	White	None
Odor	Odorless	None
Physical state	White crystalline solid	None
Melting temperature	279.5 - 280	°C
Vapor pressure (@ 20°C)	< 1.0e-16	atm
Specific gravity	1.91	None
Water solubility (@ 20°C)	4.5	mg/L
Dissolution rate in water (@ 30°C)	0.29	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log Kow)	0.17	None

4.2 FATE

4.2.1 Relevant Properties

HMX, also referred to as cyclotetramethylenetetranitramine or octogen, is commonly used in several military explosive formulations. HMX is typically mixed with other explosives, such as TNT, or used as the main explosive ingredient in plastic explosive formulations. Typical HMX percentages are in the range of ≈ 70 to 90% of the formulation by mass. For example, LX-14-0 contains 95.5% HMX and 4.5% polyurethane and most octol formulations are either 70% HMX / 30% TNT or 75% HMX / 25% TNT. It is also present in RDX as an impurity resulting from synthesis and processing methods. Some data are available regarding the fate, transport, and toxicity of HMX. However, since it is not used as frequently or in as many formulations as TNT or RDX, the amount of data available for HMX is not as large as that for TNT and RDX. HMX,

like RDX, is in the class of nitramine explosives, which are distinguished from other explosive classes (e.g., nitroaromatics) in that they contain nitro groups bonded to an amine functional group.

Chemically, HMX comprises an eight-membered ring of alternating carbon and nitrogen atoms with a nitro group attached to each nitrogen atom in the ring [1] (Figure 4-1). This is comparable in structure to RDX, which comprises a six-membered ring of alternating carbon and nitrogen atoms. As a result, HMX has chemical and physical properties similar to RDX. In its pure form, HMX is a non-descript, odorless, white powder. In use, it is typically press-loaded into explosive formulations or mixed as a solid slurry component of cast-loaded explosive formulations. HMX possesses a higher melting temperature (hence HMX standing for High Melting eXplosive in some instances); lower degree of water solubility; higher water dissolution rate; and smaller octanol-water partition coefficient than RDX.

4.2.2 Photolysis

HMX undergoes photolysis when dispersed or deposited (e.g., through advection) into surface waters such as lagoons and rivers [2, 3]. However, photolysis of HMX has been shown to occur at very slow rates. Nonetheless, photolysis and biodegradation have been identified as the two major transformation processes of HMX [4]. Because photolysis is dually identified as a main transformation pathway and a slow process, HMX is expected to persist in the environment. Data on the photolysis rates for HMX in rivers and lagoons [3] suggest that the half-lives for HMX can range from 17 days to 7,900 days. The specific half-life value is highly dependent on the depth of HMX within the aqueous matrix; the ability of sunlight to penetrate to these depths; and turbidity of the water. The photolysis half-life is expected to be longer than the half-life for biodegradation of HMX in water (≈ 1.76 days) and soil (≈ 7.39 days).

In comparison to RDX, the rate of photolysis for RDX is reportedly nearly three times that of HMX, possibly as a result of the great molar absorptivity of RDX [2, 3]. However, HMX and RDX were found to have similar photolysis-driven degradation rates when exposed to ultraviolet (UV) light and ozone [2].

End products of HMX photolytic degradation include nitrate (NO_3^-), nitrite (NO_2^-), and formaldehyde (CH_2O) [3]. The mono-, di-, and tetranitroso-derivatives of HMX were suspected in laboratory analyses; however, the identification of these compounds was not confirmed and are thought to be present only as intermediate reaction species [3]. The results from these photolysis studies on HMX also show that it is difficult to develop a conclusive pathway for HMX photolytic degradation, as secondary reactions from the photolysis of NO_3^- and NO_2^- interfere with the analysis of the initial steps in HMX photolysis [3].

4.2.3 Other Abiotic Reactions

Very little data are available on abiotic reactions of HMX in the environment [5]. The available data suggest that TNT, RDX, and HMX can be reduced by iron in the form of magnetite and ferrous iron, however, the rates of abiotic reduction for HMX by these processes is significantly less than those for TNT and RDX and are likely to be slower than biodegradation of HMX and possibly slower or on the same timescale as photolysis of RDX. The abiotic reduction of HMX

can be increased through the application of cationic surfactants, which act to increase the solubility of HMX [6].

4.2.4 Biodegradation

Several studies reported biodegradation of RDX and HMX under both anaerobic and aerobic conditions using anaerobic sludge [7], consortia, or specific isolates [8-10]. More recent laboratory work demonstrated that initial enzymatic attack by anaerobic bacteria (from a municipal sludge) leads to complete destruction of the two cyclic nitramines [11]. The microbial degradation rates of HMX are species and microbial community specific. For example, the aerobic bacteria of genus *Methylobacterium* transform HMX in less than 10 days [12] , while marine sediment communities mineralized HMX in 115 days in the presence of a carbon source [13].

Hydroxyalkylnitramines are known to be unstable in water and exist as equilibrated mixtures with their dissociated products HCHO and NH_2NO_2 [10]. The two toxic metabolites methylenedinitramine and bis(hydroxymethyl)-nitramine do not represent the only HMX ring cleavage products. None of the HMX ring cleavage products accumulated indefinitely and all disappeared and produced predominantly formaldehyde (HCHO) and nitrous oxide (N_2O).

Several studies to date, including anaerobic sludge, have demonstrated that once the HMX undergoes a change in its molecular structure, the ring collapses to produce small nitrogen-containing (N_2O, NO_2, NH_3) and small carbon-containing (HCHO, HCOOH and CO_2) products [14]. This behavior is distinguishable from that of the aromatic compound TNT, which is biotransformed under several aerobic and anaerobic conditions to produce stable intermediates (amines, acetyl derivatives, azo and azoxy compounds) while maintaining its stable aromatic ring structure [15-17]. Once the weak –N-N- bond in HMX is cleaved, the remaining chemical bonds become much weaker, causing rapid molecular decomposition involving ring cleavage of the molecule [9]. Figure 4-2 presents the possible biodegradation routes for HMX.

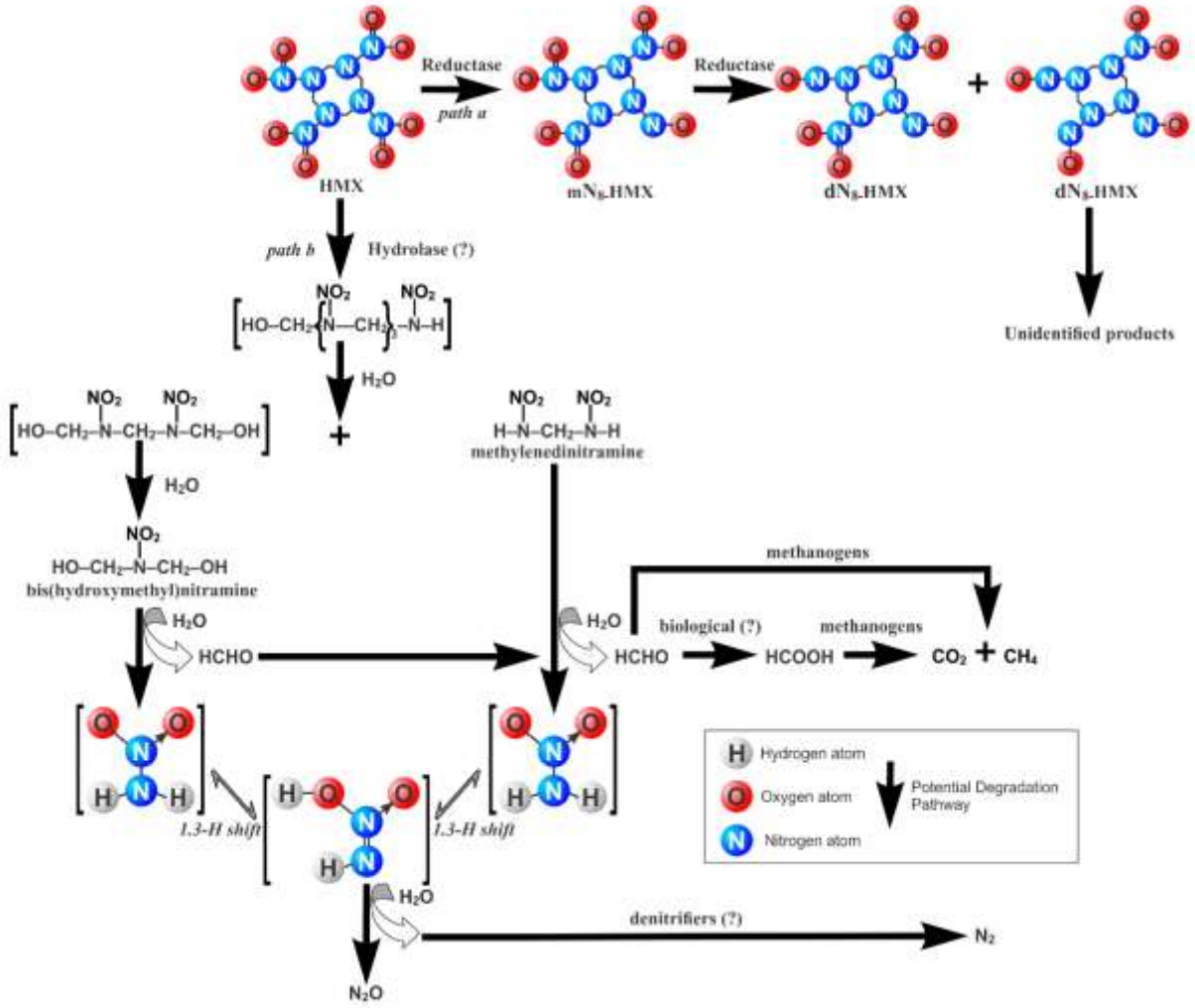

Figure 4-2. Potential Biodegradation Routes of HMX during Treatment with Anaerobic Sludge [14, 18]

Path a: reduction via nitroso route to unidentified products. **Path b**: ring cleavage followed by competing chemical and biochemical transformations. A square bracket indicates unidentified product whereas a question mark indicates potential presence that requires further experimental verification. Italicized products on the right-hand side are those detected earlier by [18].

4.2.5 Hydrolysis

There is very little information available on the hydrolysis of HMX and hydrolysis therefore is not considered a significant degradation pathway [4]. It is possible for HMX to undergo hydrolysis under alkaline conditions (pH > 10), but at a very slow rate with a half-life of ≈ 288 days [19].

Some data are available on the products that could be formed via the hydrolysis of HMX [5, 20]. The formation of ammonia (NH_3), nitrogen dioxide (NO_2), nitrous oxide (N_2O), and formaldehyde have been shown to occur from the hydrolysis of HMX at pH values ranging from 11 to 13. At a pH value of 10, 4-nitro-2,4-diazabutanl (NDAB) can also be produced.

4.2.6 Key Degradation Products

HMX exhibits a high degree of stability in the environment. The available studies on HMX fate in the environment have identified NO, N_2O, NO_2, NH_3, formic acid, formaldehyde, and CO_2 as the typical end products of degradation and transformation. Biodegradation appears to be the most significant pathway for HMX degradation, with photolysis identified as the other main pathway; data on abiotic reduction suggest this rate is slow enough to be considered insignificant. However, the rates for photolysis, as reported, are extremely slow, especially when compared to those for TNT and RDX. It would appear from the available data that HMX is expected to be much more stable in the environment than TNT and RDX, all factors being equal.

4.3 TRANSPORT

4.3.1 Transport Processes

Several studies on the transport of HMX in the environment from explosively contaminated training ranges suggest that HMX, along with RDX, appear to be the most mobile in the environment out of all of the explosives present at these ranges [2-5, 15, 21]. This mobility of HMX in the environment is a result of its low values for solubility (4.5 mg/L), dissolution, and partitioning (i.e., low probably of sorption into soils). Transport studies summarized by Pichtel [5] showed that HMX and RDX penetrated deeper into soils at various sites (Fort Greely, Fort Bliss, Fort Lewis, and others) than TNT, and that HMX and RDX have been identified in the groundwater at these sites, whereas TNT was not. This can be attributed to the high degree of mobility and recalcitrance of HMX to undergo transformation processes.

Similar to the transport processes for RDX, HMX transport is a function of the specific formulation in which it is used. HMX can be mixed with binders, waxes, and plasticizers, which can delay direct transport to the environment.

4.3.2 Transport in Soil

Transport of HMX through soil is dependent on sorption and desorption processes. If these processes are insignificant (i.e., the rates are low), then transport through the soil is primarily driven through advection via surface water bulk flow to the groundwater. Studies [2, 19] have shown that the sorption and desorption of HMX and RDX in soil are highly dependent on soil content. HMX has been shown to sorb to high clay content soils (i.e., K_d^S values of 8.0 L/kg in soil with > 87% clay content and insignificant total organic content versus 2.5 L/kg in soil with 4% clay content and 8.4 % total organic content) [19].

Work performed by Pennington et al. [21] confirms the reluctance of HMX to sorb to soil. It seems that the HMX only slowly dissolves into water, then may be transported through vadose zones to groundwater aquifers. Otherwise, HMX may persist on subsurface soil, where anaerobic degradation can take place [19].

4.3.3 Transport in Water

The water solubility of HMX (4.5 mg/L) is less than that of RDX (47 mg/L) and TNT (130 mg/L). This solubility value, taken into consideration along with the low dissolution rate in water (0.29) and poor sorption to soil as noted above, renders HMX likely to migrate through the soil and to

the groundwater after dispersion into the environment. The hydrolysis and photolysis rates for HMX are low. Furthermore, studies have shown that HMX has been found in groundwater below several training ranges, while TNT has not [4, 5, 21]. Thus, HMX is expected to be both stable and mobile in aqueous matrices. Given the low values of solubility and dissolution rates, advection of HMX is more likely to occur.

Two surveyed reports described the propensity for HMX to reach groundwater at areas where explosive use is high (e.g., training ranges) and the probability for dispersion into the environment exists [22, 23]. HMX and explosive contamination in general is not expected to leave the range footprint [23, 24]. HMX concentrations in the groundwater from one study conducted at the Arnhem Firing Range [23] were found to be less than the U.S. EPA guideline for drinking water (400 µg/L), with values as high as ≈ 92.0 µg/L. HMX transport in water was also found to be advection-driven, with low propensity for sorption, biotransformation, or aerobic mineralization. HMX dispersed onto this site remained in the crystalline phase in the impact location, dissolving into the regional aquifer at a rate of ≈ 2 to 3 g/day [23]. At Camp Edwards, concentrations of HMX in groundwater were found to be 0.02 to 0.6 mg/L [22], with unreacted HMX reaching the groundwater system as a result of partial detonations from blow-in-place operations. The results from these studies show that HMX can reach and contaminate groundwater, though ultimately it is a function on how much unreacted HMX, on average, is available.

4.4 TOXICITY DATA OF HMX

Little information is available about the potential negative health effects of HMX on humans. In one human study, no negative health effects were reported in workers who breathed HMX [25]. However, the concentrations of HMX in the workplace air were not reported and the study was limited to a small number of workers.

Studies in rats, mice, and rabbits indicate that HMX is poorly absorbed by the body following oral exposure, but may be harmful to the liver and the central nervous system if it is swallowed in very high doses. Studies conducted on animals suggest HMX is a mild skin irritant, but it is unlikely to cause any allergic reactions from skin contact and it is not irritating to the eyes [26]. No information is currently available about whether HMX can negatively affect reproduction or cause birth defects.

The U.S. EPA LHA for drinking water level of 400 µg/L was set as a protective measure in an abundance of caution since very little study of this explosive has been conducted, even though there are no known negative health effects to humans from exposure to HMX.

4.5 EXAMPLE REGULATORY GUIDELINES FOR HMX

U.S. EPA has established a LHA guidance level of 400 µg/L for HMX in drinking water. To date, HMX has not been detected above this lifetime guidance level at military installations subjected to groundwater studies. U.S. EPA and the Massachusetts Department of Environmental Protection have not established an ambient air level for HMX or a cleanup standard for HMX in soil.

4.6 DATA GAPS

In terms of data gaps, the general challenge with HMX appears to be ways to trigger and accelerate the degradation of HMX to its end decomposition products. Several studies make note of the stability and mobility of HMX in the environment and low rates of degradation. The water mobility of HMX and toxicity of cyclic nitramine explosives in particular to aquatic organisms introduces a level of urgency for addressing this challenge.

A. Fate and Transport

- **Abiotic Reduction**: There is a need to define potential means to trigger and/or accelerate abiotic reactions of HMX, since all appear to be slow compared to RDX and TNT. Moreover, information on stability and mobility of HMX in the environment needs to be generated in order to predict its transport in different media. Another great need to address relies on microbial degradation of HMX in sediments which in turn serves to determine the potential for the occurrence of natural attenuation. This improved knowledge would aid remediation efforts to mitigate HMX water mobility/access.

B. Toxicity. Toxicity data on HMX degradation byproducts need to be generated to establish their regulatory limits.

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5. 1,3,5-TRINITROPERHYDRO-1,3,5-TRIAZINE (RDX)

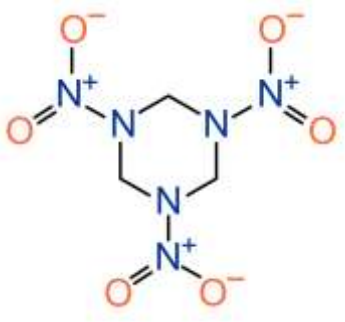

Figure 5-1. Chemical Structure of RDX

5.1 INTRODUCTION

Names: 1,3,5-Trinitroperhydro-1,3,5-triazine

Abbreviations and Other Names: Cyclonite, hexogen, 1,3,5-Trinitro-1,3,5-triazacyclohexane, 1,3,5-Trinitrohexahydro-s-triazine, Cyclotrimethylenetrinitramine, Hexahydro-1,3,5-trinitro-s-triazine, Trimethylenetrinitramine

Chemical Formula: $C_3H_6N_6O_6$

CAS No.: 121-82-4

Occurrence in Mixtures/Compositions: Composition A, B, C, CH-6, Cyclotol, HBX, H-6, PBX, Semtex, Torpex

Physical/Chemical Properties: The physical/chemical properties of RDX are listed in Table 5-1.

Table 5-1. Physical and Chemical Properties of RDX [1]

Property	Value	Units
Color	White	None
Odor	Odorless	None
Physical state	White crystalline solid	None
Melting temperature	203.3 - 205	°C
Vapor pressure (@ 20°C)	< 5e-12	atm
Specific gravity (@ 20°C)	1.81	None
Water solubility (@ 20°C)	47	mg/L
Dissolution rate in water (@ 30°C)	0.096	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log Kow)	0.87	None

5.2 FATE

5.2.1 Relevant Properties

RDX, also referred to as cyclotrimethylenetrinitramine, cyclonite, or hexogen, is a commonly used military and commercial demolition explosive. RDX is typically mixed with other explosives or waxes and binders to make formulations such as C-4, Semtex H, and sheet explosives.

Typical RDX percentages are in the range of ≈ 50 to 95% of the formulation by mass. For example, Composition B contains 59.4% RDX, 39.6% TNT, and 1% wax; C-4 contains 91% RDX, 5.3% bis(2-ethylhexyl) adipate, 2.1% polyisobutylene, 1.6% oil, and 0.1% dimethyldinitrobutane. Due to its frequent and long-term use in both military and industrial applications, much data are available regarding the transformation, degradation, and biological effects of RDX. RDX falls into

the class of nitramine explosives, which are distinguished from other explosive classes (e.g., nitroaromatics) in that they contain nitro groups bonded to an amine functional group. Other nitramine explosives include HMX, tetryl, and nitroguanidine. RDX will therefore exhibit general chemical degradation and toxicity effects inherent to the nitramine class of explosives.

Chemically, RDX comprises a six-membered ring of alternating carbon and nitrogen atoms, with a nitro group attached to each nitrogen atom in the ring [1] (Figure 5-1). Physically, in its pure form, RDX is a non-descript, odorless, white powder [2]. It is typically either press-loaded into explosive formulations (e.g., C-4) or mixed as a solid slurry component of cast-loaded formulations (e.g., Composition B) [3]; therefore, the time required for RDX to diffuse or separate out from other ingredients present in its formulation (e.g., wax binders) and into the environment should be taken into account. HMX can also be present in RDX as an impurity resulting from processing methods and manufacturing techniques; military-grade RDX contains approximately 10% HMX by weight [4].

Values for the water solubility, dissolution rate, and octanol-water partitioning coefficient (log K_{ow}) imply, respectively, that RDX is only slightly soluble in water; slow to dissolve in water; and more likely to be found in water than organic material. These values presented in Table 5-1 and discussed in detail in this report have been collected from previous relevant laboratory and field studies to provide a guide for the environmental fate of RDX starting from its dispersion in the environment, be it water or soil matrices, through its transport processes, and ending at the fate and degradation.

5.2.2 Photolysis

One recent study [5] investigated the data gaps of RDX photolysis rates and products formed in aqueous solution versus solid state, and the factors influencing photolytic degradation in direct sunlight. Most photolysis studies on RDX involved laboratory studies of RDX in solution and exposed to simulated sunlight or set wavelengths of light; only a few studies have explored photolysis of dissolved or solid RDX under exposure to natural sunlight. Bordeleau et al. [5] conducted outdoor photolysis experiments with aqueous and solid RDX samples at a northern latitude, in an effort to better understand the noted variables affecting RDX photolysis for the improvement of existing reaction rate numerical models.

The results showed that aqueous RDX samples underwent photolytic degradation ≈ 50 to 100 times faster than solid RDX particles. Half-lives for dissolved RDX particles were in the range of 0.8 days (for July time period) to 2.5 days (for October time period). The half-life for solid-state RDX particles ranged from 76 days (for moist sand) to 103 days (for dry sand). In comparison, biodegradation half-lives for RDX in water and soil are ≈ 1.89 and 6.22 days, respectively. Photolysis half-lives for RDX are dependent on several factors such as soil type, time of year, and average cloud cover. Variables such as the spectral intensity of the sunlight, latitude, altitude, plant cover, and average amount of cloud cover could have significant impacts on the photolysis rates, implying that training ranges in northern latitudes (e.g., Canada and Europe) contaminated with RDX may have a data set for photolytic degradation of RDX that is distinct from a data set taken from a southern latitude site.

Different products of photolytic degradation of RDX may form, depending on the wavelength of light exposure [6]; however, there appears to be no known mechanism proposed to link the products formed to specific light wavelengths, and this is a technical data gap. What is proposed, though, is that RDX photolysis can produce ammonia (NH_3), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), formaldehyde (CH_2O), formic acid (CH_2O_2), and *n*-nitroso-methylenediamine via photolysis [5-7] and that the photolysis of RDX starts with cleaving of the N-N bond [8].

5.2.3 Other Abiotic Reactions

Abiotic reduction of RDX is thought to require activation via a catalyst, including iron compounds, minerals found in clay, organic molecules [6], and sulfides [9]. Reduction of RDX by zero valent iron and iron (Fe^{2+}) in aqueous suspensions of magnetite has been documented [6, 10], producing hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX); hexahydro-1,3-dinitroso-5-nitro-1,3,5- triazine (DNX); and hexahydro1,3,5-trinitroso-1,3,5-triazine (TNX) in a step-wise reduction process. Negligible reduction of RDX occurred in aqueous suspensions of Fe^{2+} or magnetite alone. Half-life values were in the range of ≈ 20 to 30 hours, with higher concentrations of Fe^{2+} producing shorter half-life values.

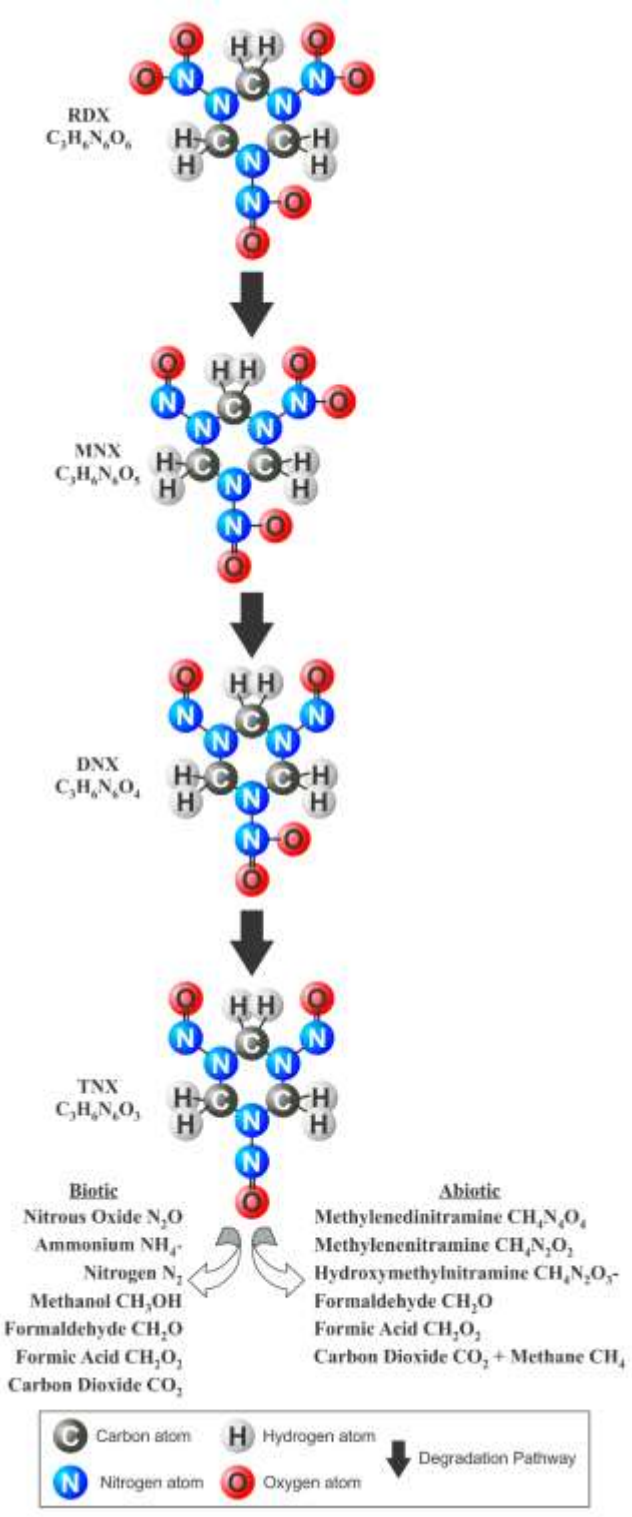

Figure 5-2. RDX Biodegradation Pathway

Sample analyses from these same tests with iron (Fe^{2+}) in an aqueous suspension (representative of anoxic sediments or engineered environments where Fe^{2+} is abundant) of magnetite suggest that these MNX, DNX, and TNX "intermediate" products can undergo further transformation in these solutions, resulting in the production of ammonium (NH_4^+), N_2O, and formaldehyde. Additional analysis of zero valent iron (Fe^0) has also demonstrated the potential to reduce RDX in both soil and aqueous matrices [6, 10].

NH_4^+ was produced as an end product in these experiments; the levels of the intermediate compounds MNX, DNX, and TNX (Figure 5-2) disappeared completely within 96 hours. In a study of RDX degradation in the presence of carbonate and sulfate green rusts, formaldehyde, N_2O, and NH_4^+ were identified as the end products of degradation.

The presence of RDX intermediate versus end products appears to be environment-dependent. Field studies [11] have shown that TNX is stable in field soil samples and MNX and DNX were shown to be stable in field soil samples except for soils with high clay, high organic content. One report [12] suggested that methylenedinitramine (MDNA) can also be produced as an intermediate product in the abiotic reduction process.

The main takeaway from these studies is that MNX, DNX, TNX are formed from RDX degradation via abiotic processes. These products can be further transformed to other compounds if certain conditions are satisfied, or if additional biotic processes, hydrolysis or photolysis factors are present.

5.2.4 Biodegradation

There is little existing information regarding biodegradation of cyclic nitramines such as RDX, pertaining to ring cleavage products, the enzymes and the metabolic pathways that lead to their formation [13, 14, 15]. RDX and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine) are reportedly degraded by anaerobic sludge [15]; under nitrate-reducing, sulfidogenic, and/or methanogenic conditions; by specific isolates or by consortia [16]. A pathway based on the sequential reduction of RDX to MNX, DNX, and TNX was suggested (Figure 5-2) and the nitroso compounds were proposed to undergo further transformation to unstable hydroxylamino-RDX derivatives, which subsequently undergo ring cleavage to eventually yield HCHO, CH_3OH, NH_2NH_2, and $(H_3C)_2NNH_2$.

RDX biotransformation reactions occur via co-metabolic processes under anaerobic conditions [16]. As with most other cases, the co-metabolic degradation rate of RDX is much slower than the direct metabolism of the compound [17].

Metabolites may undergo further reduction prior to ring cleavage and transform into toxic hydroxylamino-RDX intermediates, which in another ring cleavage reaction may yield formaldehyde, methanol, hydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine.

5.2.5 Phytotransformation

Laboratory studies on the uptake and transformation of RDX by plants have been completed on plant types including, but not limited to, reed canary grass [18]; poplar trees [18]; and parrot feather grass [19]. Yoon et al. [20] summarize these studies and state that RDX is typically absorbed into the plant via the root system, then translocated to the leaves. The data summarized by Yoon et al. and cited from a study by Thompson et al. [21] note that this translocation process occurs much more readily for RDX (60% of RDX taken up by poplars was found in the leaves of poplar trees after 2 days) than it does for TNT (78% of TNT taken up by poplar trees remained in the roots). Field studies [22] have also confirmed this uptake and translocation to the leaves.

Upon RDX translocation to leaf tissues (which can take ≈ 2 days), RDX can undergo reduction and photolysis reactions [18], which occur at similar rates (i.e., days) and the latter of which is driven particularly by unabsorbed UV light that penetrates the tissues [18]. A three-step process for RDX degradation within plant leaves has been suggested for these degradation mechanisms [18]. The first step involves reduction of RDX to MNX and DNX, regardless of the presence of light; these products are also what can be formed from abiotic iron reduction. From there, in the second step, photolysis reactions transform the MNX and DNX to formaldehyde and methanol. In the final step, mineralization of one-carbon metabolites occurred. Data from studies using reed canary grass [18] suggest that this RDX photolysis in plant tissue can also result in the formation of N_2O, NO_2^-, and formaldehyde, which is to be expected given the discussions on the known products of RDX photolysis. The presence of 4-NDAB in plant tissues was also detected under simulated sunlight.

The fate of RDX in plant rhizospheres has also been recently studied [23]. Data showed that plants grown in soil inoculated with *Ps. fluorescens* with *xplA* contained approximately 30% less RDX than control soil samples. Field soil samples taken from Eglin Air Force Base showed that RDX degradation activity was favored with the addition of exogenous carbon sources to the soils. The results from laboratory experiments suggest that bioaugmentation (with *xplA*-enabled species) and biostimulation (with exogenous carbon sources) are useful methods for RDX degradation in the rhizosphere. Otherwise, without both of these factors, RDX deposited on soils is likely to migrate into the subsurface.

5.2.6 Hydrolysis

Amine-based compounds, including nitroamine explosives, can undergo hydrolysis. Hydrolysis of RDX has been reported [24] in alkaline solutions at pH levels greater than 10, forming end products including NO_2^-, formaldehyde, formic acid (CH_2O_2), NH_3, and N_2. The half-life of this process is ≈ 100 hours, slower than aqueous photolysis and biodegradation.

The hydrolysis of RDX in an aqueous solution involves denitrification, accompanied by formation of nitrite and formation of the key ring cleavage product 4-nitro-2,4-diazabutanal (4-NDAB), with the remaining carbon and nitrogen content accounted for in the formaldehyde, formic acid, N_2O, and NH_3 products. The RDX degradation intermediate MNX also undergoes hydrolysis via denitrification to produce NO_2^-, followed by ring cleavage and denitrification to N_2O, formaldehyde, and 4-NDAB. The half-life of this reaction is ≈ 10 hours.

5.2.7 5.3 Key Degradation Products

The intermediate and final products resulting from RDX hydrolysis, photolysis, and biotransformation reactions are similar [6], thus isolating the effects of one degradation process from another based on the end products present. The main difference among these degradation pathways is the rate at which these reactions and processes occur. MNX, DNX, TNX, and possibly MDNA can be formed as intermediate products during RDX degradation. End products of RDX degradation include formaldehyde, formic acid, N_2O, and NH_3, which are all common, characterized compounds. Fate, transport, and toxicity data on these end products are available and well-researched.

5.3 TRANSPORT

5.3.1 Transport Processes

RDX has been used as an explosive material dating back to World War II. Its release to the environment, either at training ranges or manufacturing plants in the United States, has resulted in concentration levels as high as 30 mg/L in groundwater systems and 13,900 mg/kg in soils [4]. Energetic materials are transported through the soil (via absorption) or water (via dissolution). In general, volatilization of energetic materials, including RDX, is not expected to occur as a result of their extremely low vapor pressure values.

RDX transport in the environment is linked to the mass of starting material released to the environment. Ammunition factories that continuously process and work with RDX, for example, can have significant groundwater impacts as compared to training ranges in which low concentrations of unreacted RDX are dispersed into the environment. However, if dispersed in large enough quantities, RDX can pose a risk of migrating offsite due to its high mobility, resulting from low values for dissolution rate and octanol-water partition coefficient, and slight solubility in water. RDX is expected to travel with flowing water sources (including runoff) via advection. A comparison to this propensity for mobility can be made to TNT, which possesses a higher octanol-water partition coefficient value than RDX, implying that TNT more readily binds to organic matter and is less likely to migrate upon dispersion into the environment; i.e., it is more likely to be subjected to soil attenuation processes [6, 11, 20].

RDX transport is also a function of the specific formulation within which it is used. RDX is typically mixed with binders, waxes, and plasticizers which may inhibit access of water to the RDX particles, or release of RDX particles from the formulation [25].

5.3.2 Transport in Soil

RDX sorption is insignificant [11, 25, 26], though RDX has been noted to partition to organic content (log $K_{oc} \approx 0.88 - 2.44$) and not sorb significantly to clay soils [27]. RDX is generally expected to be highly mobile through soil systems [6]. How quickly and widespread the RDX is dispersed within a given soil matrix is dependent on several factors, including, but not limited to: the amount of starting, unreacted RDX dispersed into an environment through, for example, a low-order detonation; the other ingredients present in the energetic formulation that may impede the mobility of RDX; the amount of rainfall or access to water within the dispersed environment; the rates of dissolution and propensity for RDX particle advection; and the sorption of RDX into soil.

Starting with dispersed RDX at the soil surface, some RDX may be moved throughout or within the soil via fluid advection, or through dissolution in water. Due to the relatively low solubility of RDX in water and low dissolution rates, dispersed RDX is expected to be continuously released to the environment over an extended period of time [6]. For a comparison to the transport processes for other energetic materials, the rates of dissolution follow the order TNT > HMX > RDX. Likewise, the octanol-water partition values for these energetic materials are in the order TNT > RDX ≈ HMX. As a result, in transport studies [11], HMX and RDX penetrated deeper into soils than did TNT, and RDX and HMX were found in groundwater samples below several training ranges, whereas TNT was not.

5.3.3 Transport in Water

RDX is expected to be transported to water systems where it can undergo photolysis reactions; however, this depends on the depth within the water system and the availability of the sunlight to penetrate to such depths [1]. Thus, RDX that is deposited in aqueous matrices devoid of or lacking exposure to sunlight may persist for a long duration, unless biodegradation pathways are available or the alkalinity of the water system promotes hydrolysis (although this reaction is significant at pH > 10).

From the range studies conducted in the surveyed literature, the propensity for RDX to reach groundwater appears to depend significantly on the type of activity occurring at the site [28-30]. RDX has not been found at many training ranges in significant quantities (i.e., $\approx < 0.05$ µg/L) or to leave the range footprint [29, 30], although RDX was found in groundwater samples at Camp Edwards at higher concentrations (i.e., 0.4 to 8.9 mg/L) [28]. The results from these studies show that RDX can reach and contaminate groundwater, though ultimately it is a function of how much unreacted RDX, on average, is available. Ranges where live-fire testing takes place typically have a smaller concentration of unreacted RDX compared to an ammunition factory where pristine RDX is routinely handled, processed, or disposed of, or blow-in-place operations where unreacted RDX from partial detonations can reach the groundwater [29].

5.4 TOXICITY DATA OF RDX

Potential exposure to RDX could occur by dermal contact or inhalation exposure; however, the most likely route of exposure is ingestion of contaminated drinking water or agricultural crops irrigated with contaminated water [31]. The U.S. EPA has assigned RDX a weight-of-evidence carcinogenic classification of C (possible human carcinogen) based on the presence of hepatocellular adenomas and carcinomas in female mice that were exposed to RDX [32]. For the general population, including children, exposure to RDX is limited to areas around Army ammunition plants where it is manufactured, used in munitions, packed, loaded, or released through the demilitarization of antiquated munitions [33, 34]. The most likely route of exposure is ingestion of contaminated drinking water or agricultural crops irrigated with contaminated water. Exposure can also occur through dermal contact with soil containing RDX or by inhaling contaminated particulate matter produced during incineration of RDX-containing waste material.

Occupational exposure to RDX can occur when workers handle RDX at Army ammunition plants. Under these conditions, exposure can occur as a result of release of dust into the workroom air, principally during dumping of dried RDX powder, screening and blending, and cleanup of spilled material. Exposure to RDX can also occur through dermal contact during manufacture, handling, and cleanup of RDX. RDX was detected at a concentration of 0.052 mg/m^3 (0.47 ppm) in the particulate fraction of only one of eight indoor air samples taken from the incorporation area of Holston Army Ammunition Plant in Tennessee in 1986. Based on the observed concentration, the potential for exposure to RDX is considered to be negligible [34].

There is limited information on the toxicity of RDX in humans with the majority of data focusing on studies of workers exposed to RDX dust, soldiers using C-4 (a plasticized explosive containing 91% RDX) as a cooking fuel, and case reports of individuals ingesting RDX. Detected neurologic dysfunction, primarily seizures and convulsions, was the most commonly reported effect.

Additionally, studies in laboratory animals support neurological effects as a sensitive end point of RDX [35]. Seizures, convulsions, and tremors have been reported in rats, deer mice, dogs, and monkeys orally exposed to RDX for acute, intermediate, or chronic durations. In addition to these neurological effects, decreases in motor activity and impaired learning were observed in rats following administration of a single gavage dose of 12.5 mg/kg/day; however, no alterations in motor activity were observed in rats administered 10 mg/kg/day for 16 or 30 days [35].

The animal data suggest that there may be other targets of RDX toxicity, including the hematological system and liver following oral exposure [36]. Small, although significant, decreases in hemoglobin and erythrocyte levels were observed following intermediate-duration exposure, but this was not consistently found in other intermediate or chronic studies. Several studies found minor changes in serum chemistry parameters suggestive of a slight impairment of liver function.

The carcinogenic potential of RDX was evaluated in orally exposed rats and mice; no evidence of carcinogenicity was observed in two rat studies. In mice, an increase in the combined incidence of hepatocellular adenomas and carcinomas was observed in females only. However, a re-evaluation of these data using current diagnostic criteria resulted in a reclassification of some hepatocellular adenomas as foci of cytoplasmic alterations [37]. As a result of the re-analysis, the combined incidence was significantly higher than concurrent controls at 35 mg/kg/day, but not at 100 mg/kg/day and the incidence in the 35 mg/kg/day group was within the range of historical control data. The investigators suggested that the study provided equivocal evidence of carcinogenicity.

5.5 EXAMPLE REGULATORY GUIDELINES FOR RDX

In 1993, the U.S. EPA assigned RDX a chronic oral reference dose (RfD) of 3×10^{-3} milligrams per kilogram per day (mg/kg/day) [32] and the Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.2 mg/kg/day for acute-duration oral exposure (14 days or less), 0.1 mg/kg/day for intermediate-duration oral exposure (15 to 364 days) and 0.1 mg/kg/day for chronic-duration oral exposure (365 days or more) to RDX [38].

Additionally, the U.S. EPA has assigned an oral slope factor for carcinogenic risk of 0.11 mg/kg/day, and the drinking water unit risk is 3.1×10^{-6} micrograms per liter (µg/L) [32]. Data from the risk assessments indicated that the drinking water concentration representing a 1×10^{-6} cancer risk level for RDX is 0.3 µg/L. Thus, the U.S. EPA has established drinking water health advisories for RDX, which are drinking water-specific risk level concentrations for cancer (10^{-4} cancer risk) and concentrations of drinking water contaminants at which noncancer adverse health effects are not anticipated to occur over specific exposure durations [39].

The LHA guidance level for RDX in drinking water was established at 0.002 milligrams per liter (mg/L). The health advisory for a cancer risk of 10^{-4} is 0.03 mg/L. The U.S. EPA also established a 1-day and 10-day health advisory of 0.1 mg/L for RDX in drinking water for a 10-kilogram child. For RDX in tap water, U.S. EPA has calculated a screening level of 0.61 µg/L [40]. The U.S. EPA included RDX on the third Contaminant Candidate List, which is a list of unregulated contaminants that are known to or may occur in drinking water and may require regulation under the Safe Drinking Water Act [40].

Moreover, numerous states have established regulations on explosives for air quality control, solid waste disposal, storage, manufacture and use. Regulatory agencies in states such as Colorado and New York have specified RDX cleanup levels for water of less than 1 part per billion (ppb) [41]. The State of Massachusetts has established a reportable concentration of 0.001 mg/L for the GW-1 category (based on the use of groundwater as drinking water) and 50 mg/L for the GW-2 category (based on the potential for volatile material to migrate into indoor air). For soil, Massachusetts established a reportable concentration of 1 mg/kg for the S-1 category (based on sensitive uses of the property and accessible soil) and 60 mg/kg for the S-2 category (based on property uses associated with moderate exposure and accessible soil) [42].

5.6 DATA GAPS

Previous research has been greatly expanded in the area of fundamental understanding on how RDX behaves in soil. This research has resulted in some new treatment technologies. However, ongoing testing and training with legacy munitions continues to contaminate soil. In terms of data gaps, the general challenge with RDX appears to be related to its biotic degradation. Although the basic knowledge governing the environmental fate of RDX is known, accurate predictions of RDX's persistence in soil remain elusive. Moreover, more work needs to be performed to understand toxicity of its byproducts.

A. Fate and Transport. RDX is recalcitrant to biodegradation in the environment and while bacteria can degrade it, it is stable and persists at contaminated sites for many years. Understanding RDX deposition and stability in soil is one of the biggest gap areas within the fate and transport research.

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6. 1-METHYL-2,4-DINITRO BENZENE (2,4-DNT)

6.1 INTRODUCTION

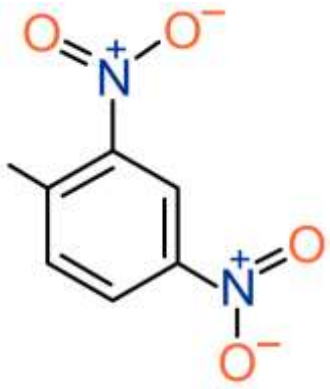

Figure 6-1 Chemical Structure of 2,4-DNT

Names: 1-methyl-2,4-dinitro benzene
Abbreviations and Other Names: dinitrotoluene, dinitrotoluol, methyldinitrobenzene, 2,4-DNT
CAS No.: 121-14-2
Chemical Formula: $C_7H_6N_2O_4$
Occurrence in Mixtures/Compositions: Several single-base and some double-base gun and rocket propellant formulations (e.g., M1, M6, M10); byproduct of TNT synthesis and processing; or formed during biotic or abiotic transformation of TNT [1]
Natural Occurrence: 2,4-DNT does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of 2,4-DNT are provided in Table 6-1.

Table 6-1. Physical and Chemical Properties of 2,4-DNT

Property	Value	Units
Color	Yellow	
Physical state	Solid	
Melting temperature	71	^oC
Vapor pressure (at 20^{o}C)	6.7e-6	atm
Specific gravity	1.32	None
Water solubility (at 20^{o}C)	270	mg/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.98	None

6.2 FATE

2,4-DNT and 2,6-DNT are the most common DNT isomers used in energetic materials. The chemical structure of 2,4-DNT is shown in Figure 6-1. Historically, DNTs have been used as a burn-rate modifier or flash suppression ingredient in gun propellants, such as M1 propellant, or as an impurity in TNT manufacturing processes. In the latter case, these two isomers are usually found in a four to one mass ratio of 2,4-DNT to 2,6-DNT [2]. The environmental fate of these DNT isomers has been studied primarily due to their toxicity.

The fate of DNTs is of particular interest when used in propellant formulations, as these formulations are hydrophobic due to the high percentage of nitrocellulose comprising the formulation. The nitrocellulose blocks DNT dissolution into or mobility within water systems [3]. As a neat energetic material (i.e., not confined within a nitrocellulose matrix), DNT's mobility and transport in the environment is somewhat similar to that of TNT [1]. Therefore, the fate and

transport of DNTs is highly dependent on the type of formulation in which it is used, more so than explosives such as TNT, RDX, and HMX.

6.2.1 Relevant Properties

Selected properties of 2,4-DNT are provided in Table 6-1. The water solubility values of these DNT isomers are close to that of ammonium perchlorate (200 mg/L) and TNT (130 mg/L), and greater than RDX (47 mg/L) and HMX (4.5 mg/L). Therefore, solubilization with water is expected to occur and has a significant influence on DNT fate and transport. The dissolution rate for 2,4-DNT is not available, however, the dissolution information for 2,4-DNT in the M1 propellant [3] is provided in Section 6.2.3 of this report.

6.2.2 Photolysis

2,4-DNT solubilizes in water, where it undergoes photolysis [1, 4, 5]. The technical information regarding the fate of DNTs published by the U.S. EPA [4] identifies photolysis as the primary means for DNT degradation in oxygenated water. Rates of photolysis are dependent on the type of water system (e.g., seawater, estuaries, fresh water). Photolysis of 2,4-DNT and 2,6-DNT has been reported to occur rapidly in seawater [4, 5]. 2,4-DNT photolytic half-lives in fresh water systems range from 2.7 to 9.6 hours. In seawater, this rate is ≈ 15 hours, and in high-purity laboratory water, this rate is > 100 hours [6, 7]. For comparison, values for the half-lives of 2,4-DNT from biodegradation in water and soil are 15.9 and 8.99 days, respectively. These photolysis rates are slightly slower than those of 2,6-DNT (12 minutes in freshwater; 5 hours in seawater; and 20 hours in high-purity laboratory water).

In freshwater systems, the depth of the system and distribution of 2,4-DNT may affect the photolysis rate [5]. For example, the wavelengths of light that govern photolytic conversion of DNT may not be able to penetrate deeply into freshwater sources, or significant concentrations of organic matter and particulates in natural water systems may compete for access to the incoming sunlight. This effect is not as widely observed in coastal waters since the concentrations of dissolved organic matter and particulates are lower and there is more vertical mixing, leading to less settling of DNT.

Products of 2,4-DNT photolysis include 2,4-dinitrobenzyl alcohol (2,4-DNBOH; 2,4-dinitrobenzaldehyde [2,4-DNBCHO]), and 2-amino-4-nitrobenzoic acid (2A4NBA) [5]. These products of 2,4-DNT photolysis can undergo additional photolytic reactions and at faster rates than the parent explosive compound. However, 2A4NBA was shown to not undergo photolysis. Therefore, 2A4NBA may accumulate in the environment [5].

6.2.3 Other Abiotic Reactions

Few data were available regarding abiotic reduction of DNTs (either 2,6- or 2,4-DNT). In general, DNTs are resistant to chemical and biological oxidation properties and hydrolysis resulting from their electron withdrawing properties [8]. The general reduction process for DNTs (either isomer) is a step-wise, two-electron transfer reaction with the generation of nitrosobenzene and *n*-hydroxylaniline intermediates with the formation of aniline [1].

6.2.4 Biodegradation

Two identical biodegradation pathways, involving dioxygenation, nitro group cleavage, and ring cleavage, have been identified in *Burkholderia cepacia* and *Hydrogenophaga palleronii.*

The degradation pathways for 2,4-DNT and 2,6-DNT are similar to those for nitrobenzene and 2-nitrotoluene in that a Rieske-type dioxygenase catalyzes the initial oxidation and removal of a nitro group [9, 10] (Figure 6-2). The products of this reaction are methylnitrocatechols, further degraded by slightly different pathways dependent on the nitrotoluene isomer.

In *Burkholderia sp*. strain DNT [11] and *Burkholderia cepacia* R34 [12, 13] the 4-methyl-5-nitrocatechol produced from 2,4-DNT is oxidized by a monooxygenase to remove the second nitro group, forming 2,4,5-trihydroxytoluene, which is a substrate for meta ring cleavage. In contrast, metabolism of 2,6-DNT by *B. cepacia* JS850 and *Hydrogenophaga palleronii* JS863 yields 3-methyl-4-nitrocatecho, which is a direct substrate for meta ring cleavage; trihydroxytoluene does not appear to be an intermediate as in 2,4-DNT degradation, and the second nitro group is removed after ring cleavage. These microbial strains can degrade approximately 20 mg/L of 2,4-DNT in 24 to 48 hours in reactor settings.

Anaerobic degradation of 2,4-DNT was reported in fluidized-bed granular carbon bioreactors. 2,4-DNT was completely transformed to 2,4-diaminotoluene (DAT) by methanogenic culture with ethanol as the primary substrate [14]. Subsequently, 2,4-DAT was easily degraded aerobically (16 mg/L of 2,4-DAT were mineralized within 9 hours in the batch activated sludge reactors).

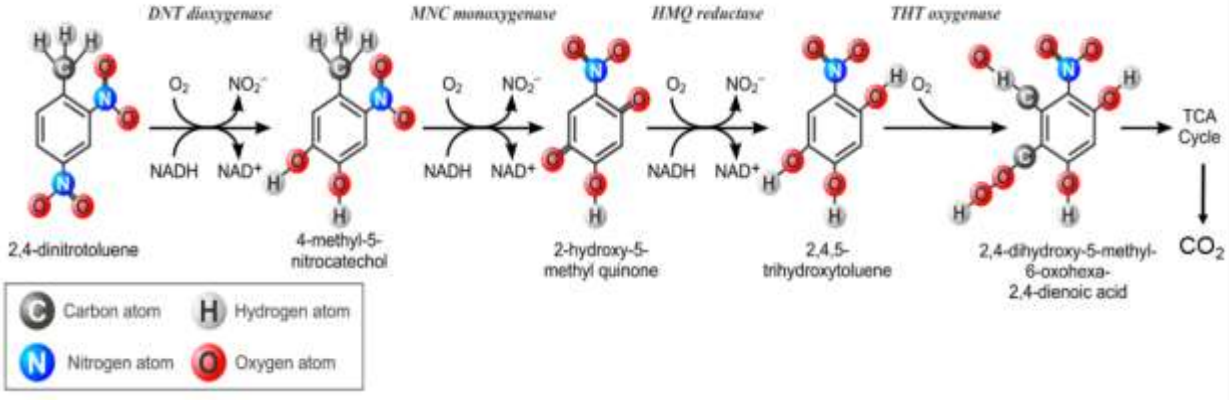

Figure 6-2. 2,4-DNT Biodegradation Pathway

6.2.5 Phytotransformation

Direct observation and measurement of plant uptake of 2,4-DNT has yet to be made. However, plant uptake is a likely fate pathway due to the low octanol-water partitioning coefficient of the DNTs, and based on the chemical structural analogy with 1,3-DNT and 4-nitrotoluene. One challenge in evaluating the probability of plant uptake is understanding the initial condition, soil properties, and water availability to dispersed 2,4-DNT. In terms of the initial condition, 2,4-DNT can be directly dispersed into a soil matrix, perhaps as a contaminant in TNT or trapped in a solid matrix of hydrophobic nitrocellulose. The latter condition can impede transport to a plant system.

Likewise, DNTs exhibit moderate solubility rates, thus transport within water systems dictates the proximity and availability of 2,4-DNT to plant materials.

Results from limited laboratory-based studies have shown that plant uptake of DNTs can occur. In studies using cell suspension cultures of separate plantlets, 2,4-DNT and 2,6-DNT were taken up by yellow weed and soap wart plantlets. Identified products of phytotransformation included 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene [15].

6.2.6 Hydrolysis

Specific studies on the hydrolysis of 2,4-DNT appear to be lacking, though predictive models suggest that DNT is resistant to hydrolysis [1, 16]. Nitroaromatic explosives, including TNT and DNTs, can undergo hydrolysis in highly alkaline systems; Sviatenko's work [16] suggests that 2,4-DNT may only be hydrolyzed in very alkaline systems (pH = 13) due to the high electron density of DNTs, which renders attack by nucleophilic bases more difficult. The half-life of this reaction is ≈ 600 min (10 hours). 2,6-DNT was not included in this study and data appear to be unavailable for 2,6-DNT hydrolysis rates for comparison. Furthermore, this work suggests that products of 2,4-DNT hydrolysis, in the event that it does occur, could involve direct substitution of a nitro group by a hydroxide ion.

6.2.7 Key Degradation Products

Key degradation products of 2,4-DNT include 2,4-DNBOH, 2,4-DNBCHO, 2A4NT, 4A2NT, DAT, aniline, and 2A4NBA. 2A4NBA appears to be of significance because of its ability to accumulate in the environment, though data on its toxicity are incomplete.

6.3 TRANSPORT

6.3.1 Transport Processes

The environmental transport of DNTs has received significant attention due to the classification of 2,4- and 2,6- isomers as the U.S. EPA priority pollutants [3]. Moreover, the propellants that comprise DNTs are used in live-fire trainings, which can produce significant levels of DNT contamination at a range in a relatively short amount of time, depending on the volume of tests conducted.

In general, transport of DNTs from its initial energetic material matrix (e.g., within nitrocellulose) and soil matrices to water matrices is not well understood [2]. However, recent data from transport studies on DNT [1-3, 17-19] can be used to evaluate the transport process in soil and water matrices. Some general conclusions can be drawn based on the findings from these reports and understanding of those properties of DNTs (e.g., water solubility) pertinent to transport. These general conclusions include:

1.) The moderate water solubility and low octanol-water partition coefficient values for 2,4- and 2,6-DNT and low octanol-water suggest that 2,4-DNT readily leaches from soil to groundwater [1, 4];

2.) The data available from relevant studies suggest that some sorption of 2,4-DNT to soils, reversible or irreversible, can occur, but is highly dependent on soil chemistry and organic matter content [4];

3.) DNTs have been found in soil, surface water, and groundwater at hazardous waste sites that contain buried ammunition wastes. Therefore, transport via surface or groundwater outweighs the tendency for 2,4-DNT sorption to sediments [6, 7]; and

4.) 2,4-DNT, once transported to water matrices, is expected to persist unless it is exposed to abiotic, biotic, or light that can drive degradation and transformation [4].

6.3.2 Transport in Soil

Transport of 2,4-DNT in soils depends on presence of nitrocellulose in propellant formulations. In these instances, the 2,4-DNT is impregnated within an insoluble matrix and 2,4-DNT diffusion is affected [1, 3, 18, 19]. As a result, the dissolution for 2,4-DNT is inhibited and subsequently 2,4-DNT accumulates on surfaces of training ranges [18]. 2,4-DNT within the soil can be reversibly bound, irreversibly bound, or transformed through, for example, abiotic processes [19]. Thus, it is difficult to provide a detailed transport model for 2,4-DNT in soil due to several processes that affect both fate and transport.

Soil adsorption of DNTs is a factor in preventing mobility in the environment. However, the propensity for soil adsorption is highly dependent on the chemical properties and organic content of the soil [1]. 2,4-DNT and 2,6-DNT both have log K_{oc} values of 1.79, indicating that partitioning to the organic carbon in soils is limited. For clay soils, absorption of DNTs is significant in clay and phyllosilicate clay soils. In general, 2,4-DNT will sorb more readily in these soils than 2,6-DNT [1, 3]. The lower rate of adsorption of 2,6-DNT is thought to be a result of the steric hindrance of the nitro group in the *ortho* position [1]. Data on the adsorption coefficients for 2,4-DNT and 2,6-DNT in clay soils have been summarized by Pichtel [1] to range from 690 to 740 L/kg for 2,4-DNT and 10 to 125 L/kg for 2,6-DNT. One study on soil transport in volcanic soils [17] showed that adsorption of DNT (2.7 g/cm^3) was higher than TNT (2.6 g/cm^3), RDX (1.5 g/cm^3), and HMX (1.8 g/cm^3). Volcanic soils were studied due to their mineralogical composition (i.e., an abundance of 1:1 clays, sesquioxides or iron and aluminum, and presence of amorphous and poorly crystallized minerals), presence of water-stable aggregates in the soil, and high degree of hydraulic conductivity and water retention.

6.3.3 Transport in Water

Better understanding of the dissolution rates of 2,4-DNT from soil matrices to water is needed to comprehensively evaluate DNT transport phenomena, particularly once the 2,4-DNT has dissolved from its propellant matrix into a soil solution [19]. DNTs do exhibit moderate solubility in water, although how readily 2,4-DNT reaches groundwater typically depends on four main factors [19]. The first factor is how much 2,4-DNT is initially deposited onto the soil. Second, the rate of accumulation of these residues should be identified (e.g., the number of average firings per year). The third factor is the rate of dissolution of 2,4-DNT out of its initial propellant matrix. Finally, the probability of 2,4-DNT undergoing transformation or degradation processes versus transport within a water matrix will influence transport, dispersion, and persistence.

6.4 TOXICITY DATA OF 2,4-DNT

There is a small likelihood for exposure to 2,4-DNTs unless living near facilities involved in its manufacturing, use, storage, and disposal. Drinking water contaminated by 2,4-DNT, breathing air or oral digestion of contaminated soil may contribute to potential exposure. The most common and direct 2,4-DNT exposure pathways include inhalation, dermal contact and incidental ingestion, usually in occupational settings [20, 21]. Several studies indicate that 2,4-DNT is readily adsorbed via oral or inhalation exposure and can be adsorbed through skin in toxic amounts [21, 22]. Some DNT degradation products, in particular 2A4NBA and aniline, are hazardous. 2A4NBA is considered an irritant. Aniline is classified as a Class 6.1 poisonous material by the U.S. Department of Transportation.

Recent toxicity studies had evaluated factory workers, munitions handlers and mining workers and showed adverse health effects posed by chronic DNT exposure identified in the central nervous system, heart and circulatory system of humans [21]. The symptoms of long-term exposure include nausea, dizziness, methemoglobinemia, jaundice, anemia and cyanosis [21, 23, 24]. Moreover, studies of workers indicate that exposure to 2,4-DNT and 2,6-DNT can lead to increased incidences of mortality from ischemic heart disease [21, 24, 25].

2,4-DNT and 2,6-DNT have both shown adverse impacts to neurological, hematological, reproductive, hepatic and renal functions in studies of rats, mice and dogs [25, 26]. Animal studies have also shown that 2,4-DNT is a hepatocarcinogenic and can cause liver cancer. In a recent study, symptoms such as cyanosis, anemia, increased splenic mass and hepatocellular lesions were observed in rats exposed to 2,4-DNT and 2,6-DNT for 14 days [27].

6.5 EXAMPLE REGULATORY GUIDELINES FOR 2,4-DNT

EPA's Integrated Risk Information System (IRIS) database includes a chronic oral RfD of 2×10^{-3} milligrams per kilogram per day (mg/kg/day) for 2,4-DNT based on neurotoxicity [28]. Based on a provisional peer-reviewed toxicity value (PPRTV) assessment conducted by the EPA for both 2,6-DNT and 2,4-DNT, EPA established a provisional chronic RfD screening value of 3×10^{-4} mg/kg/day for 2,6-DNT and 9×10^{-4} mg/kg/day for Tg-DNT. The PPRTV assessments are developed for use in the EPA Superfund program and provide toxicity values and information about adverse effects of the chemical [29, 30].

The Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.05 mg/kg/day for acute-duration oral exposure (14 days or less), 0.007 mg/kg/day for intermediate-duration oral exposure (15 to 364 days) and 0.001 mg/kg/day for chronic-duration oral exposure (365 days or more) to 2,4-DNT [20, 31]. The cancer risk assessment for the 2,4-DNT and 2,6-DNT mixture is based on an oral slope factor of 6.8×10^{-1} mg/kg/day and a drinking water unit risk of 1.90×10^{-5} micrograms per liter (μg/L) [25, 28]. EPA risk assessments indicate that the drinking water concentration representing a 1×10^{-6} cancer risk level for 2,4-DNT and 2,6-DNT mixture is 0.005 μg/L [28]. The EPA has established drinking water health advisories for DNT, which are drinking water-specific risk level concentrations for cancer (10^{-4} cancer risk) and concentrations of drinking water contaminants at which non-cancer adverse health effects are not anticipated to occur over specific exposure durations [32].

EPA established a 1-day and 10-day health advisory of 1.0 mg/L for 2,4-DNT in drinking water for a 10-kilogram (kg) child. The drinking water equivalent levels for 2,4-DNT and 2,6-DNT are 0.1 mg/L and 0.04 mg/L, respectively. Moreover, EPA established an ambient water quality criterion of 0.11 μg/L for ingestion of water and organisms and 9.1 μg/L for ingestion of organisms only for 2,4-DNT at a 1×10^{-6} risk level [21, 25]. EPA has also calculated a residential soil screening level (SSL) of 7.2×10^{-1} mg/kg and an industrial SSL of 2.5 mg/kg for the mixture of 2,4-DNT and 2,6-DNT. The soil-to-groundwater risk-based SSL is 1.3×10^{-4} mg/kg.

6.6 DATA GAPS

In reviewing the literature, the following data gaps were identified. Addressing these gaps would help complete the understanding on the fate of 2,4-DNT, particularly on the chemical and physical properties of its degradation products and their propensities to accumulate and pose toxic threats to the environment.

A. Fate and Transport

- **Degradation rates**: A complete understanding of the degradation process for 2,6-DNT versus 2,4-DNT is needed to highlight the similarities and differences (if any) with these processes.
- **Transport** (general): A complete understanding of the transport processes of 2,4-DNT in soil and water matrices is needed, including a guide on how properties of the local environment (e.g., soil composition, rainfall data, access to groundwater) can influence the mobility, dispersion, degradation, and transformation of 2,4-DNT in the environment;
- **Fate of 2,4-DNT in energetic formulations**: More data are needed on the presence and fate of 2,4-DNT prior to dissolution into soil and water systems, especially for 2,4-DNT which is "trapped" in nitrocellulose matrices, particularly on the effect(s) of the NC matrix on abiotic reactions and their rates.

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7. 1-METHYL-2,6-DINITRO BENZENE (2,6-DNT)

7.1 INTRODUCTION

Names: 1-methyl-2,6-dinitro benzene
Abbreviations and Other Names: Dinitrotoluol, methyldinitrobenzene, 2-Methyl-1,3-dinitrobenzene; 2,6-DNT; Benzene, 2-methyl-1,3-dinitro-; 1-Methyl-2,6-dinitrobenzene
CAS No.: 606-20-2
Chemical Formula: $C_7H_6N_2O_4$
Occurrence in Mixtures/Compositions: Several single-base and some double-base gun and rocket propellant formulations (e.g., M1, M6, M10); byproduct of TNT synthesis and processing; or formed during biotic or abiotic transformation of TNT

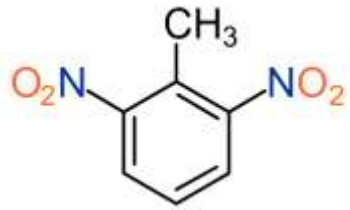

Figure 7-1. Chemical Structure of 2,6-DNT

Natural Occurrence: 2,6-DNT does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of 2,6-DNT are provided in Table 7-1.

Table 7-1. Physical and Chemical Properties of and 2,6-DNT [4-6]

Property	Value	Units
Color	Yellow to red	
Physical state	Solid	
Melting temperature	66	°C
Vapor pressure (at 25°C)	2.37e-5	atm
Specific gravity	1.28	None
Water solubility (at 20°C)	180	mg/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.98	None

7.2 FATE

2,4-DNT and 2,6-DNT are the most common DNT isomers used in energetic materials. Historically, DNTs have been used as a burn-rate modifier or flash suppression ingredient in gun propellants, such as in M1 propellant, or are present as impurities in TNT. In the latter case, these two isomers are usually found in a four to one mass ratio of 2,4-DNT to 2,6-DNT [1], and the presence of DNTs gives TNT its distinct yellow color. The fate of these DNT isomers in the environment has been studied primarily as a result of their known, documented toxicity.

As noted in the munitions constituent (MC) suite for 2,4-DNT, the fate of 2,6-DNT is of particular interest for gun propellants whose formulations comprise DNTs and nitrocellulose. Nitrocellulose, the primary ingredient in these formulations, is hydrophobic and blocks DNT dissolution into

water systems [2]. Otherwise, without this inhibition and as a neat energetic material, DNTs will exhibit mobility and transport processes similar to TNT [3]. This highlights the importance of the type of DNT-containing energetic material, especially since other energetic materials such as RDX, HMX, or TNT are typically not mixed with such significant percentages of nitrocellulose or other hydrophobic materials.

7.2.1 Relevant Properties

Key properties related to fate and transport of 2,6-DNT are provided in Table 7-1 and the chemical structure of 2,6-DNT is provided in Figure 7-1. 2,6-DNT exhibits a slightly lower water solubility (180 mg/L) compared to the 2,4-DNT isomer (270 mg/L); however, this value is still higher than that of TNT (130 mg/L) and significantly higher than those of RDX (47 mg/L) and HMX (4.5 mg/L). Similar to what was noted for 2,4-DNT, the dissolution rate for 2,6-DNT is not provided in Table 7-1 due to the finding from the surveyed literature that these data for the neat energetic compound appear to be lacking. Some data are available for the dissolution of these chemicals from M1 propellant [2] and will be described in the Section 7.2.3 of this report.

7.2.2 Photolysis

Both 2,4-DNT and 2,6-DNT readily solubilize in water, where they undergo photolysis [3, 6, 7]. The half-life for 2,6-DNT photolysis is ≈ 12 minutes in river water and ≈ 0.67 to 1.0 days in distilled water. Rates of photolysis are dependent on the type of water system and the availability of solar radiation. In natural waters, this reaction occurs so readily and rapidly that technical information regarding the fate of DNTs published by the U.S. EPA [6], identifies photolysis as the primary means for DNT degradation in oxygenated water. For comparison, the biodegradation half-life in water for 2,6-DNT is 20.6 days.

Products of 2,6-DNT photolysis include 2,6-dinitrobenzyl alcohol (2,6-DNBOH) and 2,6-dinitrobenzaldehyde (2,6-DNBCHO) [7]. The direct products of DNT photolysis can undergo additional photolytic reactions and at rates faster than that of 2,6-DNT [7]. Of note is that one byproduct of 2,4-DNT photodegradation, 2-amino, 4-nitrobenzoic acid (2A4NBA), may accumulate unless transformed by biodegradation processes. This compound does not appear to be formed during 2,6-DNT photolysis.

7.2.3 Other Abiotic Reactions

Similar to what was described for 2,4-DNT, few data were available regarding the abiotic reduction of 2,6-DNT. In general, energetic materials containing nitro functional groups, of which nitroaromatic compounds including DNT belong, can undergo abiotic reduction with the nitro groups reduced to amino groups in the process [3]. The general reduction process for DNTs (either isomer) is a step-wise, two-electron transfer reaction with the generation of nitrosobenzene and *n*-hydroxylaniline intermediates with the formation of aniline as the end product [3].

7.2.4 Biodegradation

The degradation pathways for 2,4-DNT and 2,6-DNT are similar to those for nitrobenzene and 2-nitrotoluene in that a Rieske-type dioxygenase catalyzes the initial oxidation and removal of a nitro group [8, 9]. Two identical biodegradation pathways, involving dixoxygenation, nitro group

cleavage, and ring cleavage, have been identified in *Burkholderia cepacia* and *Hydrogenophaga palleronii*. Studies involving diverse anaerobic inocula have generally cited aminonitrotoluenes as primary end products from both 2,4-DNT and 2,6-DNT transformation [10]. Complete reduction of 2,4-DNT to 2,4-diaminotoluene has been observed in a mixed methanogenic culture with ethanol as the primary substrate [10]. Under anoxic nitrate-reducing conditions, a limited extent of 2,4-diaminotoluene production has been observed along with aminonitrotoluene isomers (primary products), acetamidotoluenes, 6-nitrodazole, 2-nitrotoluene, and 4-nitrotoluene [10]. The biodegradation rates of 2,6-DNT depend on microbial species and environmental conditions under which the degradation is occurring. For example, *Burkholderia cepacia* and *Hydrogenophaga palleronii* species remove 2,6-DNT in culture during 7-day incubation, while *Alcaligenes denitrificans* isolated from a contaminated site degraded 2,6-DNT after 2 to 3 days of incubation [9].

Based on several studies, the following pathway was proposed for the biodegradation of 2,6-DNT [11] (Figure 7-2):

- Dioxygenase attacks either of the nitro groups and converts 2,6-DNT to 3-methyl-4-nitrocatechol with the elimination of nitrate.
- The aromatic ring is opened by an extradiol ring cleavage dioxygenase resulting in 2-hydroxy-5-nitro-6-oxohepta-2,4-dienoic acid.
- By analogy to the 3-methyl-catechol meta ring cleavage pathway, hydrolytic attack would produce 2-hydroxy-5-nitropenta-2,4-dioenoic acid accompanied by the loss of acetate.

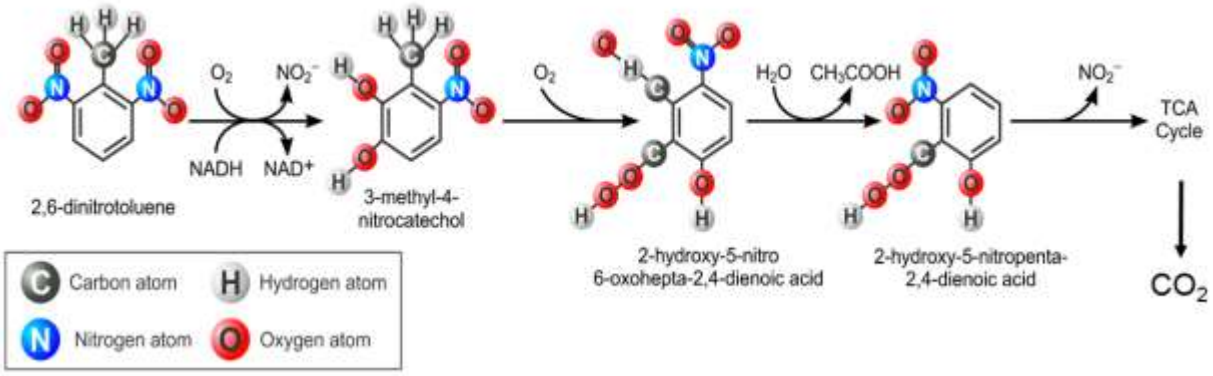

Figure 7-2. 2,6-DNT Biodegradation Pathway[11]

7.2.5 Phytotransformation

Similar to what was described for 2,4-DNT, direct observation and measurement of plant uptake and degradation or transformation of 2,6-DNT have yet to be made [12]. However, plant uptake is a likely fate pathway due to the low octanol-water partitioning coefficient of the DNTs, and based on the chemical structural analogy with 1,3-DNT and 4-nitrotoluene [12]. One challenge in evaluating the probability of plant uptake is understanding the initial condition, soil properties, and water availability to dispersed DNT. In terms of the initial condition, DNT can be directly

dispersed into a soil matrix, perhaps as a contaminant in TNT, or trapped in a solid matrix of hydrophobic nitrocellulose. The latter condition can impede transport to a plant system. Likewise, DNTs exhibit moderate solubility rates. Thus, transport within water systems will dictate the proximity and availability of DNT to plant materials.

Results from limited laboratory-based studies have shown that plant uptake of DNTs can occur. In studies using cell suspension cultures of separate plantlets with 2,4-DNT (and not 2,6-DNT), the 2,4-DNT was taken up by yellow weed and soap wart plantlets. The identified products of phytotransformation included 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene [12]. It is assumed that similar compounds could be produced from 2,6-DNT uptake and phytotransformation, although more data are required to assess this assumption.

7.2.6 Hydrolysis

Specific studies on the hydrolysis of 2,6-DNT appear to be lacking, though predictive models suggest that DNT is resistant to hydrolysis [3, 13]. Nitroaromatic explosives, including TNT and DNT, can undergo hydrolysis in highly alkaline systems; however, Sviatenko's work [13] suggests that 2,4-DNT may only be hydrolyzed in very alkaline systems (pH 13) due to the high electron density of DNT, which renders attack by nucleophilic bases more difficult. The half-life of this reaction is ≈ 600 min (10 hours). 2,6-DNT was not included in this study. Furthermore, this work suggests that products of DNT hydrolysis, in the event that it does occur, could involve direct substitution of a nitro group by a hydroxide ion, along with the formation of trace concentrations of polymeric products and Meisenheimer complexes.

Some information related to hydrolysis of 2,6-DNT can be withdrawn from U.S. EPA data on the photolysis [14]. Such data showed that 2,6-DNT in a seawater solution and under simulated solar radiation was reduced by 89% within 24 hours. Without simulated solar radiation, the 2,6-DNT concentration was only reduced by 3.2% within 92 hours. This example demonstrates, albeit in more general terms, that photolysis, rather than other degradation processes associated with aqueous systems (e.g., hydrolysis), will dominate.

7.2.7 Key Degradation Products

The key degradation products of 2,6-DNT that have been identified in the surveyed literature include 2,6-DNBOH, 2,6-DNBCHO, and aniline. More data may need to be obtained regarding the products from phytodegradation of 2,6-DNT, though it is thought that amino-nitrotoluene compounds will be produced. Products of 2,4-DNT degradation include 2,4-DNBOH, 2,4-DNBCHO, aniline, and 2A4NBA. Analogues of these products may be produced for 2,6-DNT degradation, though data need to be collected to confirm this.

7.3 TRANSPORT

7.3.1 Transport Processes

The environmental transport of DNTs has received significant attention due to the 2,4- and 2,6-isomers being classified as U.S. EPA priority pollutants [2]. Adding importance to the transport processes is the fact that propellants comprising DNTs are used in live-fire training, which can produce significant levels of DNT (both 2,4-DNT and 2,6-DNT) contamination at a range in a

relatively short amount of time, depending on the volume of tests being conducted. Typically, higher percentages of 2,4-DNT are used in propellant formulations comprising DNTs; for example, M1 propellant contains 87.6% nitrocellulose, 7.3% 2,4-DNT, 0.57% 2,6-DNT, 1.06% diphenylamine, and 3.48% dibutyl phthalate. In general, transport of DNTs from its initial energetic material matrix (e.g., within nitrocellulose) and soil matrices to water matrices is not well understood [1]. However, recent data from transport studies of DNT (both 2,4-TNT and 2,6-TNT) [1-3, 15-17] can be used to evaluate the transport process in soil and water matrices, and some general conclusions can be drawn based on the findings from these reports and understanding of those properties of DNTs (e.g., water solubility) pertinent to transport.

These general conclusions include:

1.) The moderate water solubility and low octanol-water partition coefficient values for 2,4-DNT and 2,6-DNT and low octanol-water suggest that DNTs will readily leach from soil to groundwater [3, 6, 12];

2.) The data available from relevant studies suggest that some sorption of DNT to soils, be it reversible or irreversible, can occur, but is highly dependent on soil chemistry and organic matter content [6];

3.) DNT has been found in soil, surface water, and groundwater at hazardous waste sites that contain buried ammunition wastes. Therefore, transport via surface or groundwater outweighs the tendency for DNT sorption to sediments [14]; and

4.) DNT, once transported to water matrices, is expected to persist unless it is exposed to abiotic, biotic, or light that can drive degradation and transformation [14].

7.3.2 Transport in Soil

An important factor in describing DNT transport in soil is if the DNT is used in a propellant formulation containing nitrocellulose. In these instances, the DNT is impregnated within an insoluble matrix and DNT diffusion is thus affected [2, 3, 16, 17]. This results in an inhibited rate of dissolution for DNT and subsequent accumulation of DNT on surfaces of training ranges [16]. DNT within the soil can be reversibly bound, irreversibly bound, or transformed through, for example an abiotic process [17]. Thus, it is difficult to provide a detailed transport model for DNT in soil due to several processes that affect both fate and transport.

Soil adsorption of DNTs is a factor in preventing mobility in the environment. However, the propensity for soil adsorption is highly dependent on the chemical properties and organic content of the soil [3]. Regarding clay soils, soils with higher soil organic carbon content and clay content more readily adsorbed DNTs. In general, 2,4-DNT will sorb more readily in these soils than 2,6-DNT [2, 3]. The lower rate of adsorption of 2,6-DNT is thought to be a result of the steric hindrance of the nitro group in the *ortho* position [3]. Data on the adsorption coefficients for 2,4-DNT and 2,6-DNT in clay soils have been summarized by Pichtel [3] to range from 690 to 740 L/kg for 2,4-DNT and 10 to 125 L/kg for 2,6-DNT. One study on soil transport in volcanic soils showed that adsorption of DNT was higher than TNT, RDX, and HMX [15].

7.3.3 Transport in Water

Better understanding of the dissolution rates of 2,4-DNT and 2,6-DNT from soil matrices to water are needed to better evaluate DNT transport phenomena, particularly once the DNT has dissolved from its propellant matrix into a soil solution [17]. DNTs do exhibit moderate solubility in water, although how readily the DNT reaches groundwater typically depends on four main factors [17]. The first factor is how much DNT is initially deposited onto the soil. Second, the rate of accumulation of these residues should be identified (e.g., the number of average firings per year). The third factor is the rate of dissolution of DNT out of its initial propellant matrix. Finally, the probability of DNT undergoing transformation or degradation processes versus transport within a water matrix will influence transport, dispersion, and persistence.

Residues from live-fire training had energetic contents similar to, but ~ 20% lower than, their unfired parent. The appearance of the residue was dictated by the shape of the original propellant grain. Microscopically, NC and crystalline NQ could be distinguished but the distribution of 2,4-DNT or NG was unable to be mapped in the nitrocellulose matrix, information important for understanding how these compounds dissolve out of the nitrocellulose. Dissolution of 2,4-DNT is slower than that for NG or NQ. The 2,4-DNT interacted strongly with soils and had the highest adsorption and transformation rates measured. There was also a strong correlation between soil adsorption and organic matter content in the soil. This result is consistent with lack of 2,4-DNT in groundwater under firing points even when it is deposited and detected in soils.

7.4 TOXICITY DATA OF 2,6-DNT

There is a small likelihood for exposure to 2,6-DNTs unless living near facilities involved in its manufacturing, use, storage and disposal. Drinking water contaminated by 2,6-DNT, breathing air or oral digestion of contaminated soil may contribute to potential exposure. The most common and direct 2,6-DNT exposure pathways include inhalation, dermal contact and incidental ingestion, usually in an occupational setting [5, 18, 19]. Several studies indicate that 2,6-DNT is readily adsorbed via oral or inhalation exposure and can be adsorbed through skin in toxic amounts [5, 20].

The up-to-date toxicity studies had evaluated factory workers, munitions handlers and mining workers and showed adverse health effects posed by chronic DNT exposure identified in the central nervous system, heart and circulatory system of humans [5]. The symptoms of long-term exposure include nausea, dizziness, methemoglobinemia, jaundice, anemia and cyanosis [5, 21]. Moreover, studies of workers indicate that exposure to 2,4-DNT and 2,6-DNT can lead to increased incidences of mortality from ischemic heart disease [5, 18, 21, 22].

2,4-DNT and 2,6-DNT have both shown adverse impacts to neurological, hematological, reproductive, hepatic and renal functions in studies of rats, mice and dogs [5, 23]. Animal studies have also shown that 2,6-DNT is a hepatocarcinogenic and can cause liver cancer. In a recent study, symptoms such as cyanosis, anemia, increased splenic mass and hepatocellular lesions were observed in rats exposed to 2,4-DNT and 2,6-DNT for 14 days [8, 24, 25].

7.5 EXAMPLE REGULATORY GUIDELINES FOR 2,6-DNT

Based on a provisional peer-reviewed toxicity value assessment conducted by the EPA for both 2,6-DNT and Tg-DNT, EPA established a provisional chronic RfD screening value of 3×10^{-4} mg/kg/day for 2,6-DNT and 9×10^{-4} mg/kg/day for 2,4-DNT. The PPRTV assessments are developed for use in the EPA Superfund program and provide toxicity values and information about adverse effects of the chemical [26, 27].

The ATSDR has established a MRL of 0.09 mg/kg/day for acute-duration oral exposure (14 days or less), 0.004 mg/kg/day for intermediate-duration oral exposure (15 to 364 days) and 0.001 mg/kg/day for chronic-duration oral exposure (365 days or more) to 2,4-DNT [18, 19]. The cancer risk assessment for the 2,4-DNT and 2,6-DNT mixture is based on an oral slope factor of 6.8×10^{-1} mg/kg/day and a drinking water unit risk of 1.90×10^{-5} micrograms per liter (μg/L) [22, 28]. The U.S. EPA risk assessments indicate that the drinking water concentration representing a 1×10^{-6} cancer risk level for 2,4-DNT and 2,6-DNT mixture is 0.005 μg/L [22]. The U.S. EPA has established drinking water health advisories for DNT, which are drinking water-specific risk level concentrations for cancer (10^{-4} cancer risk) and concentrations of drinking water contaminants at which non-cancer adverse health effects are not anticipated to occur over specific exposure durations [29].

The U.S. EPA established a 1-day and 10-day health advisory of 1.0 mg/L for 2,6-DNT in drinking water for a 10-kilogram (kg) child. The drinking water equivalent levels for 2,4-DNT and 2,6-DNT are 0.1 mg/L and 0.04 mg/L. For 2,6-DNT, U.S. EPA has calculated a residential soil screening level (SSL) of 3.3×10^{-1} mg/kg and an industrial SSL of 1.2 mg/kg. The soil-to-groundwater risk-based SSL is 5.8×10^{-5} mg/kg. The U.S. EPA has also calculated a residential SSL of 7.2×10^{-1} mg/kg and an industrial SSL of 2.5 mg/kg for the mixture of 2,4-DNT and 2,6-DNT. The soil-to-groundwater risk-based SSL is 1.3×10^{-4} mg/kg.

7.6 DATA GAPS

Many of the same data gaps identified for 2,4-DNT can be applied to 2,6-DNT. As described with 2,4-DNT, addressing these gaps would help complete the understanding of the fate and transport of 2,6-DNT, particularly on the chemical and physical properties of its degradation products and their propensities to accumulate and pose toxic threats to the environment. These gaps include:

A. Fate and Transport

- **Degradation processes**: Complete understanding of the degradation process for 2,6-DNT versus 2,4-DNT to highlight the similarities and differences (if any) with these processes. Abiotic reduction via Fe^{2+}, for example, has different degradation rates.
- **Transport**: Complete understanding of the transport processes of 2,6-DNT versus 2,4-DNT in soil and water matrices, including a guide on how properties of the local environment (e.g., soil composition, rainfall data, access to groundwater) can influence the mobility, dispersion, degradation, and transformation of 2,6-DNT in the environment.

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8. NITROTOLUENE (NT)

8.1 INTRODUCTION

Figure 8-1. Chemical Structure of 2-nitrotoluene

Names: 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene
Abbreviations and Other Names: *o*-nitrotoluene, *o*-methylnitrobenzene, 2-ethylnitrobenzene, ortho-nitrotoluene; 1-methyl-3-nitro-benzene, *m*-nitrotoluene; 1-methyl-4-nitrobenzene, *p*-nitrotoluene
CAS No.: 88-72-2, 99-08-1, 99-99-0
Chemical Formula: $C_7H_7NO_2$
Occurrence in Mixtures/Compositions: Nitrotoluenes are typically produced as a result of TNT manufacture via nitration of toluene with mixed acids.
Natural Occurrence: NTs do not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of NTs are provided in Table 8-1.

Table 8-1. Physical and Chemical Properties of Selected NTs

Property	2-nitrotoluene	3-nitrotoluene	4-nitrotoluene	Units
Color	Yellow	Yellow	Yellow	
Physical state	Liquid	Liquid (typ.)	Solid	
Melting temperature	-10.4	15.5	51.6	°C
Vapor pressure (at 25°C)	2.4e-4	1.4e-4	1.4e-4	atm
Specific gravity	1.16	1.16	1.16	None
Water solubility (at 20°C)	609	450	288	mg/L
Dissolution rate in water	NA	NA	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	2.30	2.42	2.40	None

8.2 FATE

2-, 3-, and 4-nitrotoluene (i.e., 2-NT, 3-NT, and 4-NT, respectively) are the NT isomers (Figure 8-1) encountered in the production and use of toluene-based energetic materials (e.g., trinitrotoluene, TNT). They are mainly discharged to the environment as a result of being used as the starting materials in TNT manufacturing processes. 2-NT and 4-NT are typically used in larger concentrations than 3-NT during these manufacturing processes, as the presence of 3-NT can result in unsymmetrical TNT (e.g., 2,3,4-TNT, 2,4,5-TNT, and 3,4,5-TNT) versus the more desirable 2,4,6-TNT [1]. NT concentrations can accumulate in the groundwater at sites where TNT

production is significant. For example, studies conducted at the Radford Ammunition Plant [2] have detected 2-NT groundwater concentrations as high as 0.82 µg/L.

8.2.1 Relevant Properties

A summary of the relevant properties related to fate and transport for 2-NT, 3-NT, and 4-NT are provided in Table 8-1. Of note are the water solubility values for all three isomers, which are higher than those values for other compounds involved in the synthesis or use of TNT; e.g., 2,4-DNT (270 mg/L), 2,6-DNT (180 mg/L), and TNT (130 mg/L). The octanol-water partitioning coefficients for the NTs are also higher than those values for the DNTs (1.98) and TNT (1.86), suggesting that, although still relatively hydrophilic, the NTs would more readily sorb to soils and sediments than DNTs and TNT.

2-NT is the ortho-isomer, 3-NT is the meta-isomer, and 4-NT is the para-isomer of NT; all three isomers are pale yellow in color, with a distinctive, strong odor typical of nitroaromatic explosives [1]. As shown from the melting temperature values presented in Table 8-1, 2-NT and 3-NT are typically in liquid form under ambient conditions, while 4-NT is a solid. As a result, the environmental fate of NT is dependent on the isomers involved and their associated properties.

8.2.2 Photolysis

Nitroaromatic compounds, including TNT, DNTs, and the NT isomers, are known to absorb sunlight in the ultraviolet and blue spectral regions and undergo photolysis [3], particularly in aquatic systems. NTs have been shown to undergo photodegradation in air (vapor-phase) as well as when released to water [3, 4]. Two main sources of NT photodegradation were identified in the surveyed literature: direct photolysis in aquatic systems and air; and indirect, vapor-phase reactions with photochemically generated hydroxyl radicals in air [3, 4].

Photolysis studies specifically on 2-NT [3] showed that the major products of 2-NT photolysis include 2-methyl-6-nitrophenol and 2-methyl-4-nitrophenol, which can be formed in photolysis reactions occurring in either air or water. Similarly, studies specific to 4-NT photolysis reported the formation of 4-methyl-2-nitrophenol as the photolysis product of 4-NT [4].

Data on the photolysis reactions of 2-NT and 4-NT have come from laboratory studies; what appears to be lacking in the surveyed literature are specific data on fate and photolysis rates under environmental conditions. In lieu of such information, one report [3] has estimated a "worst case" photolysis half-life of 24 days for 2-NT in aquatic systems. 4-NT has been reported to have a photolysis half-life of 6 hours in surface waters [5]. Data from the laboratory studies do suggest that the photolysis rates will depend on the type of aquatic system (e.g., freshwater versus seawater) and microbial populations. Direct photolysis of NTs in air has been reported; however, the half-life of these reactions appears to be unknown [5]. Indirect photolysis via the hydroxyl radical in air has been shown to occur with a half-life period of 23 days for 2-NT and 20.8 days for 4-NT [5], assuming a mean concentration of 5×10^5 molecules/cm^3 concentration of the hydroxyl radicals.

For rate comparison, the half-life for 2-NT biodegradation in water is ≈ 31.4 days and for soil is ≈ 6.79 days.

8.2.3 Other Abiotic Reactions

Aside from the discussed photolysis-driven degradation reactions, NTs typically do not readily undergo abiotic degradation via oxidation or hydrolysis in the environment [3, 4].

8.2.4 Biodegradation

The only reported microbial strain to degrade 2-NT in aerobic conditions is *Acidovorax* sp. strain JS42 [6, 7]. During the microbial metabolism, 2-NT is used as a sole carbon, nitrogen and energy source for growth while the compound is oxidized to two and three positions with the formation of unstable nitrohydrodiol complex, which spontaneously rearranges to 3-methylcatechol with the release of nitrate (Figure 8-2) [8]. A standard *meta*-cleavage pathway is then utilized to complete metabolism of 3-methylcatechol to TCA cycle intermediates [9, 10].

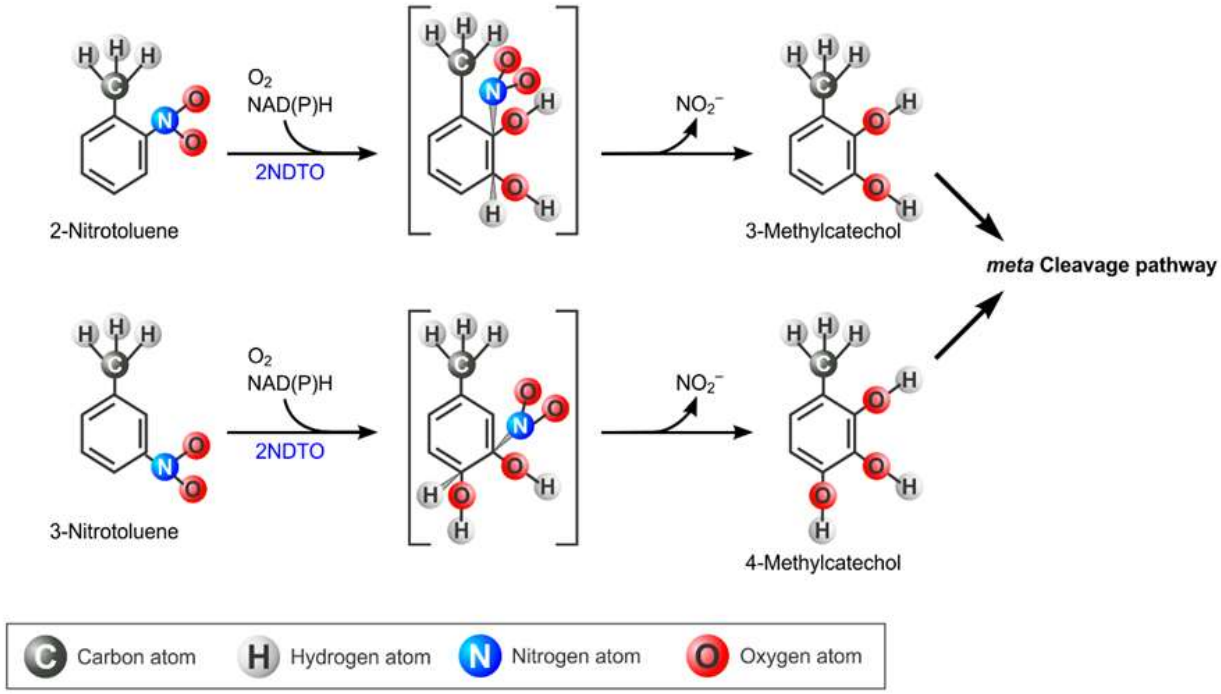

Figure 8-2. Microbial Degradation of 2- and 3-nitrotoluenes

Commonas sp. strain JS765 is able to aerobically use 3-NT as the sole carbon, nitrogen and energy source. A nitrobenzene dioxygenase oxidizes 3-nitrotoluene and 4-methylcatechol (Figure 8-2), which is then cleaved by the same *meta*-cleavage pathway as the one used by the JS42 strain [6, 10, 11]. Aside from JS765, no other microbial strains have been able to grow on 3-NT. However, *Pseudomonas putida* strain OU3 was shown to transform 3-NT in step-wise reactions into 3-nitrobenzyl alcohol, 3-nitrobenzaldehyde, 3-nitrobenzoate, and finally, 3-nitrophenol [10, 12] that show lower toxicity than the parent chemical. The nitro group is removed in subsequent transformations of 3-nitrophenol. However, strain OU3 was not shown to grow directly on 3-NT or any of the degradation intermediates.

Three microbial strains have been isolated by their aerobic growth on 4-NT [10, 13]. *Mycobacterium* sp. strain HL 4-NT-1 initiates degradation of 4-NT by reducing the nitro group and following formation of 4-hydroxylaminotoluene, which is then converted to 6-amino-meta-cresol [13]. Similar to the case in the nitrobenzene degradation pathway in *P. pseudoalcaligenes* JS45, the amino group is removed after meta ring cleavage [14]. In contrast, degradation of 4-NT in *Pseudomonas* sp. strain 4-NT and *P. putida* TW3 is initiated by sequential oxidations at the methyl group to form 4-nitrobenzoate. Following reduction to 4-hydroxylaminobenzoate, deamination occurs, resulting in the formation of protocatechuate [15, 16]. Depending on the strain, protocatechuate either enters the β-ketoadipate pathway, as in *P. putida* TW3 (161), or undergoes meta ring cleavage (*Pseudomonas* sp. 4-nitrotoluene) with production of low toxicity byproducts [17-19].

p-toluidine has also been identified as a product of anaerobic biodegradation of 4-NT [4]; however, more data are needed to fully assess the significance of anaerobic processes as effective biodegradation pathways.

8.2.5 Hydrolysis

Hydrolysis of NTs is not expected to occur [3-5].

8.2.6 Key Degradation Products

The key degradation products of NTs that have been identified in the surveyed literature include 2-methyl-6-nitrophenol, 2-methyl-4-nitrophenol, 4-methyl-2-nitrophenol, 3-methylcatechol, and 4-methylcatechol. Methylnitrophenols and methylcatechols are considered hazardous according to 29 CFR 1910.1200 [20], though more information is needed regarding their environmental fate, persistence, and toxicity.

8.3 TRANSPORT

NTs primarily reach environmental matrices through manufacturing and processing operations [5], as opposed to energetic material testing or use. Although several processing plants have controls in place to mitigate discharge of NT to the environment, NTs have been found in the wastewater of munitions factories and in leachates and groundwater from decommissioned munition sites [5].

Unlike the energetic materials such as HMX, RDX, and TNT, which have low vapor pressures and are not expected to volatilize, NTs are reported to have a "moderate" potential for volatilization [5] from an aqueous solution, resulting from the vapor pressure values and calculated values for Henry's Law constants. Therefore, transport in air is considered here along with transport in soil and water.

8.3.1 Transport in Air

When in use or part of a manufacturing process, NT vapors can be dispersed into the local atmosphere. For example, data from ambient air sampling at a processing plant in Deepwater, New Jersey, reported a 2-NT concentration of 47 ng/m^3 and 4-NT concentrations ranging from 59 to 89 ng/m^3 [21]. When released to the air, the NTs are anticipated to undergo direct photolysis or indirect photodegradation reactions with hydroxyl radicals [4].

8.3.2 Transport in Soil

Most of the surveyed literature regarding NT transport used data from manufacturing and processing plants, in which NTs were fed directly into waste streams or leached directly into the groundwater from these sites, unlike similar transport studies involving energetic materials, which may have some data on soil transport following open burn/open detonation tests or other processes that may produce direct soil contamination. However, if deposited directly onto the soil, NTs should be stable and are not expected to sorb to soils and sediments. Sorption to soil by forming electron-donor acceptor complexes with clays may be possible, since this is a feature common with nitroaromatic explosives. More data are needed to determine if NT sorption is clay content-dependent. Given the low probability of soil sorption, high degree of solubility, and moderate potential for volatilization, NTs therefore should exhibit moderate to high mobility in the soil and volatize slowly from dry soil surfaces [4].

8.3.3 Transport in Water

When deposited into aqueous systems, NTs can be susceptible to photolysis, volatilization, and biodegradation processes. Hydrolysis is not expected to occur [4]. Due to the high solubility values for 2-NT, 3-NT, and 4-NT and physical states of 2-NT and 3-NT, dissolution into and transport with aqueous systems to groundwater is expected to occur. Adsorption to sediments or bioaccumulation is not expected to significantly affect NT transport and ultimate fate in water. NTs are not expected to accumulate in aqueous systems; for example, the half-life of 4-NT in a river 4 to 5 m deep is estimated to be approximately 2.7 days [4]. Once deposited into water systems, the NTs can degrade and produce 2-methyl-6-nitrophenol and 2-methyl-4-nitrophenol or 4-methyl-2-nitrophenol through photolysis, depending on the NT present or the compounds formed from biodegradation processes [4].

8.4 TOXICITY DATA OF NITROTOLUENES

Occupational exposure to NTs may mostly occur during their production and use. The major routes of exposure are inhalation and dermal contact. Exposure may occur during sampling, loading and unloading drums containing the chemical [22].

2-NT is absorbed via the gastrointestinal tract, the lungs and through the skin [23, 24]. Due to its low acute toxicity, the main exposure symptoms are associated with methemoglobin formation and central nervous system damage. Repeated oral administration causes damage to the liver, sleep, kidneys and testes [24, 25]. The carcinogenicity of 2-NT has been investigated and showed a clear increase in the incidence of mesotheliomas in the epididymis of the male rat and in short-term tests in the mouse, which also provide evidence of weak carcinogenic potential. 2-NT has neither embryotoxic nor teratogenic potential but it has adverse effects on fertility in males and females [26]. 3-NT may cause elevation of blood methemoglobin levels in cases of acute poisoning. However, the increase produced by 3-NT is relatively small compared to that produced by other methemoglobin-forming agents [27]. 4-NT absorption generally causes methemoglobinemia and associated symptoms such as headache, cyanosis, debilitation, vertigo, ataxia, respiratory disturbances, tachycardia and vomiting [28]. The effects on the endocrine and reproductive systems in humans have not been reported.

8.5 EXAMPLE REGULATORY GUIDELINES FOR NITROTOLUENES

EPA added 2-NT to the list of toxic chemicals subject to reporting under Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986 and Section 6607 of the Pollution Prevention Act (PPA) of 1990. 2-NT has been classified by the National Toxicology Program in its 12th report on carcinogens as "reasonably anticipated to be a human carcinogen." EPA has determined that o-nitrotoluene meets the EPCRA Section 313(d)(2)(B) criteria because it can reasonably be anticipated to cause cancer in humans.

8.6 DATA GAPS

Despite several decades of research work, several data gaps pertaining to NT degradation and transformation pathways exist. Major data gaps are listed below:

A. Fate and Transport

- **Phytotransformation and Abiotic Degradation**: Information on transformation pathways of NTs as well as sorption of NTs to clay/ soil particles appears to be one of the data gaps identified during evaluation of this compound. Moreover, little to no information is available on plant uptake and NT phytotransformation.
- **Evaluation of Fate and Transport Data:** Because NTs, along with DNTs, are present during or resulting from the manufacture of TNT, a fate/transport/toxicity/remediation summary and evaluation among all of these NT-based compounds (as well as nitrobenzene and any other nitroaromatics) may be warranted to find, for example, commonalities for remediation.

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9. NITROBENZENE (NB)

9.1 INTRODUCTION

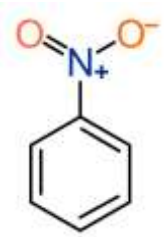

Figure 9-1. Chemical Structure of Nitrobenzene

Names: Nitrobenzene
Abbreviations and Other Names: NB, nitrobenzol
CAS No.: 98-95-3
Chemical Formula: $C_6H_5NO_2$
Occurrence in Mixtures/Compositions: Degradation product or impurity in nitroaromatic explosives (e.g., TNT, TNB, DNT)
Natural Occurrence: NB does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of NB are provided in Table 9-1.

Table 9-1. Physical and Chemical Properties of NB [2]

Property	Value	Units
Color	Yellow	
Physical state	Liquid	
Melting temperature	-5.6	°C
Vapor pressure (at 25°C)	3.7e-4	atm
Specific gravity	1.2	None
Water solubility (at 20°C)	2100	mg/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.85	None

9.2 FATE

In the area of explosive or energetic materials, NB (Figure 9-1) is typically found as a key precursor in the formation of dinitrobenzene (DNB) or trinitrobenzene (TNB) explosives during their manufacturing processes, or as a degradation product of these and dinitrotoluene (DNT) and trinitrotoluene (TNT) explosives. However, the cost to produce TNB and DNB is so high that the use and availability of these explosives is minimal. NB appears to be of particular concern due to the formation and dispersion in soil and water systems at ranges and installations associated with DNB, TNB, DNT, and TNT handling and use [1]. NB is used in other applications outside of explosives, including the synthesis of aniline, polymers, rubber chemicals, dyes, drugs, and pesticides [2].

9.2.1 Relevant Properties

Properties of NB relevant to environmental fate and transport are provided in Table 9-1 [2]. Some of these properties provide indicators to the transport of NB in the environment. For example, NB is a liquid at normal environmental temperatures; is highly soluble in water (2100 mg/L); and has

an octanol-water partition coefficient value associated with a relatively high level of hydrophilicity (1.85).

Although NB is not used as an explosive material, some comparisons can be made with other explosive materials to help evaluate the propensity for transport. In terms of specific gravity, NB, with a specific gravity of 1.2, is less dense than the nitroaromatic explosives 2,6-DNT (1.3 specific gravity), 2,4-DNT (1.3), TNT (1.3), DNB (1.6), and TNB (1.8). The log octanol-water partition value of NB (1.85) is greater than those of TNB (1.18) and DNT (1.49), and less than those of 2,4-DNT (1.98) and 2,6-DNT (1.98); it is nearly equivalent to that of TNT (1.86). All of these values are in relative close range, suggesting that the transport and perhaps fate of NB will fall in line with what has been reported for DNTs, TNB, DNB, and TNT. However, the solubility value of NB (2100 mg/L) could be the property that distinguishes NB from most of the nitroaromatic compounds presented. NB has a much higher solubility than DNTs, DNB, and TNT. Out of these compounds, only TNB has a solubility value (3500 mg/L) higher than that of NB.

9.2.2 Photolysis

NB will degrade in the atmosphere primarily by photolysis from ultraviolet (UV) light to produce *o*-nitrophenol, *p*-nitrophenol, and nitrosobenzene. 38% degradation of the source material occurred over a 5-hour long laboratory test [3]. NB will also undergo photolysis in aqueous solutions [4]; however, this is a fairly slow process and, aqueous photolysis may not be an effective wastewater treatment method. Aqueous photolysis can generate *o*-nitrophenol, *p*-nitrophenol, and *m*-nitrophenol as intermediates; nitrohydroquinone, nitrocatechol, and catechol as secondary products; and nitrite and nitrate ions. In natural waters, NB photolysis may be an important degradation pathway, but only if sources for biodegradation are poor or lacking [2].

9.2.3 Other Abiotic Reactions

Abiotic reduction of NB by ferrous iron (Fe^{2+}) has been demonstrated, yielding aniline as the product of transformation [5] using montmorillonite and ferruginous smectite. The rate of transformation is dependent on the concentration of Fe(II) in clay soils and the molecular properties and aqueous concentration of NB. The half-life for this transformation in a high (≈ 2.8 mmol/g) Fe(II) concentration clay soil sample was ≈ 15 hours; for a moderate (≈ 0.3 mmol/g) concentration sample this value was ≈ 60 hours (2.5 days). These rates appear to be faster than the half-life for the biodegradation of NB in water (12.1 days) and soil (5.84 days) and slower than NB photolysis.

9.2.4 Biodegradation

NB is a challenging compound for microbial degradation. Most of the bacterial strains cannot effectively degrade more than 200 mg/L of NB. However, from recent reports, *Micrococcus luteus* [6] completely degraded 200 mg/L NB under aerobic conditions after 120 hours, but increasing NB to 250 mg/ L required more time for total degradation (192 hours).

To date, two different strategies have evolved for microbial degradation of NB (Figure 9-2). The partially reductive pathway is favorable and faster and as identified in *Pseudomonas pseudoalcaligenes* JS45 species was isolated from contaminated soil and groundwater collected

from Pascagoula, Mississippi. This microorganism has an ability to grow on NB as a sole carbon, nitrogen, and energy source [7]. The genes encoding the entire pathway for NB degradation in JS45 have been identified, and several of the enzymes have been characterized in great detail.

NB degradation through the partially reductive pathway follows the steps below [8-11]:

1. Hydroxylaminobenzene is reduced (Figure 9-2A) through a nitrosobenzene intermediate (not shown) by the action of NB nitroreductase.
2. Hydroxylaminobenzene undergoes mutation reaction to 2-aminophenol by intramolecular transfer of hydroxyl groups.
3. 2-Aminophenol is further metabolized by a metacleavage pathway. Similar to catechol 2,3-dioxygenase, 2-aminophenol-1,6-dioxygenase breaks the benzene ring of 2-aminophenol to produce 2-aminomuconic semialdehyde (Figure 9-2B).
4. 2-Aminomuconic semialdehyde is subsequently oxidized in a NADH-dependent reaction to 2-aminomuconate, which is deaminated to form 4-oxalocrotonate (2-oxo-3-hexene-1,6-dioate).
5. Metabolism then proceeds through decarboxylation, followed by hydrolysis and then cleavage by an aldolase, to eventually yield pyruvate and acetaldehyde. An acetaldehyde dehydrogenase scavenges the acetaldehyde by oxidation to acetate, which feeds into the TCA cycle.

Moreover, *Pseudomonas sp*. strain AP-3 (191) and *Pseudomonas sp.* strain HS12 use similar pathways and enzymes for NB degradation to those of JS45. However, in AP-3, 2-aminomuconate may undergo decarboxylation prior to deamination during the formation of 2-oxo-4-pentenoate. Considering that the reduction of the nitro group is a highly favorable reaction, it is not surprising that the reductive pathway for NB degradation is the prevalent one.

The lone exception is *Commonas sp.* strain JS765, which utilizes NB in an oxidative pathway. Instead of using a three-step conversion process, JS765 uses a dioxygenase to oxidize NB to catechol in a single enzymatic step which releases nitrite (Figure 9-2C). JS765 uses a standard metacleavage pathway like that in *Pseudomonas* strains (32), to metabolize catechol to acetaldehyde and pyruvate (Figure 9-2D).

9.2.5 Phytotransformation

Limited data on the plant uptake of NB are available [12]. NB in solution was shown in laboratory studies with soybean plants to be absorbed into the roots, with a half-life of less than 24 hours. Transportation of NB to other regions of the plants did not occur.

9.2.6 Hydrolysis

Hydrolysis of NB is not expected to occur [3].

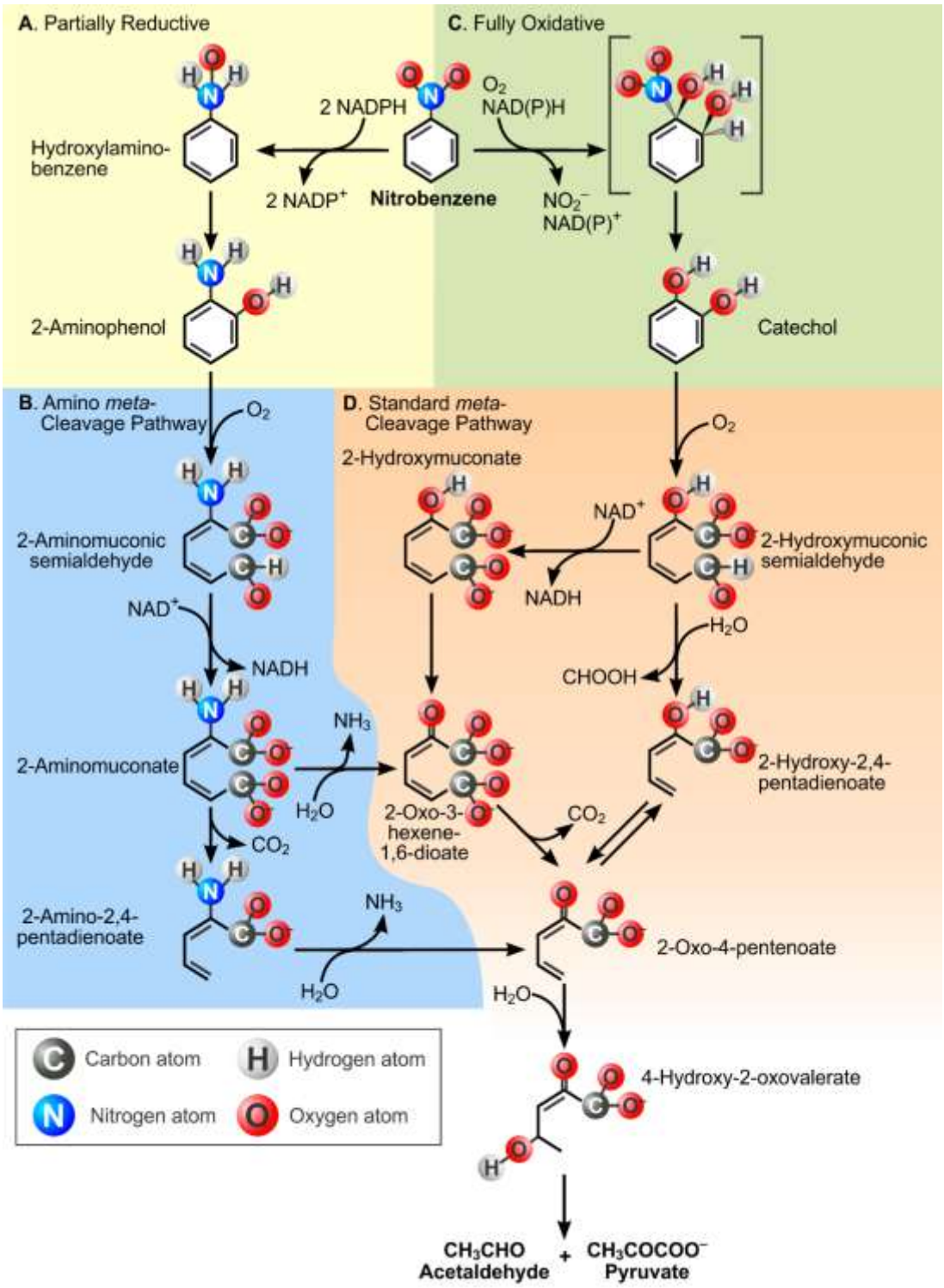

Figure 9-2. Microbial Degradation of Nitrobenzene [7]

9.2.7 Key Degradation Products

NB degradation has been shown to produce nitrophenols, nitrohydroquinone, nitrocatechol, catechol, nitrosobenzene, and nitrite and nitrate ions through photolysis; aniline through abiotic reduction with Fe(II); and acetaldehyde and pyruvate, with several intermediate products, via biodegradation.

Toxicity is the primary concern with these degradation products, particularly aniline and the nitrophenols, especially at military production plants, where several nitroaromatic compounds may be produced, most, if not all, of which can produce NB and these degradation products as wastes.

9.3 TRANSPORT

9.3.1 Transport Processes

NB can reach soil and water systems via waste effluents from explosive production sites or as a result of degradation of an explosive compound (e.g., TNT) [13]. NB does appear to be a contamination issue on military ranges, although quantitative data on the amount of NB contamination appear to be lacking.

NB is likely to be released to air, soil, or water directly as a result of NB manufacturing processes [2]. NB can also typically reach soil systems as a result of the use of a nitroaromatic explosive material (e.g., TNT) that can break down in the environment. Taken into consideration along with its high mobility in water, it may be challenging to trace the presence of NB back to its source and to determine whether it was generated as a result of manufacturing processes or use.

A review of values for the water solubility, volatility, and octanol-water partitioning coefficient for NB suggests that NB will be highly mobile in water and will unlikely bioaccumulate. This is confirmed by several studies that have provided evidence of NB in groundwater systems [2].

9.3.2 Transport in Air

Discharge of NB to air will likely come from manufacturing processes. Any NB generated from use of explosive materials is likely to occur once the energetic material has reached soil or water and sources or conditions for degradation are available. Existing EPA controls are in place to prevent the discharge of NB to air; air contaminated with NB from production processes is required to be passed through activated charcoal filters [2]. If discharged to air, NB can undergo photolysis; however, air ultimately appears to be a low probability transportation route [2].

9.3.3 Transport in Soil

NB will generally exhibit weak-to-moderate sorption to soil organic content [2]. Moderate sorption was noted for clay mineral soils [14]; nitroaromatic compounds in general demonstrate good sorption to clays. NB accumulation in soil appears to be difficult; reports [15, 16] investigating the presence of explosive compounds and their degradation products in soil report little to no NB contamination. It is more likely that, once discharged to soil, NB will undergo photolysis, biodegradation, or be diffused into and transported with water [3].

9.3.4 Transport in Water

Once in contact with water, NB is expected to be mobile due to its liquid state at normal environmental conditions and high solubility value. It is not expected to volatize from water; rather, it will tend to sink due to its higher density [3]. NB will also not readily hydrolyze. Therefore, NB could persist in water matrices unless the presence of other degradation pathways, namely, photolysis, biodegradation [3], and abiotic reduction [5] are available to attenuate and transform NB concentrations.

NB will be mobile in water matrices and has the potential to reach and travel with groundwater. NB is also expected to persist if no sources of degradation are available and sink in water, which could lead to the development of NB plumes. However, none of the available literature sources presented any findings of NB plumes.

9.4 TOXICITY DATA OF NB

NB is used to manufacture aniline. The most common route of exposure to NB is during its manufacture. Additionally, populations occupying areas near NB production and processing facilities [2] may be exposed to this compound. The most common assessment strategy to estimate exposure to NB is by measurements of blood methemoglobin levels; however, this method is not specific to NB, as many chemicals may produce methemoglobin. For chronic NB exposures, the presence of its breakdown products in urine can be used as indicators.

Acute and chronic inhalation, oral, and dermal exposure of humans to NB result in most commonly found methemoglobinemia [17]. Methemoglobinemia is a result of conversion of hemoglobin to methemoglobin parallel with lowering the amount of oxygen released to the tissues of the body [2, 18]. Thus, the lower oxygen concentration in blood may cause dizziness, fatigue and headaches. At higher concentrations, depressed respiration, bluish-gray skin, disturbed vision, and coma may occur [17, 18]. No information is available on the reproductive, developmental, or carcinogenic effects of NB in humans. Animal studies indicate that inhalation exposure to NB does not result in developmental effects, while reproductive effects, such as decreased fertility, reduced testicular weights, and decreased sperm production, have been noted. EPA has classified NB as a Group D, not classifiable as to human carcinogenicity [18, 19].

9.5 EXAMPLE REGULATORY GUIDELINES FOR NB

A provisional reference concentration (RfC) was calculated by EPA and reported at 0.002 milligrams per cubic meter (mg/m^3) for NB based on hematological, adrenal, renal, and hepatic effects in mice. The RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious non-cancer effects during a lifetime. It is not a direct estimator of risk but rather a reference point to gauge the potential effects [19].

At exposures increasingly greater than the RfC, the potential for adverse health effects increases. Lifetime exposure above the RfC does not imply that an adverse health effect would necessarily occur. The provisional RfC is a value that has had some form of Agency review, but it does not appear on IRIS [18]. The reference dose (RfD) for NB is 0.0005 mg/kg body weight per day

(mg/kg/d) based on hematologic, adrenal, renal, and hepatic lesions in rats and mice. EPA has medium to low confidence in the study on which the RfD was based because it is not an oral study, a limited number of animals/sex/dose were tested, and a no-observed-adverse-effect level (NOAEL) for the critical toxic effect (i.e., adrenal toxicity) was not determined, although two species were used and many parameters were measured; low confidence in the database due to the fact that chronic reproductive and teratology data are missing; and, consequently, low confidence in the RfD [20].

9.6 DATA GAPS

Fate and transport data for NB originate from studies on industrial production and discharge of NB. Only a few sources focus on the production and fate of NB at military installations. Thus, quantitative data on the amounts of NB that could be generated from explosive material production and use are needed. Although development of NB remediation technologies is currently ongoing, identification of effective remediation methods for removal of NB is needed. Additional data gaps identified for NB are listed below:

A. Fate and Transport:

- More specific data on NB soil transport, particularly on the sorption rates of different soils is needed, including the influence of the type of clay soil on sorption.
- NB quantities at military installations and qualifying the significance or concern with NB contamination.
- More information is needed on NB uptake by plants and the phytotransformation process.

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10. NITROGLYCERIN (NG)

10.1 INTRODUCTION

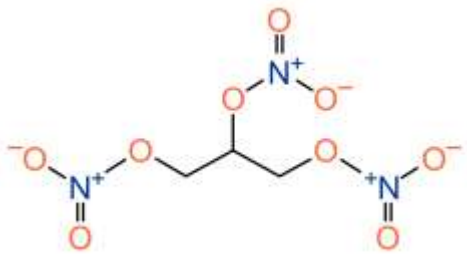

Figure 10-1. Chemical Structure of NG

Names: NG (NG), glycerol trinitrate (GTN), 1,2,3-propanetriol trinitrate, nitroglycerol, trinitroglycerol

Abbreviations and Other Names: 1,2,3-Propanetriol, trinitrate, 1,2,3-tris(nitrooxy)propane

CAS No.: 55-63-0

Chemical Formula: $C_3H_5N_3O_9$

Occurrence in Mixtures/Compositions: Primarily used in dynamite formulations and in double-based and triple-based propellants.

Natural Occurrence: NG does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.

Physical/Chemical Properties: The physical/chemical properties of NG are provided in Table 10-1.

Table 10-1. Physical and Chemical Properties of NG [1, 2]

Property	Value	Units
Color	Clear (pure form) Yellow (commercial form)	NA
Physical state	liquid	NA
Melting temperature	13.5	^oC
Vapor pressure (at 25^{o}C)	2.33E-6	atm
Specific gravity	1.596	None
Water solubility (at 20^{o}C)	173	mg/L
Dissolution rate in water	≈ 59.2 (est.)	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.62	None

10.2 FATE

NG is an explosive nitrate ester, known for its sensitivity to ignition and powerful explosive output. It is commonly used in double-based and triple-based smokeless powder propellant formulations as an absorbed ingredient added to reduce smoke output while increasing energy output. It is also used as the main explosive ingredient in commercial blasting dynamites. In military-grade dynamites RDX substitutes for the NG due to sensitivity issues associated with long-term storage. In all of these formulations, NG is rendered less sensitive to ignition through the use of stabilizers (i.e., adsorbents), primarily diphenylamine and ethyl centralite (1,3-diethyl-1,3-diphenylurea), which are toxic. It is not clear from the surveyed literature how quickly these stabilizers may leach out from a double- or triple-based propellant formulation. Formulations containing NG and these stabilizers include, but are not limited to:

- M5 Propellant (81.95% nitrocellulose; 15% nitroglycerin; 1.4% barium nitrate; 0.75% potassium nitrate; 0.6% ethyl centralite; 0.3% graphite)
- M7 Propellant (54.6% nitrocellulose; 35.5% nitroglycerin; 7.8% potassium perchlorate; 1.2% carbon black; 0.9% diphenylamine)
- M9 Propellant (57.75% nitrocellulose; 40% nitroglycerin; 1.5% potassium nitrate; 0.75% diphenylamine).
- M13 Propellant (57.3% nitrocellulose; 40% nitroglycerin; 1.5% potassium sulfate; 1% diphenylamine; 0.2% triacetin; 0.05% carbon black)

10.2.1 Relevant Properties

Properties of NG pertaining to its behavior and fate in the environment are provided in Table 10-1. Due to its ignition sensitivity and liquid form at room temperatures, NG is typically absorbed into other ingredients of an energetic formulation. As a result, the release of NG from a formulation into the soil or water will not be immediate, which is why the value in Table 10-1 for the dissolution rate in water is an approximate value.

10.2.2 Photolysis

The half-life of photolysis of NG is dependent on the type of environment [3]. The predicted photolysis half-lives of NG in water, moist sand, and dry sand environments were predicted to be ≈ 27, 111, and 126 days, respectively [4]. Dinitroglycerol (DNG), followed by mononitroglycerol (MNG) are formed (step-wise) as byproducts of NG photolysis, with glycerol formed as the final product. The DNG and MNG byproducts photodegrade at rates equivalent to or faster than NG, suggesting that photolysis should prevent the accumulation of these toxic compounds in the environment.

10.2.3 Abiotic Reactions

Laboratory studies focused on remediation technologies have demonstrated the ability of cast iron to reduce NG through a step-wise reduction to glycerol via 1,2-diNG (1,2-DNG), 1,3-diNG (1,3-DNG), 1-monoNG (1-MNG), and 2-monoNG (2-MNG). Nitrite is also produced in this process and is further reduced to ammonium. Additional laboratory tests demonstrated reduction of NG to glycerol in the presence of magnetite [5].

10.2.4 Biodegradation

Biodegradation of NG has been extensively studied in the laboratory using various microorganisms, and a degradation pathway has been identified under aerobic and anaerobic conditions (Figure 10-2). The biodegradation of NG consists of a step-wise denitration of the molecule [6, 7], with generation of more toxic, soluble, and volatile intermediate products, such as 1,2-dinitroglycerol, 1,3-dinitroglycerol, 2-mononitroglycerol and 1-mononitroglycerol, than NG itself. Upon complete denitration, the usual end product is glycerol, which may further mineralize to CO_2 [7].

Another possibility for the last degradation step is the transformation of the partial degradation product 1-mono-NG (1-MNG) by phosphorylation instead of the usual release of the last nitro

group to form glycerol, with the resulting molecule being assimilated by the microorganisms responsible for this transformation [8]. Depending on the microorganisms, complete denitration is not always achieved. There is less information about the enzymatic removal of the second nitrate ester group, although there is an evidence that a single enzyme can sequentially catalyze the elimination of both the first and second nitrate ester groups. Both 1-mononitroglycerol (1-MNG) and 2-MNG are produced as a result of the reduction process with preferential production of 1-MNG. Also, in addition to the partially denitrated products, biodegradation of NG involves the release of nitrite ions (NO_2^-), which then oxidize to nitrate (NO_3^-) in the presence of oxygen. Although NO_3^- (MCL of 45 mg/L as NO_3) is less toxic than NG, it is stable in oxidizing conditions and is one of the most common contaminants in shallow aquifers.

Environmentally friendly biological treatment methods for NG destruction are preferred over physicochemical treatments due to complete transformation (i.e., complete denitration without accumulation of glycerol dinitrates or glycerol mononitrates) of the compound and lower cost.

Early studies of aerobic NG biotransformation focused on the use of activated sludge, in batch and continuous bioreactors, supplemented with excess primary carbon sources [9]. A step-wise NG biotransformation pathway via the dinitrate and mononitrate glycerol esters was proposed, with successive steps proceeding more slowly. However, the presence of residual dinitrates and mononitrate isomers in spent batch and continuous bioreactor medium question complete NG denitration [10]. High destruction efficiencies of NG were reported in a sequencing batch reactor study, when treatment was performed with munitions wastewater from a ball powder production facility [11]. It is unclear if complete denitration of NG was achieved, since no attempts were made to measure concentrations of GDNs or GMNs. Cometabolism was again suggested to be the mechanism of NG biotransformation, since NG-acclimated cultures were incapable of utilizing GTN as the sole carbon source in bench-scale reactors [11].

Several pure bacterial cultures were recently found to utilize GTN as a sole nitrogen source [12, 13]. An *Agrobacterium radiobacter* strain denitrated GTN with the formation of both GDN isomers and subsequent conversion to 1-GMN and 2-GMN; the strain was not able to denitrate the GMN isomers, resulting in GMN accumulation [13]. A purified GTN reductase of *A. radiobacter* was NADH dependent and mediated the reductive scission of GTN to GDN only [13, 14]. *Pseudomonas putida* and *Pseudomonas fluorescens* are capable of utilizing NG as a sole nitrogen source [12, 15]. NG reductase catalyzes the NADPH-dependent denitration of NG. The *Pseudomonas* NG reductases were shown not to be reactive with mononitrate glycerol esters. However, NG has been shown to mineralize under anaerobic conditions [9]. Thus, the last step shown below is hypothesized to indicate that bacterial NG metabolism enters intermediary metabolism [18, 19].

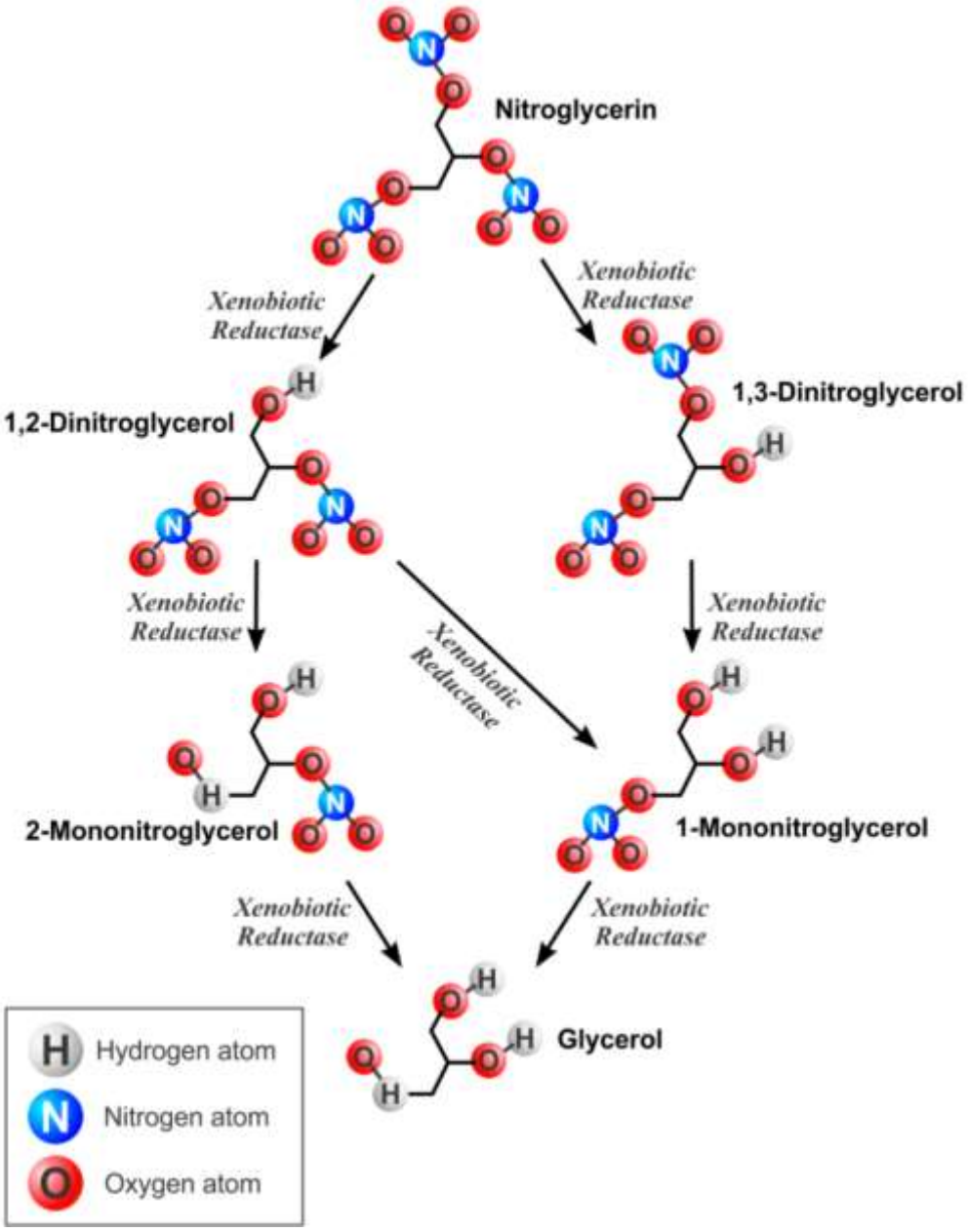

Figure 10-2. Biological Degradation of NG [16, 17]

10.2.5 Hydrolysis

NG undergoes hydrolysis, producing oxalate and nitrite and nitrate ions in the process (i.e., nitric and nitrous acid), with nitrite production favored [20]. This reaction rate increases with increasing temperature [20], and with increasing alkalinity [3]. For example, experiments on the alkaline hydrolysis of NG produced a reaction half-life of 37 days at pH 9 [3]. At normal temperatures and pH values in the range of 3 to 8, the hydrolysis half-life of NG is predicted to be more than 1 year [1]. With such a slow rate of hydrolysis at normal environmental conditions, the generation rates

of the nitrite and nitrate hydrolysis products, which can cause methemoglobinemia in mammals, are not considered a concern to wildlife [1].

Hydrolysis appears to be a degradation pathway when NG is released to soils [1]; however, the rate and effectiveness of hydrolysis will depend on the alkalinity of the soil and competition with much faster NG biodegradation processes. The biodegradation half-life of NG in soil is 6.3 days and in water it is 7.48 days.

10.2.6 Key Degradation Products

DNGs and MNGs are formed from NG degradation via phytotransformative, abiotic, and biotic processes. Both compounds can possess some degree of toxicity [21]. The distribution and persistence of DNG and MNG in the environment could pose a risk of exposure to wildlife [18]; however, more data are needed to fully assess the risk.

Nitrate and nitrite ions can also be formed from NG degradation. Both are significant environmental concerns due to their high mobility in soil and water, and known toxic effects.

10.3 TRANSPORT

Estimates by the U.S. EPA conclude that 193,953 pounds of NG were released to the environment by U.S. Army facilities, gun propellant manufacturers, and others in the NG manufacturing or hazardous waste disposal industry in 2015 [22]. A significant number of recent (i.e., within the last 15 years) studies, surveys, and experiments have sought to develop a well-understood transport process for NG. These sources have involved areas such as: degradation pathways present in surface and aquifer soils [23]; measurement of the release rate of NG to the environment from fired round residues [24]; dissolution of NG from non-soluble, solid matrices [25, 26]; and the effects of adsorption and desorption processes on soil mobility [27].

10.3.1 Transport Processes

Analysis and identification of the available transport processes for NG require knowledge of fate of NG in the environmental matrices. During the manufacture of explosive formulations or propellant compositions, NG is added as a liquid absorbed into other ingredients [26]. NG is often discharged to aqueous systems via wastewater from propellant manufacturing processes [5], and discharged to soil and sediments via open burn/open detonation activities or live-fire training missions [24].

NG present in aqueous systems from manufacturing processes needs to be treated before discharged to wastewater treatment plants; NG levels ranging from 180 mg/L (Badger Army ammunition plant) to 600 mg/L (Radford Army ammunition plant) have been reported [5]. The factors influencing the mobility of NG from soil to the groundwater at a particular site or location must be well understood so that proper remediation and transport mitigation actions can be taken.

When NG is discharged to soils and sediments, particularly from open burn/open detonation events or live-fire training missions, two significant factors that influence transport are present. First, open burn/open detonation or live-fire training activities involving propellants can release significant amounts of unburnt/unreacted material to the environment. For example, in one study [24], the

estimated amount of unreacted NG deposited from the firing of an M136 AT4 rocket was 95 g per round, or 73% of the starting NG amount. Soil contamination levels from such activities have ranged in concentrations of 18.1 µg/kg (CFB Shilo, Manitoba, Canada) to 130,000 µg/kg (Massachusetts Military Reservation) [23].

Second, there is an initial heterogeneous release of NG to the environment due to the competing processes of rapid dissolution of NG into the environment and NG diffusion into the absorbent energetic or propellant material [24-26]. NG exhibits a high degree of solubility with water; thus, dissolution is the key transport process. However, once NG present at the surface of an absorbent material has dissolved, any NG trapped in the absorbent material via diffusion could be locked in and not available for transport, particularly if the absorbent material is non-soluble, as is the case with NG absorbed into nitrocellulose in double-based and triple-based gun propellants [25, 26, 28]. The result is a fast initial diffusion of NG at the surface of the propellant, followed by a slow release of the trapped particles. This can lead to long-term persistence and potential accumulation of NG in the environment. Data from range characterization studies have shown that NG concentrations from source terms trapped in nitrocellulose have been found at military ranges in surface soils for durations of over 25 years [24].

10.3.2 Transport in Air

NG released directly to the atmosphere is expected to drop out of the atmosphere via gravitational settling or scouring by rain [1]. The vapor pressure of NG suggests that it may exhibit more volatility than other energetic materials such as RDX or TNT. However, this value does not appear to warrant concern about release to and significant transport in air [1, 3].

10.3.3 Transport in Soil

NG can be discharged to soil from open burn/open detonation or live-fire training activities. In these cases, the NG residues are primarily deposited onto the soil surface at firing points [26, 29], at depths ranging from 0 cm (i.e., on top of the soil) to ≈ 60 cm at one of the surveyed sites [29]. When discharged to soil and sediments, NG readily dissolves into water, unless, as noted, it is locked in a solid matrix such as nitrocellulose.

The values for K_{ow} (1.62) and water solubility (173 mg/L) for NG suggest that it will be mobile in soils and sediments [30]. However, this potential for NG mobility can be retarded by degradation processes in the environment. If NG is able to reach soils and sediments through the vadose zone (i.e., it is not locked in a non-soluble matrix), NG can undergo reversible soil adsorption/desorption, photodegradation, phytotransformation, biodegradatioin, or, in certain conditions, hydrolysis [23-27, 29, 31, 32]. These factors limit the ability of dissolved, mobile NG to reach groundwater [27] to the point where the risk of groundwater contamination from NG dispersed onto soil surfaces is low [33]. For NG to reach the groundwater table, a strict set of conditions is required, including: a source of available NG residues for transport; significant rain precipitation; a shallow, permeable unsaturated zone; and low amount of organic content [24, 28]. Complete data on the sorption to clay minerals in soil appear to be lacking; however, the authors of one report on the use of iron as a remediation technology concluded that while iron was capable of reducing NG and its products, the adsorption of NG and its products to iron was minimal [34].

10.3.4 Transport in Water

NG exhibits a relatively high rate of solubility in water [1]. Very few reports or studies have examined the fate of NG released directly to water systems. Biodegradation and photolysis are expected to play significant roles in NG degradation in water systems, though NG may persist in the absence of these two degradation processes. The high solubility of NG in water also suggests that adsorption to sediment and bioaccumulation in aquatic organisms is not a concern [1].

Groundwater contamination data for NG appear to be limited and the few open burn/open detonation and training sites that were available for groundwater sampling may not be representative of all sites across the United States and Canada [29]. No appreciable concentrations of NG were detected in groundwater samples analyzed as part of a recent range characterization survey conducted by Pennington [29] although NG has been detected in wastewaters from NG manufacturing installations [5].

10.4 TOXICITY DATA OF NG

NG may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact. Subchronic inhalation of NG was studied in mice and showed lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis [35]. In cats, subchronic or chronic inhalation or dermal administration of NG caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs and death. Chronic oral administration of NG to rats resulted in liver cancer [36].

Acute NG inhalation or dermal exposure of workers caused decreased systolic, diastolic, and pulse blood pressure due to vascular dilation (used as a medication for angina for that reason). Chronic NG exposure caused damage to the heart and reduced tolerance to alcohol. Reported symptoms of short-term exposure to NG include severe headache, dizziness, nausea and heart palpitations while chronic NG exposure results in severe chest pains and skin sensitization [37]. Thus, workers with potential exposures to NG should be monitored in a systematic program or medical surveillance to prevent and/or control occupational injury and disease.

10.5 EXAMPLE REGULATORY GUIDELINES FOR NG

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG is 0.2 mg/m^3 as a ceiling concentration which shall not be exceeded. The recommended exposure limit for NG alone or for mixtures with ethylene glycol dinitrates is 0.1 mg/m^3 determined in any 20-minute sampling period [38]. The American Conference of Governmental Industrial Hygienists threshold limit value for NG is 0.5 mg/m^3 as a time-weighted average concentration for a normal 8-hour workday and a 40-hour work week [38].

10.6 DATA GAPS

Several data gaps exist within research on NG and mostly related to the water transport of NG and its byproducts as well as their fate and transport. Additionally, effective removal technologies to transform and remediate NG from water and soil systems appear to be missing. Transition of

already existing laboratory-based technologies needs to occur so that the field solutions to the remediation of this compound are successfully applied.

Several main data gaps have been identified for NG.

A. Fate and Transport:

- **Water Transport**: The transport of NG released directly to water systems may need to be studied further to better understand the factors influencing transformation versus persistence of NG and its byproducts in such environments. The amount of NG discharged to water systems from NG manufacturing processes could be a significant source of contamination; however, specific information on the amount of NG discharged to water does not appear to be reported or available in NG transport studies. Some data have been collected, and interest in the fate and transport of NG appears to have increased within the past 15 years. Completing this data gap provides a complementary set of fate and transport data to the substantial amount of reports and range characterization studies on soil transport form open burn/open detonation and live-fire training activities.
- **Phytotransformation and phytodegradation**: Phytodegradation studies and efforts for NG removal from soil also appear to be a fledgling effort that may need to be investigated further for the benefit of range remediation efforts. The state of this data gap appears to be in transition from laboratory-scale studies using hydroponic samples or cultured plant cells to more field-relevant studies for long-term remediation.
- **Transport, fate, and toxicity of other compounds in NG formulations**: The transport, fate, and toxicity of compounds other than NG typically included in double- and triple-based propellant formulations need to be better understood. Little data appear to be available for the transport, fate, and toxicity of the stabilizing compounds (e.g., ethyl centralite) when used in propellant formulations with other compounds.

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11. NITROGUANIDINE (NQ)

11.1 INTRODUCTION

Figure 11-1. Chemical Structure of NQ

Names: Nitroguanidine
Abbreviations and Other Names: 1-Nitroguanidin, picrate, guanylnitramine
CAS No.: 556-88-7
Chemical Formula: $CH_4N_4O_2$
Occurrence in Mixtures/Compositions: Triple-based propellant formulations (M30, M31); IMX-101 explosive (TNT replacement)
Natural Occurrence: NQ does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of NQ are provided in Table 11-1.

Table 11-1. Physical and Chemical Properties of NQ [2, 3]

Property	Value	Units
Color	Colorless	NA
Physical state	Solid Crystals	NA
Melting temperature	225 – 250	°C
Vapor pressure (at 25°C)	3.95E-5	atm
Specific gravity	1.5	None
Water solubility (at 20°C)	5000	mg/L
Dissolution rate in water	≈ 71.9 (est.)	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	-0.89	None

11.2 FATE

NQ (Figure 11-1) is an explosive material from the class of nitramines, which includes explosives such as HMX and RDX. Historically, NQ has been used in triple-based gun propellants, along with nitroglycerin and nitrocellulose. It is often included as an oxidizer component and as flash and flame temperature reducing component [1]. It is also included in the new insensitive munition (IM) formulation IMX-101 as a TNT replacement.

The formulations containing NQ include, but are not limited to:

- IMX-101 (40-45% DNAN; 18-23% NTO; 35-40% NQ)
- M15 Propellant (20% nitrocellulose; 19% nitroglycerin; 54.7% nitroguanidine; 0.3% cryolite; 0.6% ethyl centrolite
- M30 Propellant (26-30% nitrocellulose; 20-24% nitroglycerin; 46-48% nitroguanidine, 1-3% ethyl centrolite; 1-3% graphite; 0.3% cryolite)

Triple-based propellants contain stabilizers for the purpose of desensitizing the nitroglycerin. These stabilizers include diphenylamine and ethyl centrolite (1,3-diethyl-1,3-diphenylurea), which are toxic. It is not clear from the surveyed literature how quickly these stabilizers may leach out from a triple-based propellant formulation.

As a result in this renewed interest and new use for NQ, an importance has been placed on a better understanding of the fate and transport processes of NQ [4].

11.2.1 Relevant Properties

Properties of NQ pertaining to its behavior and fate in the environment are provided in Table 11-1. Of particular note is the dissolution rate of NQ into water. This value is primarily a function of the type of energetic formulation matrix within which the NQ is embedded. For triple-based gun propellants, NQ is embedded in insoluble nitrocellulose. In IMX-101, NQ is embedded in low solubility 2,4-dinitroanisole (DNAN) matrix.

The value provided in Table 11-2 for dissolution is derived from experimental data for triple-based gun propellants. A review of the properties shown in Table 11-1 suggest that NQ readily dissolves into water (i.e., solubility of 5,000 mg/L) and favors the aqueous phase (i.e., log Kow of -0.89).

11.2.2 Photolysis

NQ can be readily photolyzed by sunlight and UV radiation, forming guanidine, urea, cyanoguanidine, and nitrite as the main products, with nitrosoguanidine as an intermediate [5-7]. The half-life for this process is ≈ 1 to 2 days in natural waters. Nitrosoguanidine has been shown to be toxic to aquatic life. Its photolysis rate is slightly faster than that for NQ.

The photolysis reaction rate does not appear to be strongly pH-dependent, as the NQ photolysis rate was only slightly slower at pH 10 compared to neutral pH. However, the distribution of end products could be different: at neutral pH, 80% of the carbon from NQ and all oxidized nitrogen could be accounted for; at pH 10, less than 25% of the NQ carbon could be accounted for as guanidine, urea, and cyanoguanidine, with gaseous nitrogen as a significant product.

11.2.3 Abiotic Reactions

Abiotic reduction of NQ by ferrous iron has been demonstrated in the literature [8]. NQ can be reduced to nitrosoguanidine and aminoguanidine by catalytic hydrogenation and by zero valent iron under anaerobic conditions [9]. The specific products of abiotic reduction via ferrous iron have yet to be identified; however, it has been shown that the rate of degradation increases with increasing alkalinity from pH 7 to 9 and that solid surfaces (as opposed to soluble ferrous) are required for reduction to occur. The half-life of this reduction pathway is estimated to be 30 days at pH levels 8 and 9.

11.2.4 Biodegradation

There is very little information on microbial transformation of NQ, with the most known study of Kaplan et al. [10] on transformation of NQ by activated sludge (Figure 11-2). The study showed transformation of NQ into nitrosoguanidine that further abiotically decomposed to cyanamide,

cyanoguanidine, melamine and guanidine under anaerobic conditions [11]. Moreover, aerobic NQ biotransformation in the activated sludge was negligible with cometabolic transformation to cyanamide in surface water samples under aerobic conditions [12].

It has also been reported that NQ is poorly degraded in soils by indigenous bacteria and that degradation rates are related to soil organic carbon content with higher degradation rates noted for soils with higher carbon content [10, 13, 14]. The most recent study on NQ degradation by *Virovorax* strain VC1 [15] showed that the NQ could be totally degraded to three harmless end products (melamine, guanidine and urea) by a soil isolate under aerobic conditions. Since the NQ is a one-carbon molecule, to achieve its effective degradation, organic carbon or nutrients should be available in sufficient amount or added during the degradation process.

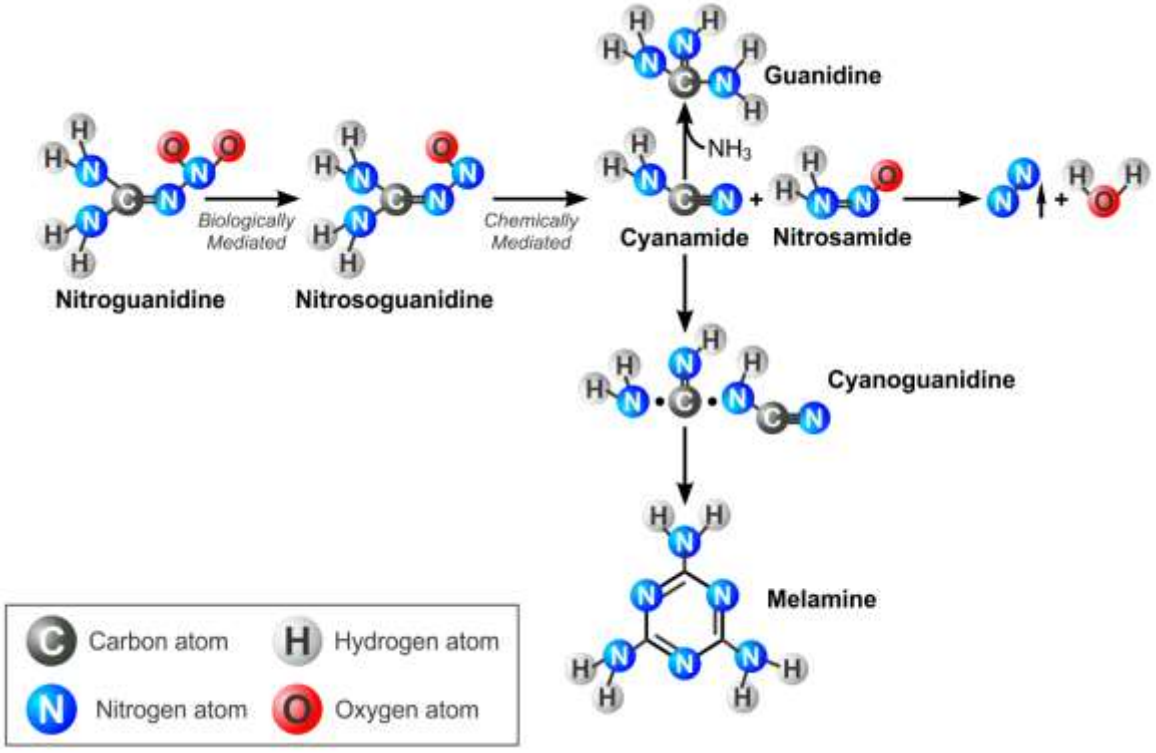

Figure 11-2. Biodegradation of NQ [11, 14]

11.2.5 Phytotransformation

Studies on the uptake of NQ by tall fescue grass and soybean plants have shown that NQ can be taken up by the roots and translocated to the leaves [16]. NQ was detected in the roots, stems, and leaves (with most of the concentration in the leaves) 96 hours after exposure to NQ-spiked soil samples. Plant uptake and phytotransformation appear to be an insignificant transformation route for NQ. Uptake by plants was in the range of 0.001 to 0.01 mg NQ/mg biomass. Data on transformation rates and products from NQ uptake appear to be lacking. NQ is suspected of undergoing phytotransformation, based on rates of recovery from these plant studies, though no analyses of transformation rates or identifications of the compounds produced were performed.

11.2.6 Hydrolysis

Hydrolysis is not expected to be an important environmental fate process for NQ because it lacks functional groups that can undergo hydrolysis [7].

11.2.7 Key Degradation Products

The key NQ degradation products from photolysis are guanidine, urea, and nitrite as the main compounds, with nitrosoguanidine as an intermediate. Nitrosoguanidine can undergo photolysis to form cyanamide [14]. Photolyzed NQ is thought to be significantly more toxic to aquatic life [5, 6].

Biodegradation processes can form nitrosoguanidine and aminoguanidine. Nitrosoguanidine can further decompose to cyanamide, cyanoguanidine, melamine and guanidine.

11.3 TRANSPORT

Most releases of NQ are from manufacturing processes [7]. NQ contamination via open burn/open detonation activities and live-fire testing could also be possible, but do not appear to be significant contamination sources [1, 17]. Some quantitative data on environmental discharges of NQ are available. For example, NQ wastewater contamination was detected at the Sunflower Ammunition Plant in DeSoto, Kansas, where M30 triple-based gun propellant was manufactured in quantities of up to 400,000 gallons per day at a production rate of 40 tons per day [5, 6]. Most information on transport comes from physical-chemical properties, as up until recently, very few studies were conducted on the transport and fate of triple-based propellants [17].

The understanding of the transport processes for NQ is of particular importance due to its likely proliferation in the environment resulting from the increased usage of new IM formulations comprising NQ. Recent data from range survey and sampling activities [1, 17] did not find significant NQ soil contamination levels, most likely due to the low use of triple-based gun propellants as opposed to single- and double-based formulations.

11.3.1 Transport Processes

In triple-based gun propellants, NQ particles are embedded within a nitrocellulose matrix. Nitrocellulose is insoluble and very stable in the environment. This embedment of NQ within nitrocellulose and resistance of nitrocellulose to dissolution results in a heterogeneous release of NQ to the environment [1, 18]. A similar release process was noted for nitroglycerin (NG), and at least one study [1] showed that the rate of dissolution of NG out of the propellant matrix is faster than that of NQ. NQ is highly soluble in water; thus, the insoluble nitrocellulose serves as a barrier or impediment to the otherwise rapid NQ dissolution. Dissolution rates for NQ from triple-based propellant residues were estimated to be 71.9 ± 4.3 $\mu g\text{-}g^{-1}\text{-}h^{-1}$ with a 0.047 ± 0.002 h^{-1} decay constant [1], with NQ exhibiting a fast initial dissolution rate [19, 20].

Use of NQ in IMX-101 also presents alternative factors to take into account when predicting or evaluating transport processes. In IMX-101, NQ is embedded in a DNAN matrix and, similar to what was described for NG embedded in nitrocellulose, its release to the environment is expected

to be controlled by the dissolution of NQ out of the DNAN matrix [21, 22]. It is also thought that IMX101 detonations may release some fraction of unreacted/neat NQ into the environment [21].

11.3.2 Transport in Air

The vapor pressure of NQ is low (0.03 mm Hg at 25^{o}C), so transport in air is not considered a concern [7] and will likely settle out of the atmosphere.

11.3.3 Transport in Soil

NQ can be deposited into soils from open burn/open detonation or live-fire testing activities, though only small levels of NQ contamination have been identified in studies that investigated NQ range contamination [1, 17]. Soil analyses from live-fire testing found NQ soil contamination levels of ≈ 0.62-4.4E-5 %; similarly, for and open burn activities, NQ soil contamination levels were ≈ 0.008 to 0.002% [17].

If released to soil, NQ has a low potential for sorption (including those onto clay minerals) and biodegradation in soils [1] and is expected to be stable in most soils [23]. Data from IMX-101 studies have shown that NQ can be taken up by plants upon release to the soil [4].

The rates of soil sorption and degradation of NQ depend on soil type and have ranged from no appreciable degradation [1, 23] to a half-life of 7.5 to 56 days [24]. The adsorption coefficient (k_d) for NQ to soils was estimated to be ≈ 0.69 to 1.36, soil type-dependent [1], and the values for the octanol-water partition coefficient of NQ (-0.89) and soil organic carbon-water partition coefficient are low [25]. As a result, the mobility of NQ in soil is high and the probability of NQ contamination reaching groundwater is high and is a concern [17, 20]. The slow release of NQ from solid triple-based propellant residues can help decrease its release to soils.

11.3.4 Transport in Water

If released directly to water, NQ can undergo photolysis [5, 6] or be biotransformed under aerobic and anaerobic conditions [10] when nutrients or organic carbon sources are present [1]. There is some concern over the toxicity of photolyzed NQ to aquatic life upon release to waters; however, the short half-life for NQ photolysis and amount of dilution that could take place within this half-life span is such that the threat to aquatic life is low [5]. Thus, in water systems, mobility is expected to be high and degradation or transformation processes are expected to be readily available to mitigate NQ levels.

11.4 TOXICITY DATA OF NQ

Although NQ has small toxicity, its transformation products such as nitrosoguanidine, guanidine, cyanoguanidine, melamine, urea and nitrate have varying degrees of toxicity [11]. Acute toxicity values for NQ and its analogues are found to be moderately toxic with no studies on the health effects of NQ in humans reported in the literature.

Acute toxicity studies identified oral LD50 values of 3.85 g/kg in mice and 10.20 g/kg in rats [26]. In subchronic 90-day studies, an increased water consumption in male and female mice and rats was found when these animals were fed 1,000 mg/kg/day NQ [27]. In chronic toxicity studies, NQ

was found to cause significant changes in hematologic indices and in the enzyme-generating function of the liver at doses of 0.05 and 0.5 mg/kg/day. No carcinogenicity studies on NQ are currently available. NQ is classified as group D: not classifiable as to human carcinogenicity [28]. NQ, however, was found to be cytotoxic or mutanogenic in microbial systems [29, 30].

11.5 EXAMPLE REGULATORY GUIDELINES FOR NQ

No specific MCLs exist for NQ to date but health advisory (HA) limits were set up for one-day and 10-day exposures, which is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to one day and 10 days of exposure and is also normally designed to protect a 10-kg child consuming 1 liter of water per day, for NQ is set at 10,000 µg/L for both HAs. Lifetime HA, which is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure, was set up at 700.0 µg/L. The reference dose of NQ is 100.0 (µg/kg/day).

11.6 DATA GAPS

Several research programs have been undertaken to study and better understand the transport processes for NQ in the environment. As the use of NQ expands to include not only triple-based gun propellants but also IM formulations, there is anticipated to be a corresponding increase in NQ contamination levels at manufacturing, open burn/open detonation, and training sites. Because IMX-101 is being developed as the replacement for TNT, it would be of value to have a body of work on the fate and transport of the explosive constituents of IMX-101 comparable to that of TNT.

Studies and efforts related to land-based treatments may be of value to address the high mobility of NQ in soils and ability to leach to groundwater. Likewise, the high mobility of NQ and its ability to reach groundwater may drive the need for more research on aqueous-based treatments.

A. Fate and Transport

- **Phytotransformation**: More data on the transformation rates and identification of the products of NQ phytotransformation are needed.
- **Transport and fate of NQ in IMX-101**: In IMX-101 discharged to soil, it is likely to find NQ "trapped" within the DNAN matrix. It has been shown that this trapping of the NQ can affect the dissolution of NQ into the environment. Other data on the fate and transport of NQ that can be influenced or altered by the trapping of NQ within DNAN needs to be obtained.
- **Transport, fate, and toxicity of other compounds in NQ formulations**: The transport, fate, and toxicity of compounds other than NQ typically included in triple-based propellant formulations need to be better understood. Little data appear to be available for the transport, fate, and toxicity of the stabilizing compounds (e.g., ethyl centralite) when used in propellant formulations with other compounds.

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12. 3-NITRO-1,2,4-TRIAZOLE-5-ONE (NTO)

12.1 INTRODUCTION

Names: 3-nitro-1,2,4-triazole-5-one
Abbreviations and Other Names: NTO
CAS No.: 932-64-924807-55-4
Chemical Formula: $C_2H_2N_4O_3$
Occurrence in Mixtures/Compositions: IMX-101, IMX-102, IMX-104, PAX-48
Natural Occurrence: NTO does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.

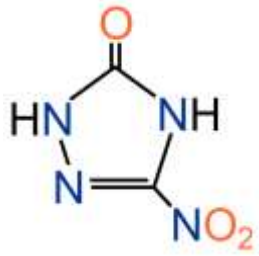

Figure 12-1. Chemical Structure of NTO

Physical/Chemical Properties: The physical/chemical properties of NTO are provided in Table 12-1.

Table 12-1. Physical and Chemical Properties of NTO [4, 5]

Property	Value	Units
Color	White to pale yellow	NA
Physical state	Crystalline powder	NA
Melting temperature	268 – 271	°C
Vapor pressure (at 25°C)	low	atm
Specific gravity	1.93	None
Water solubility (at 20°C)	1280 - 2000	mg/L
Dissolution rate in water	TBD	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	0.858	None

12.2 FATE

NTO (Figure 12-1), repurposed by the Los Alamos National Laboratory as an explosive chemical, is a less sensitive, more stable, yet equivalently performing replacement for RDX [1]. Since its discovery, it has been integrated into several explosive formulations comprising the new generation of insensitive munitions (IMs) which seek to offer equivalent or better explosive output with an improvement in safety. As a newer explosive compound, knowledge of the toxicity, fate, and transport is not as well understood as traditional explosives such as HMX, RDX, and TNT [2, 3]. However, research, laboratory studies, and field experiments have recently been completed or are underway with the goal of producing a similar body of work for NTO to provide a comprehensive assessment of the health and environmental fate of all explosive compounds. NTO is used in IM formulations including, but not limited to, IMX-101 (NTO/DNAN/NQ); IMX-104 (NTO/DNAN/RDX), and PAX-48 (NTO/DNAN/HMX).

12.2.1 Relevant Properties

NTO, in comparison to other explosive compounds, is unique due to its acidity [2, 6]. As a result, NTO is expected to exhibit lower affinity for soil absorption and therefore a higher likelihood of

environmental mobility [6]. It can also form metal salts, aliphatic amine salts, and aromatic amine salts [7], and a lower pH when dissolved in aqueous media [2]. These findings can be taken as indicators relevant to environmental effects. The dissolution rate appears to be undetermined. However, several recent studies [6, 8, 9] have investigated the propensity for NTO dissolution.

12.2.2 Photolysis

NTO undergoes photolytic degradation when in solution [6]; however, it demonstrated higher stability than TNT. Nitrites, nitrates, ammonium and carbon dioxide are the primary products from NTO photolysis [6, 10]. The half-life values for NTO transformation via photolysis range from approximately 8.3 hours to 3 days. The photolysis rate can be affected by the pH of the solution with the highest photolysis rates in alkaline solutions and slower degradation rates in neutral and acidic pH conditions [6, 8].

12.2.3 Other Abiotic Reactions

Laboratory tests have demonstrated the ability of NTO in solution to be reduced using bimetallic (iron/nickel or iron/copper) suspensions [11]. Data on the products formed through abiotic reduction appear to be unavailable; however, the half-life for this process has been estimated to range from 14 to 33 minutes (dependent on the concentration in solution). The affinity of NTO for reduction sites increased with lower pH values and was higher for molecular NTO versus the ionic form [11]. Data on the reduction of NTO by iron alone appear to be lacking; however, recent (i.e., 2015-present) SERDP/ESTCP-sponsored programs have begun to better understand iron reduction of new explosive compounds such as NTO and DNAN.

12.2.4 Biodegradation

Very little is known about the fate, toxicity, and microbial communities that degrade NTO. Some recent work on the metabolism of NTO by bacteria suggests that it is pH-dependent in aqueous systems. One recent study [12, 13] focused on determination of aerobic and anaerobic degradation rates for NTO in soil microcosms with and without supplemental carbon and nitrogen. High throughput 16S rRNA gene sequencing was used to characterize soil microbial diversity and principle components analysis was used to compare the communities between treatments. Biological degradation of NTO occurred under aerobic and anaerobic conditions. The extents and rates of biodegradation were generally greater in the presence of supplemental carbon or under anaerobic conditions. The degradation rate in aerobic conditions when cultures were supplemented with molasses were of 18.71 mg/L in second culture inoculation. The anaerobic degradation rates with thiosulfate were only 4.34 mg/L. The community analyses indicated the presence of dominant phyla belonging to the *Proteobacteria*, *Firmicutes*, *Acidobacteria*, and *Bacteriodetes*.

12.2.5 Phytotransformation

Limited data are available on plant uptake of NTO. One experiment [14] used simulated rainfall to assess uptake of IMX-101 explosive compounds by grasses. No NTO was detected in analyzed roots and shoots. However, lysimeter studies on the grass uptake of NTO [15] reported significant uptake of NTO, most likely resulting from the high concentrations of NTO in the aqueous phase in this experiment and the high propensity of ryegrass for water uptake. The availability of NTO

for uptake will rely heavily on the amount of rainfall within an area, because NTO is highly mobile in solution.

12.2.6 Hydrolysis

NTO is not expected to undergo hydrolysis in neutral, acidic, and basic solutions. Photolysis will dominate over hydrolysis for NTO in solution [6].

12.2.7 Key Degradation Products

The key NTO degradation products from photolysis are nitrites, nitrates, ammonium, and carbon dioxide. Information on other degradation products through other processes (e.g., biodegradation) appears to not yet be available due to the more recent development and use of NTO as an explosive compound.

12.3 TRANSPORT

Primarily due to NTO being a new explosive, data on the environmental transport of NTO is incomplete. Several recent studies [3, 6, 8-11, 14-18] have sought to better understand the factors that influence NTO transport through to laboratory and field-relevant experiments. Most of the available data on transport are a combination of the conclusions gained from these studies and an analysis of the physical and chemical properties of NTO.

The IM formulations comprising NTO (e.g., IMX-101, IMX-104) as one of their ingredients are melt-cast, which is a process in which one of the explosive ingredients or binders are melted into liquid form; additional explosive ingredients or binders are added as solid particles, and then the mixture is poured into a body and hardens as it cools. In IMX-101, for example, NTO is added as solid particles to the melted DNAN energetic binder.

12.3.1 Transport Processes

Models and predictions on the transport processes for NTO defer to the physical state of the NTO in the environment. In live-fire training or open burn/open detonation activities, NTO is dispersed in the environment as part of the melt-cast IM formulation. Some preliminary data on the detonation of IM formulations containing NTO in blow-in-place tests suggest that the NTO may not fully detonate, leaving a comparably high level (i.e., gram quantities) of unreacted NTO in the environment [17]. Therefore, NTO will be present as solid particles within a matrix of the melted ingredient (e.g., DNAN in IMX-101). In this case, the release of NTO to the environment now becomes not only a function of the solubility of NTO and its affinity for soil adsorption, but also how readily it can dissolve from its melt-cast matrix [8]. This places an emphasis on understanding the climate of the environment and the particle sizes used in the IM formulation to better approximate a rate of dissolution out of the IM fill, as the testing of IM formulations is expected to increase on military ranges [3].

12.3.2 Transport in Air

Similar to other solid explosives, NTO is not expected to readily vaporize and therefore transport in air is negligible.

12.3.3 Transport in Soil

When discharged to the environment as part of an IM formulation, NTO can be exposed to several processes that affect transport, including: dissolution from a solid IM matrix into water; photodegradation; soil adsorption/desorption; plant uptake; and biodegradation. Most of the data on soil transport come from studies with explosive formulations; data on waste stream contamination from NTO manufacturing sites appear to be unavailable. In general, NTO is expected to exhibit high mobility in soils and runs the risk of reaching groundwater systems fairly easily and unimpededly [6].

Starting with its deposition into soils as part of an IM formulation, NTO has the capability to quickly dissolve out of such fills, as a result of its high solubility in water and the high degree of friability of the fill, which leaves smaller portions of unreacted explosives (and therefore more surface area) available for dissolution [6, 8]. Some preliminary data on this dissolution rate are available from laboratory studies and are on the order of ≈ 10 mg dissolved per mL water [9]. This propensity for dissolution will also depend on the availability of water (i.e., rainfall) for driving the dissolution [9].

Once it is in solution, an explosive material may undergo hydrolysis or, if sunlight is available, photolysis. For NTO, hydrolysis is not a significant degradation process. Photolysis of NTO may occur, at rates that are slower than the photolysis rates for TNT but faster than those for RDX [6]. The effect of photolysis to impede the transport of pristine NTO through the soil will depend on the availability of sunlight and water, pH of the soil, and presence of natural organic matter. It is not known, at present, if photolysis is a major loss pathway for NTO dispersed onto soils [6].

Any solubilized NTO that has not degraded via photolysis is expected to be transported through the soil to groundwater with very little retardation due to soil absorption [3, 6]. Several factors are at play that limit this absorptivity/increase the mobility. The solubility of NTO (≈ 1280 to 2000 mg/L) and its octanol-water partitioning coefficient (log K_{ow} ≈ 0.858) suggest that it has the potential to reach groundwater with low probability of partitioning to soils or bioaccumulation [6, 18]. Soil pH also has a strong influence on NTO adsorption [6]. The acidic nature (pKa = 3.76) [19] of NTO and the knowledge that organic and mineral soils have net negative charges contribute to the low affinity for adsorption [18]. This net negative charge increases with soil pH; therefore, NTO adsorption decreases with increasing soil pH [8]. However, some sorption could occur via cation bridging, which is a general sorption mechanism for negatively charged organic material [6, 18]. Thus, any soil adsorption of NTO is more likely to occur in low pH/low percent organic material soils. Half-lives of NTO in soils ranged from 1.3 days (low organic matter soils) to 72 days (high organic matter soils) [8].

Studies and data on biodegradation rates of NTO and the effects of biodegradation on soil transport appear to be unavailable. This does not necessarily mean the influence of biodegradation on NTO soil transport is negligible; rather, the data may have yet to be compiled due to the more recent development and use of NTO as an explosive compound.

12.3.4 Transport in Water

Not much of the open literature describes the environmental transport following direct discharge of NTO to water systems. However, one document [11] does report that the high solubility of NTO in water renders most absorption-based techniques ineffective for remediation purposes. As discussed, the low octanol-water partitioning coefficients lower the probability of NTO bioaccumulation. Given the high solubility level and low affinity for sorption to soils and sediment, NTO is anticipated to be highly mobile in aqueous systems. What is not known is how this mobility is affected by the propensity of NTO for photolysis, which may be the main loss pathway in aqueous environments. Similar to what was stated for NTO transport in soil, biodegradation may have an influence on water transport of NTO; data may have yet to be compiled due to the more recent use of NTO.

12.4 TOXICITY DATA OF NTO

The development of occupational and environmental exposure standards for NTO is limited due to several toxicity data gaps. The acute oral LD50 for NTO is reported to be > 5 g/kg in rats and mice. In rabbit tests, NTO produced mild skin irritation but was not an eye irritant and did not induce dermal sensitization in guinea pigs [20]. A recently completed oral subchronic toxicity test in rats at doses of 0, 30, 100, 315 and 1000 mg/kg/day showed no compound-related effects on food consumption or body weight. Reduced testicular size was observed in the 315 and 1000 mg/kg/day groups and microscopic changes in testis were observed in all dose groups. The lowest observed adverse effect level (LOAEL) was determined to be 30 mg/kg/day in rats, based on microscopic changes in the testis [20]. There are no published studies on the toxicokinetics and metabolism of NTO in animals. However, the fate of NTO was investigated in vitro using rat liver microsomes and bacterial systems. Rat liver microsome catalysis of NTO under nitrogen atmosphere produced primarily amine, 5-amino-1,2,4-triazol-3-one urazole, but, in the presence of oxygen, produced a major product, 5-hydroxy-1,2,4-trizol-3-one urazole, and a minor product, an amine [21][10].

There are no published genotoxicity data for NTO. Therefore, both in vitro and in vivo genotoxicity of NTO were evaluated with regards to health and environmental risk assessment and will be published in the near future.

12.5 EXAMPLE REGULATORY GUIDELINES FOR NTO

No federal or state-wide regulatory limits exist for NTO and its degradation products.

12.6 DATA GAPS

Because NTO is a relatively new explosive currently transitioned to widespread manufacture and use, several data gaps exist in relation to its environmental fate, transport, and toxicity, and the interaction between NTO and other munitions constituents. A more in-depth understanding of degradation processes, their rates, roles as major loss pathways, and individual toxicities of NTO (and degradation products) are needed. Thus, a comparable study file on NTO can be compiled and more direct comparisons can be made to link the data on TNT, RDX, HMX, and other more traditional explosive compounds.

The specific gaps related to NTO include:

A. Fate and Transport

- **Phytotransformation**: More data are needed on NTO phytotransformation; specifically, how/where it accumulates, how it is transformed, and products of transformation and their rates.
- **Photolysis**: The influence of photolytic reactions as a loss pathway for IM formulations comprising NTO subjected to weathering and soil transport need to be better understood. The photolysis rate of NTO falls between that of TNT and RDX, taken into consideration with the low affinity of NTO to sorb to soils, and may be one of the few means to prevent migration of NTO to groundwater. NTO discharged to the environment via, for example, live-fire training, OB/OD activities, or resulting from manufacturing processes needs to be quantified to fully assess and evaluate the potential risk of groundwater contamination.
- **Iron reduction**: More data are needed on the reduction of NTO by iron alone. It appears that such studies have recently been started and data may be published soon.

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13. 2,4-DINITROANISOLE (DNAN)

13.1 INTRODUCTION

Figure 13-1. Chemical Structure of DNAN

Names: 2,4-Dinitroanisole
Abbreviations and Other Names: DNAN
CAS No.: 119-27-7
Chemical Formula: $C_7H_6N_2O_5$
Occurrence in Mixtures/Compositions: IMX-101, IMX-104, PAX-21
Natural Occurrence: DNAN does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of DNAN are provided in Table 13-1.

Table 13-1. Physical and Chemical Properties of DNAN [2, 3]

Property	NTO	Units
Color	White to pale yellow	NA
Physical state	Crystalline powder	NA
Melting temperature	268 – 271	°C
Vapor pressure (at 25°C)	low	atm
Specific gravity	1.93	None
Water solubility (at 20°C)	1280 - 2000	mg/L
Dissolution rate in water	TBD	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (K_{ow})	0.858	None

13.2 FATE

DNAN (Figure 13-1) is under evaluation for replacing TNT as an equivalently performing, yet less sensitive explosive [1]. It is intended to be used in several of the new generation of insensitive munitions (IMs), specifically in melt-cast explosive formulations, in which DNAN is melted down, other solid explosive compounds (e.g., NTO) are added, and then the mixture is cast into a casing and solidifies. As DNAN is a relatively new explosive, the body of work on the environmental fate, transport, and toxicity is incomplete when compared to data for the traditional or more conventional explosives such as RDX and TNT. DNAN falls into the class of nitroaromatic explosives, which includes TNT. As a result, most of the data generated from the ongoing research in the understanding of the environmental fate and transport of DNAN is compared against similar data sets for TNT to aid in assessing and evaluating the scope of the possible environmental or biological hazards posed by DNAN [1].

13.2.1 Relevant Properties

DNAN's water solubility values and partitioning coefficients suggest that the compound is fairly mobile in water. The specific dissolution rate of DNAN is yet to be determined. However, several

recent studies [4-8] have been conducted to investigate the propensity for DNAN dissolution out of a matrix of energetic materials (i.e., explosive formulations) containing compounds with higher and lower solubility values than DNAN.

13.2.2 Photolysis

Products of DNAN photolytic reaction are: nitrate ion, ammonium, formaldehyde, formic acid, 2-hydroxy-4-nitroanisole (2-HONAN) and 2,4-dinitrophenol (DNP) [1]. Moreover, under stimulated solar conditions, photolytic reaction of DNP produces nitrocatechol. Complete disappearance of an aqueous solution of DNAN via photolysis was reported to take approximately 21 days [1] while the photolysis half-life of an aqueous solution of DNAN under pH neutral conditions was 0.23 days [4].

13.2.3 Abiotic Reduction

Reduction of DNAN using ferrous has also been demonstrated [9]. Fe^{2+} reduction at acidic pH values was slow, however DNAN was completely reduced at pH 7 within 24 hours and within 2 hours at more alkaline pH levels.

13.2.4 Biodegradation

As the use of the IM compound DNAN increases, releases to the environment may pose a threat to local ecosystems. Little is known about the environmental fate of DNAN and the conversions caused by microbial activity. DNAN biotransformation rates were studied in sludge under aerobic (8 days when microbial slurries were supplemented with carbon and nitrogen to 34 days when slurries were supplemented with carbon source only) [10] and anaerobic conditions (up to 21 days in a bioreactor settings) [11]. The partial biotransformation of DNAN was most rapid under anaerobic conditions with H_2 as a co-substrate [10, 12, 13]. The results showed that the ortho nitro group in DNAN is region-selectively reduced to yield 2-methoxy-5-nitroaniline (MENA), and then the para nitro group is reduced to give 2,4-diaminoanisole (DAAN). Both MENA and DAAN were identified as important metabolites in all redox conditions. Azo and hydrazine dimer derivatives formed from the coupling of DNAN reduction products in anaerobic conditions. Secondary pathways included acetylation and methylation of amine moieties, as well as the step-wise O-demethylation and dehydroxylation of methoxy groups. Seven unique metabolites were identified which enabled elucidation of biotransformation pathways [13].

Another bench study showed aerobic biotransformation of DNAN in artificially-contaminated soil microcosms. DNAN was completely transformed in 8 days in soil slurries supplemented with carbon and nitrogen sources. DNAN was completely transformed in 34 days in slurries supplemented with carbons alone and persisted in unamended microcosms. A strain of *Bacillus* (named 13G) that transformed DNAN by co-metabolism was isolated from the soil [10]. Clone libraries were used to evaluate the effects of DNAN on bacterial populations within three anaerobic bioreactors [12]. Prior to the addition of DNAN more than 69% of the clones in each reactor were identified as a single *Desulfuromonales* species. However, after 60 days of treatment a clone identified as a *Levilinea* sp. became the dominant organism at greater than 27% of the clone distribution in each reactor, suggesting the species may play an important role in the reduction of DNAN and MNA. Lastly, *Nocardioides* sp. strain JS1661 was isolated from activated sludge based on its ability to grow on DNAN as the sole source of carbon and energy. Enzyme assays indicated

that the first reaction involves hydrolytic release of methanol to form 2,4-dinitrophenol (2,4-DNP). Growth yield and enzyme assays indicated that 2,4-DNP underwent subsequent degradation by a previously established pathway involving formation of a hydride-Meisenheimer complex and release of nitrite. Identification of the genes encoding the key enzymes suggested recent evolution of the pathway by recruitment of a novel hydrolase to extend the well-characterized 2,4-DNP pathway (Figure 13-2) [14].

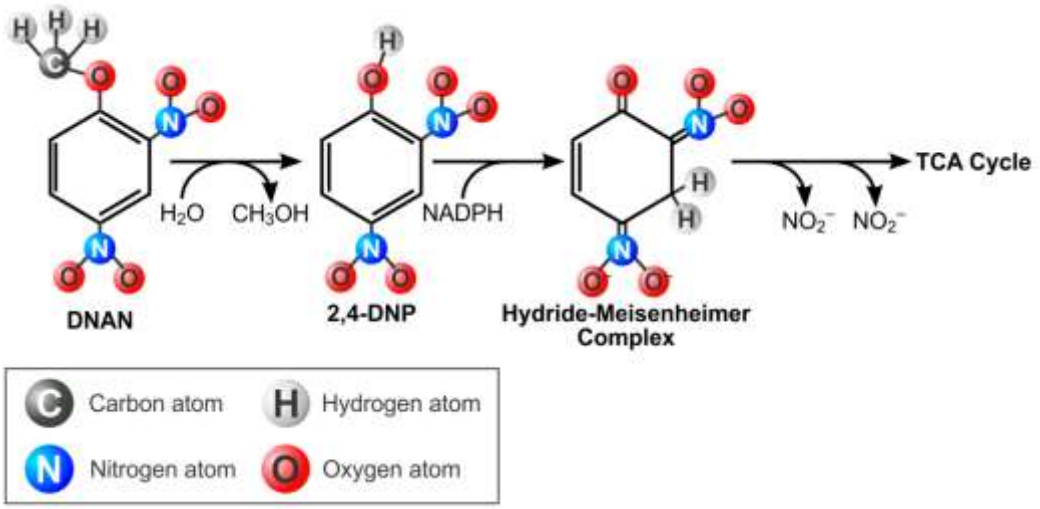

Figure 13-2. Proposed Pathway of DNAN Biodegradation by *Nocardioides* sp. JS1661

13.2.5 Phytotransformation

Studies on the uptake and transformation of DNAN by ryegrass [15] have been conducted to assess the propensity for uptake and possible DNAN phytotoxicity. The data suggest that ryegrass root uptake of DNAN followed by transport to the shoots is likely to occur. Studies of ryegrass samples in soils spiked with DNAN at ≈ 4.7 mg/kg of soil produced 2-amino-4-nitroanisole (2A-4NAN) at levels up to ≈ 37.6 µg/g dry grass tissue in 19 days.

13.2.6 Hydrolysis

Under typical environmental conditions, hydrolysis of DNAN is not a significant degradation route, however it is possible in very high alkaline solutions (i.e., pH > 12) and yields DNP as a degradation product [1].

13.2.7 Key Degradation Products

Several DNAN degradation products, such as 2-ANAN, 4-ANAN, and DAAN, have higher water solubility and lower octanol-water partition coefficient values than the parent compound [1]. Therefore, they are expected to exhibit higher mobility in water and less likely to partition to organic matter and bioaccumulate. This information is of great importance considering lack of knowledge on the fate, transport, and toxicity of these products in addition to the data gaps for DNAN. It would appear that the degradation products of DNAN have a higher probability of

mobility through the environment based on the solubility and octanol-water partitioning coefficient values, however, these products have a higher affinity for irreversible soil adsorption and mobility of these products is therefore in competition with sorption in the environment [1].

13.3 TRANSPORT

Since DNAN is a fairly new munitions constituent, not much is known on its behavior and transport in water, soil and sediments. Several laboratory-based studies as well as field demonstrations [1, 5-8] have made efforts to predict and characterize behavior and environmental factors that influence DNAN fate and transport. Most of the available data on the transport phenomena of DNAN is a combination of the information gained from these studies and an analysis of the physical and chemical properties of DNAN.

DNAN is more soluble than TNT. Its degradation products can bind irreversibly to soils, making it less environmentally hazardous than TNT [1].

13.3.1 Transport Processes

DNAN can likely reach soil and water systems via corrosion of unexploded ordnance (UXO), live-fire training or open burn/open detonation (OB/OD) activities, or through wastewaters from DNAN manufacturing. Corrosion of UXO is unlikely to occur due to the newness of DNAN and its associated IM fills. Therefore, the sources of DNAN transport are most likely to be range activities and DNAN manufacture.

Once dispersed into the environment, properties of DNAN such as solubility and partitioning coefficients will influence its mobility. Knowledge of adsorption and degradation pathways as well as their rates will determine to what extent mobility of DNAN is mitigated through irreversible and transformative processes. A comparison of the propensity for mobility against the effectiveness of adsorption and degradation pathways can be used to provide an assessment of the risk of dispersed DNAN reaching groundwater. The risk for widespread contamination of DNAN becomes significant if allowed to reach groundwater.

13.3.2 Transport in Air

DNAN is characteristic of extremely low vapor pressures. Therefore, air transport and cycling are highly unlikely.

13.3.3 Transport in Soil

No explosive detonation is 100% efficient; there will always be some unreacted residue of material. Thus, in live-fire training or OB/OD activities, DNAN can be dispersed into the environment as unreacted/undetonated residues. Some data are available on the expected amount of unreacted residues produced following the detonation of an IM explosive containing DNAN [5, 16]. High-order detonation tests of PAX-21 resulted in 99.994% reaction efficiency (i.e., 0.006% unreacted residue); tests with IMX-104 produced 99.995% and 99.99% efficiencies (i.e., 0.005% and 0.01% unreacted residues, respectively). These residues will be deposited onto range soils [6].

As noted, new IM formulations are melt-cast, a process in which DNAN is melted down and then solid particles of other explosives are added to it before solidifying. This is similar to Comp B, a conventional melt-cast explosive, in which TNT is melted down and then solid RDX particles are added. When deposited onto soils as part of an IM formulation, the chemical and physical properties of the explosive ingredients added to the DNAN matrix can influence the rate of dissolution of DNAN into water [5]. The solid explosives added to DNAN possess higher solubility values (e.g., NTO) and are typically of smaller physical size than DNAN. These smaller, more soluble particles dissolve first, subsequently leaving physical holes in the DNAN matrix [4, 6, 8]. This is noticeably different from conventional melt-cast explosive formulations (e.g., Comp B), in which the opposite occurs: the TNT dissolves first, leaving RDX particles behind [8]. The holes can increase the DNAN surface area available for dissolution. Some preliminary data on the DNAN dissolution rate from IMX-101 are available from laboratory studies and are on the order of $\approx 10^{-2}$ mg dissolved per mL water, with rates for NTO and NQ being much faster, on the order of $\approx 10^{1}$ to 10^{2} mg dissolved per mL water [7].

Once in solution, DNAN can be subjected to photolysis reactions at relatively fast rates (≈0.23 day half-life), and degrade into products that are more readily irreversibly sorbed to soil [1]. Pristine DNAN can sorb to soils [4], the affinity for which increases with increasing organic content. Sorption half-lives range from 4.1 to 48 days [4]. Nitroaromatic compounds, in general, tend to reversibly sorb to organic matter in soils or to clay minerals. DNAN has been demonstrated in laboratory experiments to exhibit reversible sorption [1]. For example, DNAN in one of these laboratory experiments was completely recovered after two months in both high-clay and high-silt content soil samples [1]. While pristine DNAN is somewhat mobile in soil, its degradation products, specifically 2-ANAN, 4-ANAN, and DAAN, are more likely to irreversibly sorb [1]. In the same experiment with DNAN sorption to high-clay and high-silt content soil samples [1], less than 40% of the 2-ANAN and less than 20% of the 4-ANAN were recovered after 2 months in either soil, while no DAAN was recovered after only 3 days in either soil. The affinity for irreversible sorption appears to increase with an increasing number of amino groups [1].

The ability for DNAN to sorb to soils or undergo degradation via biodegradation, abiotic reduction, or photolysis at relatively fast rates acts to mitigate the risk of DNAN reaching groundwater. These factors either impede (i.e., reversible sorption) or directly prevent (i.e., photolysis) DNAN deep penetration into soil layers. Reports on the environmental fate of the new IM formulations [5-8] often compare the transport or fate of DNAN to another new explosive used in IM formulations, NTO, and report that, while both have a higher solubility than RDX and TNT and therefore a higher propensity for transport to groundwater, DNAN is less mobile in the environment. NTO, which has a lower probability of retardation or transformation in the soil, is expected to more readily reach groundwater [5].

13.3.4 Transport in Water

DNAN is expected to be both mobile and stable in water unless exposed to sunlight, which would in turn drive photolytic reactions [1].

13.4 TOXICITY DATA OF DNAN

The nitroaromatic DNAN has toxicity properties very similar to other compounds of that class. Briefly, DNAN appears to be less toxic than TNT and many other nitroaromatics in mammalian and aquatic organisms. Although DNAN is used industrially in the synthesis of dyes, the information on the toxicity of DNAN and its byproducts is limited. DNAN has moderate acute toxicity, with an oral lethal median concentration (LC50) of 199 mg/kg in studies performed on rats. DNAN caused reversible eye and skin irritation, but did not cause dermal sensitization [17].

Chemical analysis of test water indicated that DNAN concentrations were relatively stable during the bioassays. Acute toxicity was similar for the two species tested, with 48-hr LC50 ranging from 37 to 42 mg/L DNAN. Chronic toxicity tests indicated that fish survival (7-day LC50 = 10 mg/L) was significantly more sensitive to DNAN relative to the invertebrate (no significant impact on survival at 24 mg/L). However, the reproduction endpoint for the invertebrate was significantly more sensitive to DNAN than survival. When assessing the most sensitive chronic endpoints, the two-test species indicated similar chronic toxicity, with lowest observable adverse impacts ranging from 10 to 12 mg/L DNAN and median effects on sublethal endpoints (growth, reproduction) ranging from 11 to 15 mg/L DNAN. Chronic no-effect concentrations ranged from approximately 6 to 8 mg/L DNAN [18].

13.5 EXAMPLE REGULATORY GUIDELINES FOR DNAN

No federal or state-wide regulatory limits exist for DNAN and its degradation products.

13.6 DATA GAPS

DNAN is an explosive compound that has only recently been transitioned to use in new IM formulations. As such, most of the data regarding the fate, toxicity, and transport of it and its degradation products is incomplete. A more in-depth understanding of degradation processes, their rates, roles as major loss pathways, and individual toxicities for DNAN and breakdown products is needed such that a comparable study file on DNAN can be compiled and more direct comparisons can be made to TNT, RDX, HMX, and other more traditional explosive compounds. Therefore, many of the same data gaps identified for NTO apply to DNAN.

A. Fate and Transport: In general, data are recommended to be collected for not only transport and fate of DNAN, but also the effects the DNAN "matrix" has on the transport and fate rates for the other explosive compounds in IM formulations comprising DNAN.

- **Soil Transport**: Ore studies should be conducted on the soil transport of DNAN to better assess and evaluate the risk of DNAN reaching groundwater, especially given the high mobility of DNAN in water.
- **Water Transport**: An assessment of the transport of DNAN in wastewater from manufacturing processes and the associated potential contamination risk appears to be incomplete. These data are critical as the use of new IM formulations and subsequent need for a DNAN supply increases.

- **Abiotic Reduction and Phytotransformation**: Reduction and phytotransformation routes for DNAN do exist, but more research may need to be done to fully evaluate these methods for remediation.

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14. TETRAZENE EXPLOSIVE

14.1 INTRODUCTION

Figure 14-1. Chemical Structure of Tetrazene Explosive

Names: Tetrazene explosive
Abbreviations and Other Names: Tetrazene; tetracene; tetrazolyl guanyltetrazene hydrate; tetrazen
CAS No.: 31330-63-9
Chemical Formula: $C_2H_6N_{10}\cdot H_2O$
Occurrence in Mixtures/Compositions: Used in lead styphnate-based percussion primer and stab detonator compositions
Natural Occurrence: Tetrazene does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of tetrazene are provided in Table 14-1.

Table 14-1. Physical and Chemical Properties of Tetrazene

Property	Value	Units
Color	Colorless or pale yellow	NA
Physical state	Crystals	NA
Melting temperature	140 – 160 (decomposes)	°C
Vapor pressure (at 25°C)	low	atm
Specific gravity	1.7	None
Water solubility (at 20°C)	insoluble	mg/L
Dissolution rate in water	Unknown	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	Unknown	None

14.2 FATE

Tetrazene ($C_2H_6N_{10}\cdot H_2O$), also known as tetracene, is a primary explosive often used in ammunition primers [1], particularly in percussion primers and stab detonator formulations (e.g., 9-mm MK1 and 7.62-mm C21 ball cartridges) [2, 3]. It is used to provide improved stability and sensitivity of ignition [4, 5]. However, it has been shown that tetrazene may be thermally unstable in instances of long-term storage at the upper extreme of storage and handling temperatures (≈ 70°C) [2] and that it is a toxic material [6]. Therefore, efforts are underway to phase out tetrazene use in primers [6].

14.2.1 Relevant Properties

Overall, little data are available on the environmental fate and transport of tetrazene. This is most likely a result of its use only in primer and detonator formulations. In these formulations, milligram quantities of tetrazene are used. For example, 9-mm MK1 ball cartridges use 17 mg of primer composition per cartridge, 4 to 5% of which (i.e., ≈ 0.85 mg) will consist of tetrazene; 7.6- to 2-mm ball cartridges comprise ≈ 1.3 mg of tetrazene [3]. A list of priming compositions containing

tetrazene and their other ingredients is provided in Table 14-2. Such ingredients include metal-based compounds (e.g., lead styphnate, barium nitrate) with significant toxicity concerns.

Table 14-2. Priming Compositions Containing Tetrazene [3]

Ingredient	Priming Composition (% Dry Weight)					
	5.56-mm No. 41 Primer	9-mm MK1 Type B	9-mm MK1 Type C	7.62-mm C21 Type A	7.62-mm C21 Type B	7.62-mm C21 Type C
Tetrazene	3	5	4	3	3	4
Lead Styphnate	40	40	37	37	40	37
Barium Nitrate	42	30	32	38	30	32
Calcium Silicide	10	0	0	13	0	0
Antimony Sulphide	0	9	15	0	9	15
Lead Dioxide	5	9	0	9	9	0
PETN	0	7	5	0	7	5
Aluminum Powder	0	0	7	0	0	7

Although tetrazene is used to desensitize/stabilize priming compositions, it does possess some degree of chemical instability/sensitivity (hence, its classification as a primary explosive). As a result, when a primer or detonator functions (i.e., is fired), the tetrazene readily and quickly decomposes, leaving trace amounts of unreacted compounds [7]. Therefore, due to the small quantities used and ease of decomposition, data regarding the fate and transport of tetrazene are lacking. Some data on the properties of tetrazene are provided in Table 14-1. Most of the discussion on the environmental fate and transport of tetrazene will primarily be inferred from the solubility until environmental fate and transport data become available or more widely disseminated. The dissolution rate into water is expected to be low as a result of its water insolubility; however, this value and the value for the octanol-water partition coefficient in Table 14-1 are listed as "unknown" though the dissolution rate is assumed to be low and the partition coefficient high as a result of the insolubility of tetrazene.

14.2.2 Photolysis

No data were found on the photolysis of tetrazene, either as a solid particle or dispersed in an aqueous solution. Other hydrocarbon-based energetic materials (e.g., TNT, HMX, RDX, and PETN) can undergo photolysis. Tetrazene may also be susceptible to this degradation pathway; however, data from experiments or studies are needed to determine if photolysis of tetrazene can occur.

14.2.3 Other Abiotic Reactions

No data were found on the abiotic reduction of tetrazene. Given the insolubility of tetrazene in water, transport of tetrazene with water through soil is likely to be insignificant. This may result in deposits of tetrazene in surface soils near firing points that, over time, could have abiotic reduction within soil matrices. However, the quantities of unreacted tetrazene discharged to the

environment are likely to be so low that abiotic reduction of tetrazene has been overlooked in environmental fate studies or is a non-factor.

14.2.4 Biodegradation

No information on biological degradation of tetrazene explosive exists to date.

14.2.5 Phytotransformation

No information was found on plant uptake or phytotransformation of tetrazene. Most hydrocarbon-based explosives can be taken up in the roots of plants and, in some instances (e.g., TNT) transported to and transformed in different plant regions. While root uptake of tetrazene could occur from a chemical composition standpoint, the availability of unreacted tetrazene in soil and water is likely limited by the small amount of tetrazene expected to be discharged to the environment and the insolubility of tetrazene in water (both also suggest low probability of mobility within soils).

14.2.6 Hydrolysis

No data were found suggesting that tetrazene will hydrolyze. It has been shown to degrade by boiling water as a result of its melting temperature being so close to the boiling point of water [8].

14.2.7 Key Degradation Products

The thermal decomposition of tetrazene has been studied fairly extensively [2], owing, in part, to its melting and decomposition occurring so close to the boiling point of water. At 90°C, tetrazene was shown to convert to 5-aminotetrazole [2].

14.3 TRANSPORT

Sources for tetrazene transport can come from manufacture or use. The low amounts of tetrazene used in primers and detonators (i.e., the use) have been discussed in the previous section. Little data are available for the fate and transport from tetrazene from a use standpoint, most likely due to these low amounts used per ammunition cartridge. The same can be said for its manufacturing: little to no data are available on the fate and transport of tetrazene from manufacturing plants. A significant supply of 5.56-mm and 7.62-mm ammunition, the primers of which are likely to contain tetrazene, are produced at the Lake City Army Ammunition Plant [4]. This could be a more significant source for tetrazene discharge to the environment as opposed to use at firing ranges. However, little to no data are available on transport resulting from tetrazene production.

14.3.1 Transport Processes

The transport processes for tetrazene are unknown or not widely distributed. Therefore, an evaluation of the potential for transport is made here, as a function of source (from manufacture or use); quantity used; and ability of pristine tetrazene to reach soil and water matrices.

Tetrazene could reach soil and water matrices directly from manufacturing processes; however, more data are needed on how much is typically discharged as a function of a production run or on a time basis (e.g., annually). Discharge of tetrazene to the environment via manufacturing may be

the more likely source for pristine or unreacted tetrazene reaching the environment, as use in live-fire operations will likely react most, if not all, of the compound. Additionally, more tetrazene is likely to be discharged on a time basis through manufacturing processes (depending on the batch size) compared to being discharged to the environment through use.

Tetrazene used (i.e., fired) at firing ranges is likely to be a low value source of discharge material, resulting from the low quantities of material used (i.e., in the milligram and sub-milligram range) and the extremely low amount of unreacted tetrazene expected from each live fired round (i.e., in the sub-microgram range). The amount of unreacted tetrazene discharged to the environment through use will also be a function of how frequently ammunition charges containing tetrazene are used in a given location.

14.3.2 Transport in Air

Air is not expected to be a significant transport source for tetrazene due to factors such as its low vapor pressure and low quantities used in primers and detonators.

14.3.3 Transport in Soil

Tetrazene could reach soil from manufacturing processes or use. Once in the soil, tetrazene could persist, due to its insolubility with water and assumed high (i.e., hydrophobic) octanol-water partition coefficient resulting from this insolubility. However, data on the soil transport of tetrazene are lacking, and research into this transport process may be warranted.

14.3.4 Transport in Water

Tetrazene is more likely to reach water systems via direct discharge; the more likely source for this discharge route is from manufacturing processes rather than use. The use of tetrazene typically occurs over soils. Tetrazene deposited onto soils will not readily dissolve into water and therefore the probability of tetrazene reaching groundwater is most likely low or will take a long period of time. Similar to the transport data in soil, research data on the water transport of tetrazene are lacking.

14.4 TOXICITY DATA OF TETRAZENE AND KNOWN DEGRADATION PRODUCTS

Tetrazene explosive material is a substituted iminourea. Dust or fumes can cause eye irritation consisting of redness, swelling, and pain. Tetrazene may cause conjunctivitis with repeated exposures and it is harmful if inhaled or swallowed. Inhalation of high concentrations may cause respiratory and nasal irritation, coughing, and difficulty breathing. Ingestion may cause nausea, vomiting, constipation, cramps, and/or stomach pain.

14.5 EXAMPLE REGULATORY GUIDELINES FOR TETRAZENE

No information on regulatory limits for tetrazene explosive exist to date.

14.6 DATA GAPS

Information on the fate and transport of tetrazene is, in general, lacking in all areas. More data are needed in each of the topics covered above, and on the properties in Table 14-1 that can help predict or evaluate transportation processes (e.g., precise values for the octanol-water partition coefficient value). Addressing these data gaps may be of particular relevance to manufacturing processes, especially if the batch volumes of tetrazene produced or discharged to the environment as waste are significant.

A. Fate and Transport:

- **Transformation Reaction Data** (including photolysis, hydrolysis, abiotic reactions, biodegradation, phytotransformation): Definitive data on rates/half-lives (even if it is not likely to occur).
- **Transport**: Little data are available from laboratory or field studies on the environmental transport of tetrazene. This is mostly due to its low quantities in priming compositions.

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15. TETRYL

15.1 INTRODUCTION

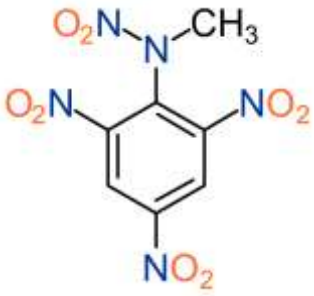

Figure 15-1. Chemical Structure of Tetryl

Names: Tetryl
Abbreviations and Other Names: Nitramine, Tetralite, Tetril, N-Methyl-N,2,4,6-tetranitroaniline, N-Methyl-N,2,4,6-tetranitrophenyl-1-amine
CAS No.: 479-45-8
Chemical Formula: $C_7H_5N_5O_8$
Occurrence in Mixtures/Compositions: Use discontinued in the United States as of 1979; previously used in Comp C-3, in tetryl formulations with TNT, and as an ingredient of detonators and primers
Natural Occurrence: Tetryl does not naturally occur, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of tetryl are provided in Table 15-1.

Table 15-1. Physical and Chemical Properties of Tetryl [3]

Property	Value	Units
Color	Yellow	NA
Physical state	Solid crystals	NA
Melting temperature	130-132	°C
Vapor pressure (at 25°C)	5.3e-13	atm
Specific gravity	1.57	None
Water solubility (at 20°C)	75	mg/L
Dissolution rate in water	unknown	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	2.4	None

15.2 FATE

Tetryl is considered to be both a nitroaromatic and nitramine explosive [1]. In 1979, the United States discontinued the use of tetryl and replaced it with RDX as a result of its instability following prolonged storage at elevated temperatures [2]. However, it could still be present at unexploded ordnance (UXO) sites as it leaches into the environment; at storage sites where it is in the process of being destroyed; or as residual explosive material remaining in the soil from open burning, manufacturing, storage, or range activities [3, 4].

15.2.1 Relevant Properties

Properties relevant to the environmental fate and transport of tetryl are provided in Table 15-1. The solubility of tetryl (75 mg/L) is lower than that of TNT (130 mg/L), but higher than that of RDX (47 mg/L). The value for the octanol-water partition coefficient, log K_{ow} (2.4), is higher than that of TNT (1.86) and RDX (0.87). Tetryl is, therefore, considered to exhibit moderate solubility

with a low potential for bioaccumulation. The dissolution rate for tetryl in water was not identified in the surveyed literature, as noted in Table 15-1.

15.2.2 Photolysis

Tetryl can undergo both hydrolysis and photolysis in aqueous systems [3, 5, 6]. However, when aqueous systems are exposed to sunlight, tetryl will more readily undergo photolysis over hydrolysis; i.e., photolysis will dominate, at a rate an order of magnitude higher than that of hydrolysis [3, 6]. In laboratory studies using aqueous samples of tetryl in distilled water exposed to sunlight at 20°C, 95.4% of tetryl was converted to degradation products via photolysis within the first 20 days of the study, while 2.3% of tetryl was converted via hydrolysis [6]. In comparison, TNT, a structurally similar chemical, had a photolysis half-life value of ≈ 30 minutes in natural water and ≈ 200 minutes (≈ 3.3 hours) in pure (distilled) water. The biodegradation half-life values for tetryl in water and soil are 7.79 and 12.2 days, respectively.

N-methylpicramide is the primary degradation product of tetryl photolysis in aqueous systems, with nitrate ions, picrate ions, and methylnitramine also formed, but in smaller amounts [3, 5, 6]. Tetryl has not been shown to undergo direct photolysis in the atmosphere, but is expected to do so based on its ability to photolyze in water [3], though more data are needed to confirm this theory.

15.2.3 Other Abiotic Reactions

Hydrolysis and photolysis are the two primary abiotic reduction pathways for tetryl. No data were found, for example, on abiotic treatment of tetryl using ferrous iron (Fe(II)).

15.2.4 Biodegradation

Small amounts of data from composting experiments indicate that tetryl may be degraded under some conditions [7]. When tetryl-contaminated sediment was added to hay-horse feed or sewage sludge-wood chip compost, 90% of the tetryl was removed after 44 days. A first-order half-life of 1.2 weeks was calculated for tetryl in a manure-hay-sawdust compost.

In a biodegradation study with two types of soils (silt-loam and sandy loam), tetryl was found to undergo rapid biotransformation via two principal pathways [8]. The principal product of biodegradation was identified as n-methyl-2,4,6-trinitroaniline. Aminodinitrophenyl-methylnitramine and other unidentified polar metabolites were identified as secondary biodegradation products.

A laboratory study was conducted to determine whether tetryl can be degraded by an anaerobic process [9]. The results indicated that the metabolic conversion of tetryl to aniline is possible by a sulfate-reducing bacterial consortium during 7-day cultivation with 0.2 mM tetryl. This consortium metabolized tetryl by co-metabolism with pyruvate as a growth substrate. For every mole of tetryl metabolized, 1 mole of aniline was produced, and the aniline was further metabolized. This metabolic conversion of tetryl is likely to be of value in the anaerobic treatment of tetryl-contaminated soil and groundwater, such as found at many military ammunition sites [9].

15.2.5 Phytotransformation

Laboratory studies on the uptake and transformation of tetryl by vegetation including bush bean plants, wheatgrass, and bromegrass [3, 10, 11] have been conducted, with the uptake and transport routes reported in terms of percent explosive sample accumulated in the plant and metabolites detected. The results from these studies show the tetryl is taken up by and accumulates in the roots of the plant or grass and then quickly transformed. For example, in the study with bush bean plants which involved 7-day exposure to tetryl-amended hydroponic cultures, only 3% of the tetryl taken up by bush bean specimens remained unchanged. 86% to 96% of the transformed products were located in the roots, while 3% to 7% was found in stem tissues and 1% to 3% found in leaf tissues [3]. Similar results were found for grass specimens, where most of the tetryl accumulated and was transformed in the roots, with some low levels detected in the shoots [10]. Tetryl taken up by vegetation is typically metabolized to N-methyl-2,4,6-trinitroaniline (N-methylpicramide), along with a variety of polar metabolites, which were not specifically identified. N-methylpicramide is also a product of photolysis and hydrolysis of tetryl.

15.2.6 Hydrolysis

Tetryl can also be degraded by hydrolysis, producing picric acid, N-methylpicramide, methylnitramine, and nitrite and nitrate ions in the process [3]; these are similar products to what is formed through tetryl photolysis and phytotransformation. Also noted in the discussion of photolysis is that an aqueous system exposed to sunlight favors tetryl photolysis significantly over hydrolysis. In aqueous systems not exposed to sunlight (i.e., "dark hydrolysis"), hydrolysis is expected to be the main abiotic reduction process [3, 6, 12]. However, even with hydrolysis as the main reduction pathway with little to no photolysis occurring, the rate of hydrolysis is still comparatively slow. Laboratory studies on the hydrolysis of tetryl in aqueous solutions at 20°C without exposure to sunlight reported a 2.3% conversion of tetryl to picric acid in 20 days and a 3.4% conversion in 90 days. The half-life for tetryl hydrolysis has been estimated to be $\approx 302 \pm 76$ days; other studies suggest that the uncertainty factor with these data may be significant, and the half-life could be as short as 33 days [3].

In aqueous systems, as noted, photolysis is expected to dominate. When deposited onto soils, however, with limited exposure to direct sunlight, tetryl is expected to be more susceptible to hydrolytic degradation [13]. This process will be slower in acidic and pH neutral soils, and somewhat faster in alkaline soils (pH 9).

Picric acid is the primary product formed as a result of tetryl hydrolysis in soil. However, in field soil studies, additional tetryl transformation products were detected in analyzed soil samples, including 4-amino-N-methyl-N,2,6-trinitroaniline and N-methylpicramide. It is thought that several degradation and transformation reactions (namely, hydrolysis, biodegradation, and phytotransformation) are present and competing against each other over a finite supply of tetryl. Therefore, the attribution of these additional transformation products to a specific mechanism of tetryl degradation (e.g., hydrolysis) or transformation is difficult [13].

15.2.7 Key Degradation Products

Picric acid has been identified as the main tetryl degradation product of concern, resulting from its high solubility in water; subsequent ability to leach through soil to groundwater; and possible

toxicological effects on humans. These effects include the destruction of red blood cells, liver impairment, and hematuria [3], though more conclusive data need to be collected to confirm these effects result from picric acid exposure. N-methylpicramide is formed from photolytic, hydrolytic, and phytotransformation processes. 4-amino-N-methyl-N,2,5-trinitroaniline has also been detected in soil samples containing tetryl.

15.3 TRANSPORT

15.3.1 Transport Processes

A review of the properties of tetryl provided in Table 15-1 provides indicators of how tetryl is suspected to be transported through the environment. These properties include, but are not limited to, the water solubility, vapor pressure, and octanol-water partition coefficient. These properties can be analyzed to determine the propensity for tetryl to partition to water or air and bioaccumulate. The information inferred from the review of these properties is supported by data from field studies collected primarily at U.S. Army ammunition plants on the fate and transport of tetryl. With the production of tetryl in the United States ceasing in the 1970s, no new releases of tetryl from manufacturing operations are expected.

15.3.2 Transport in Air

The extremely low vapor pressure of tetryl at 25ºC (5.3e-13 atm) implies that only an insignificant amount of tetryl is present in the vapor state at ambient temperatures. Any tetryl particles dispersed into the air, for example from an open burn or open detonation operation, are expected to be deposited onto land or water rather than remaining airborne [3]. Therefore, any transport processes associated with air are considered non-factors for tetryl.

15.3.3 Transport in Soil

Tetryl soil contamination and transport have been studied in the field from military sites where tetryl was manufactured and released to soil as waste effluent, tested, disposed (e.g., through open burn operations), or stored in magazines [14, 15]. Two such sites that were studied extensively for soil contamination and where most of the data regarding soil transport were taken from, was the Louisiana Army Ammunition Plant and the Joliet Army Ammunition plant, the latter of which was a production site for tetryl until 1973 [3].

Once deposited into the soil, tetryl can rapidly break down, resulting from processes such as hydrolysis (if water is available), biodegradation, and photolysis (if sunlight is available). In reviewing the properties of tetryl, a soil organic carbon-water partioning coefficient (K_{oc}) value of 406 has been calculated for tetryl, using its water solubility value of 75 mg/L [3]. Tetryl, therefore, is expected to exhibit low to moderate mobility from soil to groundwater and not significantly leach from soil to groundwater, especially if a high organic content is present in the soil. However, tetryl has been shown to be capable of moving through soil and entering underground water systems [3]. It should be noted that the ability of tetryl to be transported through the soil to water systems is also influenced by the degradation process, which can prevent tetryl from reaching groundwater. Thus, a review of the properties of tetryl alone, combined with the knowledge of the degradation process, render an assessment of soil transport somewhat challenging.

Data from a soil contamination study at the Joliet Army Ammunition Plant conducted in 1981 identified tetryl in two of five surface soil samples [3]. Tetryl levels were as high as 38,500 µg/g in surface soils near the production area and as low as 23.5 µg/g in surface soil samples taken at a site location far from the production area. The data suggest that tetryl contamination is mostly confined to the ammunition plant and mobility may be restricted due to degradation processes and low to moderate mobility of tetryl through soil. It should be noted that degradation products were not examined at these sites.

15.3.4 Transport in Water

Though tetryl may not easily travel through soil to groundwater, it can reach surface waters from runoff and leaching, or from natural processes such as soil erosion from contaminated sites. In reviewing the properties of tetryl relevant to water transport, tetryl has a water solubility of 75 mg/L at 20°C and an octanol-water partition coefficient of 2.4, suggesting that it does have the potential to accumulate in and contaminate groundwater [13]. Once tetryl reaches water systems, it is expected to undergo photolysis if sunlight is present; hydrolysis if sunlight is not present; or associate with suspended sediment particles and settle to the bottom. No data on tetryl bioaccumulation exist [3].

Laboratory studies have shown the ability for tetryl to leach from soil to water [3, 14, 15]. Additionally, site surveys have confirmed, to some extent, the ability of tetryl to reach groundwater following soil contamination [3]. A survey of the Joliet Army Ammunition Plant conducted in 1985-1986 detected tetryl in groundwater at concentrations of 67, 34, and 13.7 µg/L at a tetryl production area, TNT production area, and wastewater area, respectively. Another survey conducted in 1988 detected tetryl at a concentration of 67 µg/L in a groundwater monitoring well installed at the location that produced the highest levels of soil contamination in the 1981 survey. However, no tetryl was found in surface water and groundwater samples taken from other areas of the plant [3].

15.4 TOXICITY DATA OF TETRYL

Since tetryl has been phased out from both use and manufacturing, there is a small likelihood of exposure. Most of the information on the health effects of tetryl comes from studies on workers employed in military facilities during World Wars I and II due to the inhalation of tetryl contaminated air [16, 17]. However, the relative contribution by the three possible routes (inhalation, oral, and dermal) is not known. The oral and dermal routes of exposure, in particular, may be of concern to humans because of the potential for tetryl to contaminate drinking water and soil.

The exposure symptoms include cough, fatigue, headaches, eye irritation, lack of appetite, nosebleeds, nausea and/or vomiting. Little is known about the longer-term health effects in workers exposed to tetryl. Few data exist from animal studies with tetryl. None of the data located were reliable enough to determine levels of significant exposure. However, a few studies examined hematological effects in workers exposed to tetryl dusts. Examinations of an unspecified number of operators engaged in the making and cleaning of tetryl pellets revealed many cases of slight leukocytosis and increased levels of lymphocytes (incidences not reported) and two cases of decreased red blood cells [18]. Data regarding the toxicokinetics of tetryl in humans are limited to

information from cases of occupational exposure by the inhalation and dermal routes. These data provide qualitative evidence that tetryl may be absorbed in humans by these routes. There are no data regarding oral absorption of tetryl in humans.

15.5 EXAMPLE REGULATORY GUIDELINES FOR TETRYL

The federal government has developed standards and guidelines to protect people from the health effects of tetryl. The Department of Transportation has many regulations for the transportation of explosives such as tetryl. Although tetryl is no longer being manufactured or used, the Occupational Safety and Health Administration (OSHA) has set a regulatory level for tetryl in the workplace. The maximum allowable amount of tetryl in workroom air during an 8-hour workday, 40-hour workweek, is 1.5 milligrams of tetryl per cubic meter of air (mg/m^3) [19]. This level may apply to workers engaged in destruction of tetryl explosives and those who work in locations where tetryl is stored. The National Institute for Occupational Safety and Health recommends that workers not be exposed to air containing more than 1.5 mg/m^3 during a 10-hour workday [20].

The Agency for Toxic Substances and Disease Registry (ATSDR) has not derived maximum residue levels (MRLs) for tetryl because of the lack of reliable human or animal studies which identify levels of exposure associated with adverse health effects. In addition, U.S. EPA has not verified a reference dose for oral exposure or a reference concentration for inhalation exposure to tetryl.

The transportation of explosives including tetryl must be in accordance with the Department of Transportation hazardous material regulations (49 CFR 171-190) and motor carrier safety regulations (49 CFR 390-398). Numerous states have established regulations on explosives for air quality control, solid waste disposal, storage, manufacture, and use.

15.6 DATA GAPS

Despite a significant body of knowledge on tetryl chemistry and degradation, several data gaps exist and need to be better characterized to understand fate and transport and degradation products of tetryl decomposition. Main data gaps for tetryl are listed below:

A. Fate and Transport: Since tetryl is no longer in use (and probably only present as a soil/water contaminant from buried/submerged UXO), tetryl may be present in the soil or water primarily as degradation products. It may be of use to know which ones are most significant from a toxicity and persistence standpoint.

- **Key Degradation Products**: More information may be needed on the fate and transport of picric acid, primarily as a result of its potential toxicity and high levels of solubility and mobility in water. Picric acid may have a high potential for widespread dissemination and contamination.

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16. LEAD AZIDE

16.1 INTRODUCTION

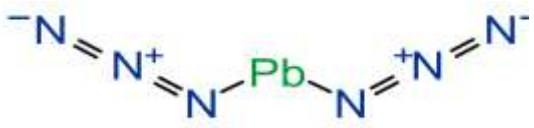

Figure 16-1. Chemical Structure of Lead Azide

Names: Lead azide
Abbreviations and Other Names: $Pb(N_3)_2$ diazidolead
CAS No.: 13424-46-9
Chemical Formula: $Pb(N_3)_2$
Occurrence in Mixtures/Compositions: Primary explosive used in detonators and primers; e.g., Detaline, DuPont blasting caps, DuPont Specialty "C" detonators
Natural Occurrence: Lead azide does not occur naturally, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of lead azide are provided in Table 16-1.

Table 16-1. Physical and Chemical Properties of Lead Azide

Property	Value	Units
Color	White	NA
Physical state	Needle-like crystals	NA
Melting temperature	245 – 250	^oC
Vapor pressure (at 25^{o}C)	Extremely low	atm
Specific gravity	4.8	None
Water solubility (at 20^{o}C)	2.3	mg/L
Dissolution rate in water	Unknown	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	Unknown	None

16.2 FATE

Lead contamination has been a significant concern at military test ranges; for the purposes of this report, is it difficult to discern what percentage of total lead contamination at these ranges is due to bullet (i.e., from an unjacketed lead bullet or lead styphnate primer) versus lead azide use. From a 2014 report, approximately 10 million devices containing lead azide (e.g., detonators) are produced annually in the US and the military consumes approximately 750 lbs of lead azide [1]. In the case of range training or testing with lead azide-based detonators, this chemical decomposes to produce nitrogen (N_2) gas and the lead contaminant, then persists in the environment. The environmental fate and transport of lead azide, therefore, relates to the presence of lead contamination at military sites and its fate and transport in the environment.

16.2.1 Relevant Properties

Lead azide is a primary explosive used almost exclusively in detonators for initiating secondary explosives for over 90 years, particularly for the more sensitive explosives HMX, RDX, and PETN [2, 3]. Lead azide is sensitive to ignition and, as a result of this sensitivity, is used in small (i.e., mg level) quantities in detonators, which is typical of primary explosives. In the US, three types

of lead azide formulations have been developed for use in detonating devices: dextrinated lead azide (DLA), colloidal lead azide (CLA), and polyvinylalcohol lead azide (PVA-LA). DLA uses dextrin as a colloiding agent to mitigate the formation of larger crystals that are more sensitive to ignition, yet suffers from some degree of hygroscopicity and is less pure (≈ 92.7%) than CLA and DLA. CLA is a high-purity lead azide (≈ 99.9%) charge with very small particle sizes, and minimal hygroscopicity but increased sensitivity. CLA is commonly used in low energy electric (LEI) detonators. PVA-LA is an improved version of DLA, featuring the same sensitivity to impact ignition as DLA, but with improved hygroscopicity and purity (≈ 96.0%).

Health and environmental impacts of lead azide contamination may be much more serious than the impacts associated with, for example, RDX due to hazards associated with lead contamination. Several properties of lead azide relevant to transport and fate are provided in Table 16-1.

16.2.2 Photolysis

Lead azide has been shown in laboratory studies to undergo photolysis in a vacuum when irradiated with 380 nm light [4, 5] and when exposed to sunlight in atmosphere can become covered with a brown film [6]. The photolysis reaction drives decomposition of lead azide, producing metallic lead and gaseous nitrogen. There are no data pertaining to the rate of lead azide photolysis in the atmosphere or within aqueous systems.

16.2.3 Abiotic Reduction

No data were found on the abiotic reduction of lead azide. Lead will readily bond to high pH clay soils and abiotic reduction of lead in soils will not occur. Lead is likely to remain in soils indefinitely [7].

16.2.4 Biodegradation

Sodium azide and azide salts impair bacterial growth by inhibition of cytochrome oxidase in Gram-negative bacteria (both aerobic and anaerobic microorganisms); thus, no biodegradation reactions are known for this compound.

16.2.5 Phytotransformation

No data were found on the phytotransformation of lead azide. Lead can be taken up by edible plants in the roots, from contaminated soils via direct foliar uptake or surface deposition. It is expected to persist once taken up by plants [8].

16.2.6 Hydrolysis

Lead azide will readily hydrolyze in aqueous systems, yielding lead and hydrazoic acid [9]. No information was found on the rate of this process.

16.2.7 Key Degradation Products

The primary degradation product of concern with lead azide is lead, which can be formed from use (i.e., functioning) of a device containing lead azide, or via lead azide hydrolysis if unreacted material is dispersed in the environment. A significant amount of toxicological and environmental

hazard data has been compiled for lead, and lead dispersed into the environment is expected to persist indefinitely.

16.3 TRANSPORT

The source of lead azide for transport through an environment can come from manufacturing or use. However, there is no longer a source of lead azide production in the United States, and most new implementations of lead azide come from an aging, stockpiled reserve [3].

16.3.1 Transport Processes

The use of lead azide-based detonators or primers can disperse fine particulates of lead into the local atmosphere. From there, the particulates can be deposited onto the soil or aqueous systems [1]. The long-term stability of lead and its propensity to dissolve into pH acidic (≈ 5) water (specific rate data were not found) place an emphasis on a solid understanding of the transport process in air, soil, and water. Some information regarding the general transport characteristics of lead azide can be derived from the data provided in Table 16-1, or from published studies and military site surveys [10]. However, lead azide appears to be somewhat overlooked in terms of transport and fate studies and not much information specific to lead azide is available. What is known is the transport processes from lead, which have primarily been taken from laboratory and field studies from weapons training ranges where lead bullets are the primary source of lead contamination. The normal operation of the range can produce soil contamination levels on the order of 10,000 ppm [11]. Therefore, where transport data specific to lead azide are not available, conclusions will be drawn from known transport data for lead.

16.3.2 Transport in Air

Air is not expected to be a significant transport source for lead azide or lead [12] due primarily to the low vapor pressure of lead azide (i.e., a miniscule amount of lead azide vapor is generated under ambient conditions) and high density of lead particles (i.e., the particles will easily drop out of air).

16.3.3 Transport in Soil

A field study [13] on the contamination levels from a former DuPont facility in New Jersey that manufactured lead azide, aluminum, and bronze-shelled blasting caps from 1902 to 1994 revealed that levels of lead were found in sediment and soils on the former manufacturing site, including the site floodplain.

No additional data specific to lead azide transport in soil appear to be available in the open literature. For lead particles, the type of soil and soil chemistry will have a significant influence on transport. In general, lead exhibits low mobility in soil [7]. Clay and organic soils can provide bonding sites for lead or precipitate lead out of solution, respectively, trapping the lead for an indefinite amount of time, with sorption typically increasing with increasing pH [7, 12]. This is the most common result of lead transport in soil [8]. However, fractured rock and coarse sand soils containing pH acidic content (e.g., granite) are at higher risk for lead mobility and dissolution into groundwater [12]. A general guideline that has been employed for determining the probability of

lead leaching from soil to groundwater is that groundwater more than 10 feet below ground surface is not affected by leaching of lead from soil [11].

16.3.4 Transport in Water

The discovery of lead discharges from the former DuPont lead azide manufacturing facility to the surrounding flood plain suggests that lead residues associated with lead azide production can migrate from soil to local aqueous systems [13], though, as noted, the mobility through soil is rather low for clay/pH basic soils.

Specific details on the transport of lead azide in water appear to be lacking. However, water transport of lead has been studied rather extensively. Lead can reach water systems via direct deposition or via mobility through soils, as discussed. The ease at which lead can be transported in water can be inferred from its solubility. The solubility of lead in water depends on the acidity of water, which is affected by, for example, the presence of acid rain contaminants in rainwater. Lead exhibits low solubility in pH neutral water, but is soluble in mildly acidic water [11, 12, 14]. Lead can be transported in water as a suspension in storm runoff, as a dissolved particle in surface runoff, or as a dissolved particle in groundwater. Whether the lead travels in water as a suspension or in solution will depend on the pH of the water [12, 14].

16.4 TOXICITY DATA OF LEAD AZIDE

Azides can be incorporated into the body by breathing vapors, droplets or dust containing azides, by skin contact (mainly with solutions or vapors), or by ingestion of solids, solutions or food containing azide. Since azides are not very stable, and may decompose when entering the body, the most dangerous mode of absorption is as vapors or droplets, mainly into the eyes or the skin. Ingesting azides interferes with all biochemical processes involving iron. It affects the neurological system and the heart.

Toxicity data for lead azide are not available. Its aqueous solution is toxic and exhibits lead poisoning effects. However, lead azide is a confirmed animal carcinogen with unknown relevance to humans.

16.5 EXAMPLE REGULATORY GUIDELINES FOR LEAD AZIDE

The Occupational Safety and Health Administration (OSHA) has set a regulatory level for lead azide in the workplace. The maximum allowable amount of lead azide in workroom air during an 8-hour workday, 40-hour workweek, is 0.05 milligrams of per cubic meter of air (mg/m^3). The OSHA recommends that workers not be exposed to air containing more than 0.050 mg/m^3 during a 10-hour workday.

16.6 DATA GAPS

Much of the research and studies conducted on contamination at military ranges resulting from lead azide have been overshadowed by the more pressing concern for lead contamination resulting from the use of lead bullets and lead styphnate, a common small arms primer. However, several data gaps for lead azide were identified:

A. Fate and Transport: Overall, a more lead azide-specific set of data on fate and transport is needed, not only to identify possible fate and transport processes unique to lead azide, but also to help discern contamination concerns resulting from lead azide use versus other lead-containing chemicals or materials.

- **Assessment of the value of conducting a full fate and transport study** for lead azide should also be conducted to determine if the amount of lead azide contamination is significant enough to warrant such a study (i.e., is there a "zero tolerance" limit for lead released to the environment specifically from the use of lead azide).

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17. LEAD STYPHNATE

17.1 INTRODUCTION

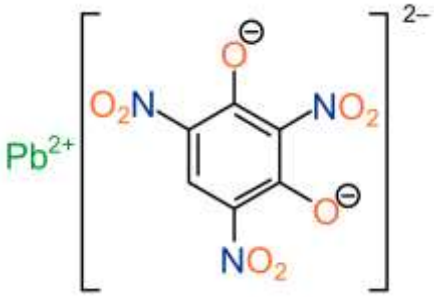

Figure 17-1. Chemical Structure of Lead Styphnate

Names: Lead styphnate
Abbreviations and Other Names: lead trinitroresorcinate; bleitrizinat
CAS No.: 15245-44-0
Chemical Formula: $C_6HN_3O_8Pb$
Occurrence in Mixtures/Compositions: Used in detonator charges and primer compositions
Natural Occurrence: Lead styphnate does not occur naturally, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of tetryl are provided in Table 17-1.

Table 17-1. Physical and Chemical Properties of Lead Styphnate

Property	Value	Units
Color	Orange-yellow to dark brown	NA
Physical state	Solid crystals	NA
Melting temperature	190	°C
Vapor pressure (at 25°C)	low	atm
Specific gravity	3	None
Water solubility (at 20°C)	8	mg/L
Dissolution rate in water	NA	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	0.006	None

17.2 FATE

Lead styphnate ($C_6HN_3O_8Pb$) is a primary explosive compound that features high ignition reliability but poor explosive power output when compared to other primary explosives such as lead azide [1]. For these reasons, it is often mixed with lead azide to provide a detonator charge with high ease of ignition and adequate output power by serving as the ignition source for the difficult-to-ignite yet powerful azide. The use of lead styphnate, lead azide, and lead bullet cores at live-fire training or test ranges is responsible for lead contamination at such sites. When used, lead styphnate produces gaseous nitrogen (N_2) and vaporized lead particles as the bullet primer composition ignites and reacts in the high-temperature and high-pressure regime of a gun barrel. Some unreacted lead styphnate may also be released, though most likely in extremely small amounts (estimated to be one microgram or less [2]). The pressures generated from the resulting burning of the gun propellant forces the vaporized lead to be ejected from the muzzle. Some lead vapor may also be released to the environment as the shell casing is ejected from the gun [3].

17.2.1 Relevant Properties

Detonator charges comprising lead styphnate with lead azide are commonly used in gun primers [1]. The NOL-130 stab primer mix comprises 40% lead styphnate, 5% tetrazene, 20% barium nitrate, 20% lead azide, and 15% antimony sulfide. The K90 percussion primer comprises 40% lead styphnate, 5% aluminum powder, 16% antimony sulfide, 30% barium nitrate, and 5% tetrazene. The total lead styphnate amount in either primer mix is ≈ 22 mg [4]. Two forms of lead styphnate can be used in such formulations: basic and normal; the main difference between the two forms is that the basic lead styphnate contains a higher lead content (59.6 to 60.2%) and lower nitrogen content (5.97 to 6.17%) than normal lead styphnate (43.2 to 44.3% and 8.87 to 9.07%), respectively.

Selected physical and chemical properties of lead styphnate are provided in Table 17-1. The primary concern with the use of lead styphnate (i.e., functioning of a detonator) appears to be the amount of lead dispersed to the environment, as the other elements present in lead styphnate may likely be released as gaseous decomposition or combustion products (e.g., NO_2) [5]. Lead styphnate is only slightly soluble in water (8 mg/L) and possesses a low octanol-water partition coefficient (0.006), suggesting that mobility and propensity for bioaccumulation are low.

17.2.2 Photolysis

No data exist regarding the photolysis of lead styphnate.

17.2.3 Other Abiotic Reactions

No data were found on additional abiotic reactions involving lead styphnate. However, lead will readily bond to clay and alkaline soils (i.e., pH 8 and greater). Abiotic reduction of lead in soils will not occur; rather, lead is likely to remain in soils indefinitely [6].

17.2.4 Biodegradation

No data exist regarding the biodegradation of lead styphnate.

17.2.5 Phytotransformation

No data were found on the phytotransformation of lead styphnate. However, lead can be taken up by edible plants in the roots, from contaminated soils: direct foliar uptake or surface deposition. It is expected to persist once taken up by plants [7].

17.2.6 Hydrolysis

No data were found on the hydrolysis of lead styphnate.

17.2.7 Key Degradation Products

The primary degradation product of concern with lead styphnate is lead, which can be formed from use (i.e., functioning) of a device containing lead styphnate. A significant amount of toxicological and environmental hazard data has been compiled for lead.

17.3 TRANSPORT

Lead styphnate has the potential to reach the environment through manufacturing processes or use. In the case of the former, lead styphnate releases to the environment appear to not be a concern [5]. In the case of the latter, releases of lead styphnate to the air, soil, and water are more likely, though still very low on a per-item basis. Repeated use of items containing lead styphnate (e.g., primers) within the same area can lead to lead contamination [3, 8], which is why the use of lead-based energetic materials and bullets is a significant concern at live-fire training and test ranges. Typically, lead styphnate releases to the environment from use may consist of its combustion products (e.g., CO, CO_2, NO, NO_2, H_2O and lead oxides), though some extremely trace amounts of unreacted lead styphnate may also be released [3].

17.3.1 Transport Processes

The primary transport process for lead styphnate is associated with its use on live-fire and testing ranges. In this case, the lead styphnate ignites, burns, and disperses airborne lead oxide particles into the air, which then settle onto the soil or indoor training ranges [2, 3, 5]. It is estimated that 80% of airborne lead on firing ranges are from the fired projectile while the remaining 20% is from the compounds present in the priming composition [5].

Some information on the transport processes of lead styphnate can be derived from the data provided in Table 17-1, or from published studies [2, 3, 5]. However, transport data from published reports and studies that are specific to lead styphnate are difficult to discern from lead contamination from other sources present at firing ranges (e.g., lead bullet cores). What is known, instead, is a more general transport process for lead from any available sources present at weapons training ranges. The normal operation of the range can produce soil contamination levels on the order of 10,000 ppm [9]. Therefore, where transport data specific to lead styphnate are not available, conclusions will be drawn from known transport data for lead.

17.3.2 Transport in Air

Outdoor air is not expected to be a significant transport source for lead styphnate based on its low vapor pressure value (i.e., a miniscule amount of lead styphnate vapor is generated under ambient conditions) and high density of lead particles (i.e., the particles will easily drop out of air). Indoor air and its occupational exposure is likely an issue as discussed above.

17.3.3 Transport in Soil

No additional data specific to lead styphnate transport in soil appear to be available in the open literature. For lead contamination at live-fire and training ranges, the type of soil and soil chemistry will have a significant influence on transport. In general, lead exhibits low mobility in soil [10]; i.e., rain and surface waters will do very little to help lead migration through soil. Lead exhibits low solubility in pH neutral water, but is soluble in mildly acidic water (pH 6) [9, 11, 12]. Therefore, lead could be transported in water as a suspension in storm runoff, as a dissolved particle in surface runoff, or as a dissolved particle in groundwater. Whether the lead travels in water as a suspension or in solution will depend on the pH of the water [11, 12].

Working against the potential for soil mobility is the ability of lead to sorb to soils. Clay soils and organic soils can provide bonding sites for lead or precipitate lead out of solution, respectively, trapping the lead for an indefinite amount of time, with sorption typically increasing with increasing pH [6, 12]. This is the most common result of lead transport in soil [7]. However, fractured rock and coarse sand soils containing compounds acidic in solution (e.g., granite) are at higher risk for lead mobility and dissolution into groundwater [12]. A general rule that has been employed for determining the probability of lead leaching from soil to groundwater is that groundwater more than 10 feet below ground surface is not affected by leaching of lead from soil [9]. Therefore, lead deposited onto soils is expected to persist and accumulate in soils if repetitive firing range activities are conducted over time.

17.3.4 Transport in Water

Specific details on the transport of lead styphnate in water appear to be lacking. However, water transport of lead has been studied rather extensively. The ease at which lead can be transported in water can be inferred from its solubility. The solubility of lead in water depends on the acidity of water, which is affected by, for example, the presence of acid rain contaminants in rainwater.

17.4 TOXICITY DATA OF LEAD STYPHNATE

Toxicity of lead styphnate depends on whether it occurs in water as organic or inorganic lead. Toxicity can then be presumed on the basis of information available about lead.

17.5 EXAMPLE REGULATORY GUIDELINES FOR LEAD STYPHNATE

No reports on regulatory limits for lead styphnate exist. However, there is information on styphnic acid regulatory indoor limits.

17.6 DATA GAPS

Much of the research and studies conducted on contamination at military ranges resulting from lead styphnate are lacking, mostly because the use of this compound is limited to small arms primers.

A. Fate and Transport

- **Fate processes**: Lead styphnate appears to be resistant to hydrolysis and photolysis; however, phytotransformation may need to be explored further given that lead is capable of being taken up by plants. No data were found on biodegradation of lead styphnate; it is not clear if this compound could be biodegraded to some extent as a result of its hydrocarbon content.

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18. AMMONIUM PICRATE

18.1 INTRODUCTION

Figure 18-1. Chemical Structure of Ammonium Picrate

Names: Ammonium picrate

Abbreviations and Other Names: Dunnite, explosive D; 2,4,6-trinitrophenol ammonium salt, ammonium picronitrate

CAS No.: 131-74-8

Chemical Formula: $C_6H_6N_4O_7$

Occurrence in Mixtures/Compositions: picratol (48% TNT and 52% ammonium picrate)

Natural Occurrence: Ammonium picrate does not occur naturally, and, therefore, there are no background levels in the soil, air, water, or food.

Physical/Chemical Properties: The physical/chemical properties of ammonium picrate are provided in Table 18-1.

Table 18-1. Physical and Chemical Properties of Ammonium Picrate

Property	Value	Units
Color	Yellow	NA
Physical state	Crystals	NA
Melting temperature	280	°C
Vapor pressure (at 25°C)	4.43e-12	atm
Specific gravity	1.72	None
Water solubility (at 20°C)	10,000	mg/L
Dissolution rate in water	NA	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	0.02	None

18.2 FATE

Ammonium picrate is an explosive material mainly used during the 1940s and 1950s in production of bombs, projectiles, and rockets due to its relatively high degree of insensitivity as compared to other explosive materials [1-3]. Ammonium picrate was typically used as a stand-alone explosive or mixed with TNT to form picratol, which allowed for faster production of bombs and projectiles to meet the demands of World War II. Its use was discontinued shortly after World War II, due to compatibility and subsequent ignition sensitivity issues that were discovered from degradation reactions between the ammonium picrate and metals present in artillery casings [1]. However, there are still existing stockpiles of ammonium picrate in the US that represent approximately 8% of the demilitarization inventory [4].

18.2.1 Relevant Properties

Properties of ammonium picrate relevant to its environmental fate and transport are provided in Table 18-1. One key characteristic of ammonium picrate is its high water solubility (10,000 mg/L) in comparison to other explosives such as TNT (130 mg/L), RDX (47 mg/L), and HMX (4.5 mg/L). This high solubility and the dissociation of ammonium picrate have significant impacts on its fate and transport.

The octanol-water partition coefficient (0.02) of ammonium picrate indicates that the compound is hydrophilic, more so than other explosive materials such as TNT (K_{ow} = 1.86) and RDX (7.41) and, like most explosive materials it is not expected to bioaccummulate. The specific gravity of ammonium picrate (1.72) is typical of most explosive materials (≈1.3 to 1.8). Data on the dissolution rate of ammonium picrate into water are not available.

18.2.2 Photolysis

A limited amount of data exist on photolysis, suggesting that ammonium picrate undergoes photolytic conversion in aqueous solutions. It was demonstrated that aqueous concentrations of ammonium picrate mixed with small amounts of hydrogen peroxide and exposed to 254 nm UV light can be effectively destroyed within 2 hours [5]. However, no data were provided on the identities or quantities of the degradation products. Moreover, no information exists on the direct (i.e., non-aqueous) photolysis of ammonium picrate.

18.2.3 Other Abiotic Reactions

No information on additional abiotic degradation pathways for ammonium picrate in the environment was found. However, if picric acid is formed through dissociation of ammonium picrate in water, this compound has been known to react with metals in shell casings and produce metal salts of picric acid, which are much more sensitive to ignition than the parent compound.

18.2.4 Biodegradation

No data exist regarding the biodegradation of ammonium picrate.

18.2.5 Phytotransformation

No data were found on the plant uptake or phytotransformation of ammonium picrate. However, given that the compound readily solubilizes in water and dissociates into the ammonium and picrate ions, it may be possible that some plant uptake of ammonium occurs via nitrification processes.

18.2.6 Hydrolysis

Ammonium picrate is expected to readily dissociate in water to the ammonium and picrate ions at pH values normally encountered in the environment (i.e., pH 4-10) [6, 7]. This dissociation has a significant impact on the transport of ammonium picrate in the environment because the transport of the ionic compound in the environment is expected to be much more rapid than other, nonionic explosive materials (e.g., HMX) [6].

If in contact with metals from, for example, a munition shell, the picrate ion could form a metal salt of picric acid [6], which can be very sensitive to ignition.

18.2.7 Key Degradation Products

The key degradation products of ammonium picrate are ammonium and picrate ions, both with a relatively high degree of mobility in the environment.

18.3 TRANSPORT

Ammonium picrate can reach water and soil systems as a result of corrosion and breaching of buried or submerged ordnance, activities such as blow-in-place or open burn/open detonation that can release unreacted explosive residues to the environment, live-fire testing, or manufacturing of explosives and loading, assembly, and packing activities [7, 8].

18.3.1 Transport Processes

With water systems, a significant concern with ammonium picrate is its direct release to such systems, especially due to use in open sea combat and training operations and deep-water ordnance disposal practices. Ammonium picrate was used in the early to mid-20th century, at a time when it was common practice to dispose of excess, obsolete, or unserviceable munitions into deep-water regions [7, 8]. The corrosion or breaching of significant quantities of munitions disposed in deep-water regions could be a source of continual ammonium picrate water contamination [8]. The Naval Surface Warfare Center, Dahlgren Division [9] collected data on the use of munitions constituents at the Potomac River Test Range, and found that ammonium picrate was the most used munition constituent by weight associated with live munitions testing over the span of 90 years. A total of 436,228 lbs of ammonium picrate was tested at the Potomac River Test Range over the 90-year span, with the majority tested during the 1940s and 1950s [9].

Ammonium picrate is not in use in the present day; therefore, most of the soil contamination is more likely to come from legacy munitions storage areas or disposal pits that were used in the early to mid-20th century. As an example of the amount of contamination that may come from a disposal pit, field studies at the Hawthorne Army Ammunition Plant [10] reported maximum ammonium picrate (desert) soil concentrations of 240 ppm at one such pit and concentrations up to 800 ppm at a second pit. Picrate has also been detected in groundwater sampling wells at the Louisiana Army Ammunition Plant [11]. However, the presence and detection of ammonium picrate in soil and water samples ultimately may be tied to how resistant an ordnance item containing ammonium picrate is to corrosion. For example, one field study involving the detection of ammonium picrate in soils [12] did not detect ammonium picrate in soil samples surrounding six buried, intact 76-mm rounds.

18.3.2 Transport in Air

The vapor pressure and physical state (solid) of ammonium picrate under ambient conditions suggests that direct volatilization to air is not a significant transport route. However, if ammonium picrate is able to dissociate to the ammonium and picrate ions, some gaseous loss of of ammonia (NH_3) to the atmosphere may occur [13].

18.3.3 Transport in Soil

Transport of ammonium picrate in soil may be highly variable. More experiments and subsequent data sets are needed to fully assess soil transport characteristics. Ammonium picrate directly deposited to soil is expected to be resistant to biological or photochemical degradation processes [4]. Therefore, it is likely to persist unless it comes into contact with water. The solubility of ammonium picrate in water, low octanol-water partitioning coefficient, and ionic property does render the compound highly mobile in soil [11]; however, some soil sorption could occur that can impede mobility [4, 14], but may be highly dependent on the organic and mineral composition of soils. Experiments with picric acid mixed with solutions containing calcium ions and calcium clays showed a high degree of picric acid removal; mixtures with solutions containing sodium ions and clays showed no sorption of ammonium picrate.

Despite the lack of conclusive studies and information on the soil absorption of ammonium picrate, field studies [6] of soil disposal pits known to contain ammonium picrate munitions have provided evidence of the extreme mobility of ammonium picrate compared to other explosive materials. In one data set from this study, picric acid concentrations were greater at 12-inch pit depth level (800 ppm) than at the pit surface (160 ppm), compared to concentrations of HMX (46 ppm), tetryl (120 ppm), and PETN (130 ppm) at this same 12-inch pit depth.

18.3.4 Transport in Water

Ammonium picrate may reach water systems via soil transport in solution or direct release from deep-water munitions disposal sites. If ammonium picrate is contained within a submerged munition, the release from the munition and subsequent transport is highly variable, driven by several factors including the physical condition of the munition (e.g., seal integrity and size of the breach hole), resistance of the munition to corrosion, dissolution rate of the ammonium picrate, and properties of the water (e.g., current velocity) [15]. Ammonium picrate that reaches water systems via this route is expected to immediately dissociate. Ammonium picrate that reaches water systems via soil transport is also expected to be in its dissociated form. In either transport route, the picrate ion is not expected to partition to sediment or bioaccummulate (i.e., its octanol-water partition coefficient is low [0.02]) [7].

18.4 TOXICITY DATA OF AMMONIUM PICRATE

Direct exposure to ammonium picrate may cause moderate skin, eye and mucous membrane irritations. Ammonium picrate ingestion can cause a bitter taste, nausea, diarrhea, vomiting, abdominal pain, skin eruptions, stupor, and possible death. Breathing high levels can damage the kidneys, liver, and red blood cells. Long-term exposure effects include skin allergy, liver, kidney, and blood cell damage. The most common occupational health problem in workers exposed to ammonium picrate was dermatitis, due to sensitization and not primary irritation by the picrate. Upper respiratory disease was negligible and systemic toxicity was not recognized among the workers. The cutaneous lesions appeared usually on the exposed parts of the upper extremities. Persons least exposed seemed more liable to acquire dermatitis, which did not develop in those engaged in operations where there was the heaviest exposure. Ammonium picrate can produce nausea, vomiting, diarrhea, staining of the skin, dermatitis, circular eruptions of the skin, coma, and seizures. Ammonium picrate was also examined for mutagenic activity in a series of in vitro microbial assays employing *Salmonella typhimurium* and *Saccharomyces cerevisiae* indicator

organisms. The compound was tested over a series of concentrations such that there was either quantitative or qualitative evidence of some chemically-induced physiological effects at the high dose. The results of the mutagenicity tests were all negative. Ammonium nitrate is harmful to aquatic organisms.

18.5 EXAMPLE REGULATORY GUIDELINES FOR AMMONIUM PICRATE

No information on regulatory limits of ammonium picrate exist to date.

18.6 DATA GAPS

The body of work on the fate and transport of ammonium picrate compared to other explosives such as TNT, RDX, and HMX is not as complete, primarily due to ammonium picrate being phased out from use [11]. Data gaps for ammonium picrate include:

A. Fate and Transport: More data are needed for a better understanding of ammonium picrate photolysis, biotransformation, soil absorption, and phytotransformation (and any other abiotic processes). Addressing these data gaps is not a primary concern, however, based on a recent study on the water range and operating areas at the Potomac River Test Range [9] which concluded that ammonium picrate contamination from buried munitions does not pose a significant threat to the ecological and human health.

B. Toxicity: Information on the toxicity of ammonium picrate degradation products and their risk assessments (i.e., if the quantities produced are above some threshold limit) should be evaluated.

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19. PICRIC ACID

19.1 INTRODUCTION

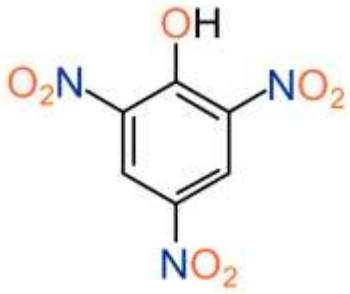

Figure 19-1. Chemical Structure of Picric Acid

Names: Picric acid

Abbreviations and Other Names: Carbazotic acid, phenol trinitrate, picronitric acid, trinitrophenol, 2,4,6-trinitro-1-phenol, 2-hydroxy-1,3,5-trinitrobenzene, TNP, melinite

CAS No.: 88-89-1

Chemical Formula: $C_6H_3N_3O_7$

Occurrence in Mixtures/Compositions: Booster charges; grenades; mines

Natural Occurrence: Picric acid does not occur naturally, and, therefore, there are no background levels in the soil, air, water, or food.

Physical/Chemical Properties: The physical/chemical properties of picric acid are provided in Table 19-1.

Table 19-1. Physical and Chemical Properties of Picric Acid

Property	Value	Units
Color	yellow	NA
Physical state	crystals	NA
Melting temperature	121.8	^oC
Vapor pressure (at 25^{o}C)	9.87e-10	atm
Specific gravity	1.77	None
Water solubility (at 20^{o}C)	13.1	g/L
Dissolution rate in water	high	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.33	None

19.2 FATE

Picric acid is an explosive compound belonging to the class of nitroaromatic explosives. It was used in grenade and mine formulations during the early to mid-20th century [1, 2]. Its use was discontinued in favor of less expensive, easier to manufacture, and safer to use (picric acid can form unstable metal salts over time when in contact with metal surfaces of ordnance shells) energetic materials such as TNT and RDX [3]. Not much attention has been given to the fate and transport of picric acid due to its discontinuation in the mid-20th century [3]. However, unexploded ordnance and stockpiles of old ammunition containing picric acid do exist, and the fate and transport of picric acid may need to be better understood because such munitions have been in storage or buried in contact with soil and water for over 50 years.

The fate of picric acid is also important because it can be a degradation product formed from other explosive compounds, namely ammonium picrate and tetryl [4].

19.2.1 Relevant Properties

Relevant properties pertaining to the fate and transport of picric acid are provided in Figure 19-2. One key property of picric acid that is a strong indicator of its environment fate and transport is its water solubility. Picric acid is highly soluble (13.1 g/L) and will readily dissolve (i.e., present as the picrate anion) in water [1, 3].

19.2.2 Photolysis

There appear to be some incomplete data on the photolysis of picric acid. Picric acid can undergo photolysis and form picramic acid [2, 3]. However, the technical literature also states that picric acid discharged to the environment is not expected to be significantly degraded via photochemical processes [1]. A more complete study on the propensity and factors affecting picric acid photolysis may be warranted.

19.2.3 Other Abiotic Reactions

Little data were found on other abiotic processes for picric acid. However, in general, nitroaromatic compounds can be reduced via ferrous iron (Fe^{2+}) [2, 5].

19.2.4 Biodegradation

The three nitro groups of picric acid create a highly positive redox potential that is susceptible to reductive rather than oxidative processes. An initial reductive attack on the aromatic ring converts picric acid to the hydride-TNP Meisenheimer complex. In *Rhodococcus (opacus) erythropolis* HL PM-1 [6], *Nocardioides* sp. strain CB 22-2 [7] and *Nocardioides* simplex (formerly *Arthrobacter*) FJ2-1A [8], elimination of nitrite is thought to proceed through this intermediate. However, Rieger et al. [9] stated this elimination requires an unlikely C-3 to C-2 hydrogen migration. Studies show that C-2 protonation of the hydride species occurs readily at physiological pH and suggests the protonated hydride complex is the reactive intermediate for nitrite elimination to 2,4-dinitrophenol. Reduction of the aromatic nucleus in 2,4-DNP forms the hydride-DNP Meisenheimer complex.

A second pathway involves a two component enzyme system which catalyzes two hydration reactions of picric acid to form a dihydride Meisenheimer-complex [10]. The nitro form of this dihydride complex remains as a dead-end metabolite; the acid form undergoes elimination of nitrite, after which the two metabolic pathways of picric acid merge [8]. The enzyme catalyzing denitration of the dihydride Meisenheimer-complex of picric acid to form the hydride Meisenheimer-complex of 2,4-dinitrophenol and also the hydrolase enzyme for subsequent reaction have been recently purified [11]. It has been known for more than a decade that 4,6-dinitrohexanoate undergoes further mineralization, with a minor amount remaining as a dead-end metabolite [6]. However, the further metabolites have not yet been identified.

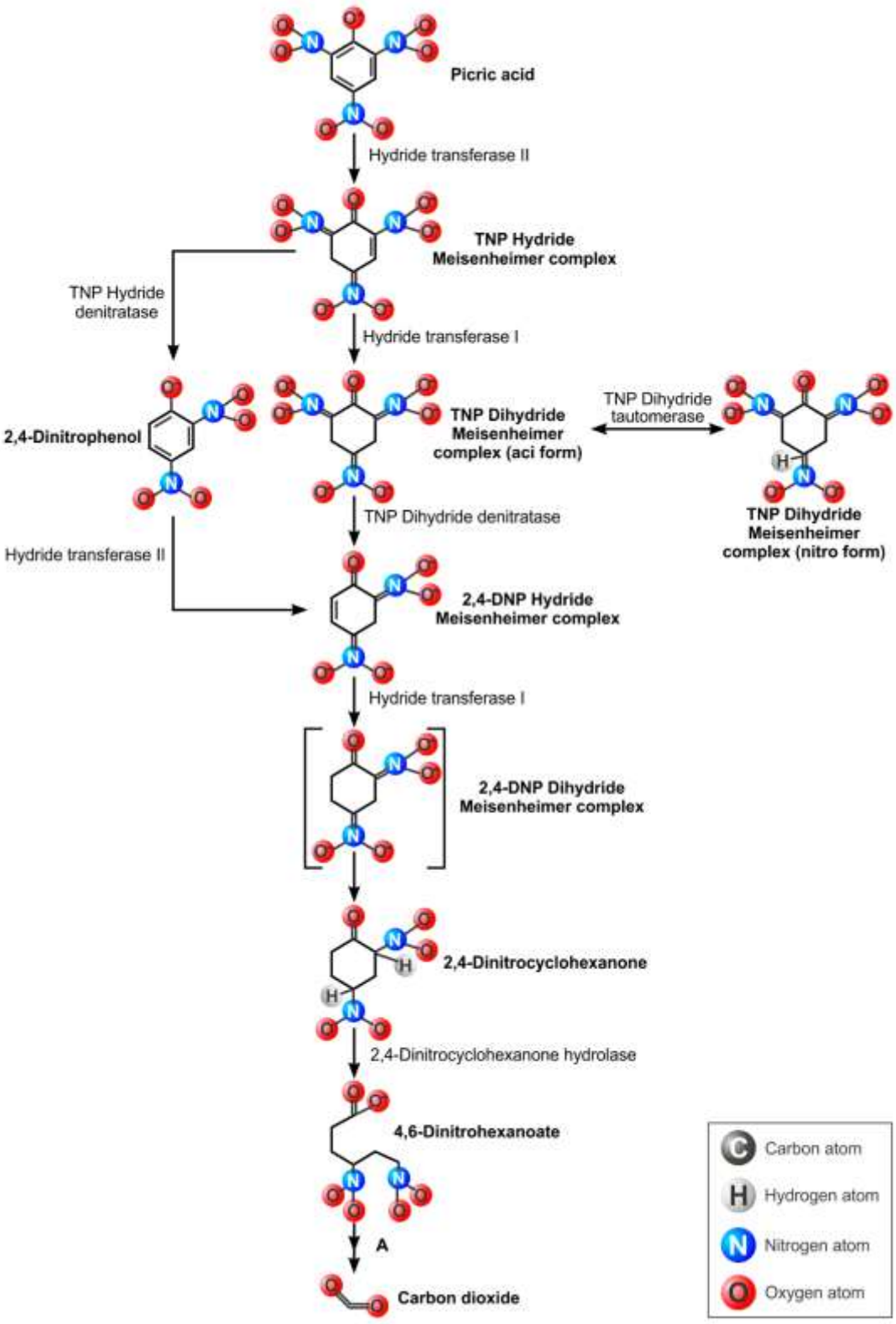

Figure 19-2. Microbial Degradation of Picric Acid [8, 10, 11].

19.2.5 Phytotransformation

No data were found on the plant uptake or phytotransformation of picric acid.

19.2.6 Hydrolysis

Picric acid will not undergo hydrolysis; rather, the compound will dissociate to yield the picrate anion when dissolved in water. It should be noted that picric acid can also be formed from the hydrolysis of tetryl [3].

19.2.7 Key Degradation Products

The key degradation products of picric acid should be known primarily from a safety standpoint. Picric acid can react with metals to form chemically unstable metal salts. Picric acid can also form picramic acid via abiotic reduction by Fe(II) and photolysis. Picramic acid is a flammable, potentially explosive, and toxic compound.

In aqueous solutions, picric acid will dissolve and dissociate, though this is a chemically stable process and does not result in the formation of a new compound.

19.3 TRANSPORT

Picric acid has not been actively used as a military explosive since the mid-20th century. As a result, most sources of environmental contamination are from munitions stockpiles and buried unexploded ordnance (UXO), rather than use or test/training range activities. Releases of picric acid to the environment typically originate from leaching of the material out of these munitions.

19.3.1 Transport Processes

Most of the sources for picric acid soil contamination are likely to come from legacy munitions storage areas or disposal pits that were used in the early to mid-20th century. A unique concern with picric acid and ammonium picrate, typically not seen with other explosive compounds, is the direct release to aqueous systems. Picric acid was used at a time when it was common practice to dispose of excess, obsolete, or unserviceable munitions in deep-water regions [12, 13]. This, combined with the use of such ordnance in open sea combat and training operations, can result in a significant, continual source of picric acid in aqueous systems, the release rate of which will depend on the corrosion or breaching of these munitions [13]. The Naval Surface Warfare Center, Dahlgren Division [14], collected data on the use of munitions constituents at the Potomac River Test Range, and found that ammonium picrate, which can degrade to picric acid, was the most used munition constituent by weight associated with live munitions testing over the span of 90 years. A sum total of 436,228 lbs of ammonium picrate was tested at the Potomac River Test Range over the 90-year span, with the majority tested during the 1940s and 1950s.

19.3.2 Transport in Air

The vapor pressure and physical state (solid) of picric acid under ambient conditions suggests that direct volatilization to air is not a significant transport route.

19.3.3 Transport in Soil

Picric acid directly deposited onto soil is expected to be resistant to biological or photochemical degradation processes [1]. It is likely to persist until it comes into contact with water. It is known that contact with rainwater will result in the solubilization, dissociation (into the picrate anion), and movement of picric acid particles [3]. Anions tend to be highly mobile in the soil and do not typically sorb as strongly to soils containing organic content and clay as a neutral compound [3]. As a result of this high solubility, anionic form of the acid in water, and low octanol-water partitioning coefficient (1.33), picric acid should be highly mobile in soil [3]. Picric acid could be thought to have, in turn, a high probability for reaching groundwater systems. It has been detected in groundwater samples at the Louisiana Army Ammunition Plant, though it was not detected at the Massachusetts Military Reservation, where picric acid-containing munitions were known to have been used [3].

Despite this anticipated high mobility, the transport of picric acid in soil and its propensity to reach groundwater ultimately depend on the soil type. Picric acid transport through the soil is highly variable [1]. The picrate anion is not expected to partition from water to organic sediments [1], based on data from laboratory studies; however, some sorption to humic compounds may occur [1]. In laboratory studies, picric acid sorbed to solutions containing calcium ions and calcium clays, no sorption was observed with sodium ions and sodium clays, and intermediate sorption occurred in mixtures of sodium ions with calcium clays or calcium ions with sodium clays.

Despite these factors that can affect picric acid transport in soil, the general consensus from reports on this topic is that picric acid is mobile in the environment and retention of picric acid can, but is less likely, to occur. More experiments and subsequent data sets are needed to fully assess soil transport characteristics and build a complete soil transport model. The available data from field studies are inconclusive as to how susceptible groundwater may be to picric acid contamination at sites that handled, stored, or used picric acid-based ammunition. It appears that the type of activity may influence the ability of picric acid to reach groundwater. Manufacturing activities could be higher probability sources of direct release of picric acid to the environment compared to UXO (the release from which is a function of the burial depth, corrosion rates, and physical integrity of the munitions components).

19.3.4 Transport in Water

Picric acid can reach water systems via soil transport (as discussed) or from direct release from deep-water munitions disposal sites. The release of picric acid from the munition and subsequent transport is driven by several factors including the physical condition of the munition (e.g., seal integrity and size of the breach hole), resistance of the munition to corrosion, dissolution rate of the picric acid, and properties of the water (e.g., current velocity) [15]. Picric acid released from a submerged munition is expected to immediately dissociate to form the picrate anion.

19.4 TOXICITY DATA OF PICRIC ACID

Picric acid is toxic by all routes of entry. Picric acid is corrosive to the eyes and skin and may cause permanent eye injury and scarring. It is considered an occupational skin sanitizer. Once sensitized, contact with even a small amount can cause an allergic reaction with symptoms such

as skin redness, itching, rash and swelling. This reaction can spread from the hands or arms to other parts of the body. Picric acid is harmful if swallowed.

Symptoms from picric acid exposure may include headache, nausea, vomiting, diarrhea, abdominal pain, itching, urinary dysfunction, stupor, convulsions, and death (liver and kidney damage may also occur). The severity of the symptoms depends on the degree of exposure. Dermal exposure may cause irritation and can lead to allergic reactions, skin damage, and staining at the contact site. Ingestion and absorption may cause poisoning.

19.5 EXAMPLE REGULATORY GUIDELINES FOR PICRIC ACID

No information on regulatory limits of ammonium picrate exist to date.

19.6 DATA GAPS

Similar to the data gaps described for ammonium picrate, the body of work on the fate and transport of picric acid compared to other explosives such as TNT or RDX is not as complete due to picric acid no longer being in use.

A. Fate and Transport

- **Photolysis:** More in-depth laboratory and field studies on the persistence of picric acid may also be warranted. Some data suggest that picric acid will undergo photolysis, though no data on the rate of photolysis were found, and more information on what environmental conditions facilitate photolysis is needed.
- **Reduction via Fe(II)**: More data are needed to determine if Fe(II) is capable of reducing picric acid. The existing data suggest that Fe(II) can reduce nitroaromatic explosives, but no data specific to this reduction method for picric acid were found.
- **Transport:** Because picric acid is no longer in use, it will likely contaminate the environment through release from a corroded or compromised munition. Some work has been done to develop models for predicting the corrosion and release of energetic materials (including picric acid) in UXO buried in deep waters. As these models are refined and improved, data on the potential environmental and toxicological effects (i.e., how high are the picric acid levels that are released per unit time) should be analyzed.

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20. PENTAERYTHRITOL TETRANITRATE (PETN)

20.1 INTRODUCTION

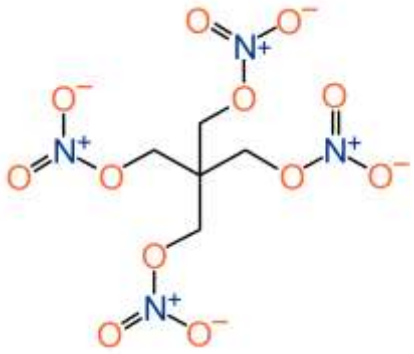

Figure 20-1. Chemical Structure of PETN

Names: Pentaerythritol tetranitrate (PETN)
Abbreviations and Other Names: Pentrite, nitropenta, corpent
CAS No.: 78-11-5
Chemical Formula: $C_5H_8N_4O_{12}$
Occurrence in Mixtures/Compositions: Pentolite; Semtex; PTX-2; detonating cord; some sheet explosives
Natural Occurrence: PETN does not occur naturally, and, therefore, there are no background levels in the soil, air, water, or food.
Physical/Chemical Properties: The physical/chemical properties of PETN are provided in Table 20-1.

Table 20-1. Physical and Chemical Properties of PETN [1, 4, 5]

Property	Ammonium Picrate	Units
Color	White	NA
Physical state	Crystalline solid	NA
Melting temperature	143.3	^oC
Vapor pressure (at 25^{o}C)	7.1e-12	atm
Specific gravity	1.76	None
Water solubility (at 20^{o}C)	1.5	mg/L
Dissolution rate in water	NA	$\mu g\text{-}g^{-1}\text{-}h^{-1}$
Octanol-water partition coefficient (Log K_{ow})	1.61	None

20.2 FATE

PETN is an explosive compound belonging to the class of aliphatic nitrate esters, which includes other explosive compounds such as nitroglycerin and nitrocellulose. The ease of detonation, or sensitivity, of PETN is the accepted standard for defining a primary explosive versus a secondary explosive. Explosives more sensitive than PETN (e.g., lead azide) fall into the former category, whereas less sensitive ones (e.g., TNT) fall into the latter. Because of this characteristic, the unique sensitivity and explosive properties of PETN justify its use as either an ingredient in detonators or as the main component in explosive charges.

PETN is used in a variety of explosive applications, including detonating cords and sheets; boosters; priming compositions; primary explosive charge formulations; and blasting caps [1]. As the main component of an explosive charge, PETN is used in explosive recipes such as Semtex formulations or Pentolite (50% PETN; 50% TNT).

The fate and transport of PETN has not been as well researched compared to data for TNT, HMX, and RDX [2]; this is because PETN is not used as widely as these explosives and subsequently is not often detected in soils [3].

20.2.1 Relevant Properties

Properties that relate to the persistence of PETN in different environments are very important in predicting its fate and transport characteristics. A review of these properties is provided in Table 20-1. The values for water solubility and the octanol-water partition coefficient provide quantitative data on how PETN may permeate through soil and water matrices and how likely PETN is to be absorbed. The water solubility of PETN (1.5 mg/L) is less than that of TNT (130 mg/L) or RDX (4 mg/L), indicating that PETN will be more reluctant to dissolve into water and therefore be less mobile in the environment. The octanol-water partition coefficient of PETN (log $K_{ow} \approx 1.61$) indicates that the compound will favor portioning to the octanol phase.

20.2.2 Photolysis

Some data suggest that PETN can undergo photolysis in aqueous matrices. Laboratory tests [6] indicate that 66% of an aqueous sample of PETN (5.6 µM) was degraded (to 1.9 µM) within 21 days following irradiation from simulated sunlight, degrading via a step-wise denitration process. This decrease in PETN was accompanied by the formation of nitrate (8.2 µM) and trace amounts of nitrate. Trace amounts of pentaerythritol trinitrate and pentaerythritrol dinitrate were also detected in analyzed samples. For comparison, half-life values for the biodegradation of PETN in water and soil are 37 and 9.92 days, respectively.

20.2.3 Other Abiotic Reactions

Laboratory studies have demonstrated the ability of PETN to be reduced via step-wise denitration to pentaerythritol and ammonium (NH_4^+) using granular iron [7]. The half-life values for PETN transformation in 100% granular iron and 30% granular iron/70% silica sand columns were 0.26 and 1.58 minutes, respectively. Pentaerythritol trinitrate and pentaerythritrol dinitrate were detected as reaction intermediates (but not quantified) in analyzed samples, along with the nitrite ion, which was released at each denitration step. The nitrite was also reduced to ammonium by the iron. All of the nitrogen content in the initial PETN sample was present as NH_4^+ within ≈ 35 minutes after the start of the reduction experiment.

20.2.4 Biodegradation

A number of bacterial strains degrade PETN and have been isolated from contaminated soil. Studies of the metabolism of PETN in mammals have shown that PETN is sequentially denitrated to produce the tri-, di-, and mononitrates in untreated or unpreserved urine and fecal matter, suggesting that microorganisms are responsible for its degradation [8].

Enterobacter cloacae PB2 utilizes two atoms of nitrogen per molecule of PETN, producing pentaerythritol dinitrate, which is subsequently oxidized to dialdehyde. An enzyme activity, designated PETN reductase, was found to reductively liberate nitrite from PETN with the production of pentaerythritol trinitrate and pentaerythritol dinitrates [8]. Moreover, a resting-cell suspension of *Agrobacterium radiobacter* grown on glycerol trinitrate as the nitrogen source metabolized 0.1 mM PETN rapidly, within 1.5 hour [9]. In each of these strains, a nicotinamide

cofactor-dependent oxidoreductase catalyzes the reductive cleavage of the nitrate ester group to yield an alcohol and nitrite [10]. The enzymes have similar amino acid sequences, and all contain flavin mononucleotide as a noncovalently bound cofactor.

20.2.5 Phytotransformation

Little to no data are available on the uptake and transformation of PETN by plants. One study [11] noted that based on data seen for other explosives (e.g., TNT) and propellants, if PETN were present in soils with access to plants, it would most likely be taken up and remain in the roots.

20.2.6 Hydrolysis

PETN can undergo hydrolysis. Laboratory studies were conducted on samples of PETN in deionized water by incubating at 50°C under different pH levels. Results showed that alkaline solutions are capable of hydrolyzing PETN. Samples in solutions of pH 12 had degradation half-life values of ≈ 20 days, while samples in solutions of pH 11 had values of ≈ 330 days [6]. Hydrolysis of PETN under normal environmental temperatures is assumed to be slow, though quantitative data appear to be unavailable. [4]. The reaction of PETN with water results in the scission of an O-NO_2 bond, which begins the step-wise denitration of PETN.

20.2.7 Key Degradation Products

The key degradation products of PETN are the denitrated compounds pentaerythritol trinitrate, pentaerythritol dinitrate, pentaerythritol mononitrate, and pentaerythritol. Pentaerythritol is a chemically-stable compound with low toxicity.

20.3 TRANSPORT

It appears from the surveyed literature that the fate and transport of PETN in the environment is not as heavily researched and well understand as RDX and TNT [6]. Nonetheless, data on the transport and fate of PETN are needed particularly due to its use in a variety of munitions and explosive formulations at live-fire training ranges.

20.3.1 Transport Processes

Once discharged to the environment, PETN can undergo degradation processes via hydrolysis, photolysis, biodegradation, or abiotic reduction [6]. PETN is also expected to have limited mobility in the environment, inferred from its water solubility value and octanol-water partitioning coefficient. These degradation processes and properties of PETN indicate that pristine PETN particles are not expected to be highly mobile in the environment to the extent that appreciable quantities are capable of reaching the groundwater.

20.3.2 Transport in Air

Dispersion and transport of PETN in air is not anticipated due to its low vapor pressure. Any PETN dispersed into the air as a result of, for example, blast testing will most likely drop out of the atmosphere via gravitational settling or scouring by rain.

20.3.3 Transport in Soil

PETN exhibits low mobility in soils, especially compared to other organic explosive compounds (e.g., TNT and RDX). The solubility value (1.5 mg/L) and octanol-water partition coefficient (3.71) indicate that PETN will not readily solubilize in water and that the compound can strongly sorb to soils [5]. Only small amounts of PETN are expected to dissolve into and be mobile in soil water following release to the environment. However, data from laboratory studies in which water was continually dripped on spherical PETN particles (to simulate rainwater exposure) showed that after 2 months of water dropping, ≈ 26% of the original mass of PETN dissolved into the water [6], demonstrating that although dissolution of PETN is limited by its low solubility with water, it still can leach out of an explosive formulation into the soil.

Laboratory studies on the ability of PETN to sorb to soils showed that PETN tends to sorb more readily with increasing organic content (i.e., a K_d value of 0.17 for soil with total organic carbon < 0.5% and a K_d value of 3.30 for soil with TOC = 2.5%) [6], which is expected given the octanol-water partition coefficient value (3.71). The results from this study suggest that PETN could migrate through the soil and potentially reach groundwater in low-TOC (i.e., < 0.5%) soils. This propensity to reach groundwater, however, will depend on how readily the source sample dissolves into water and depth of soil to traverse. Laboratory experiments [12] that analyzed PETN sorption in a variety of soils did not show any significant sorption to high clay content (48.7%) soils.

Nonetheless, little to no data appear to be available from field studies on PETN transport in soils, mainly due to the paucity of PETN residues present in soil samples. This may be a result of PETN degradation, using less PETN on average at military test ranges compared to, for example, TNT, or both.

20.3.4 Transport in Water

Little to no data were available in the technical literature regarding the direct release and transport of PETN in aqueous systems. Because of its low solubility with water, PETN is likely to exhibit limited mobility in water streams and may be more likely to deposit as crystalline sediment in a stagnant water pool [13].

20.4 TOXICITY DATA OF PETN

Structurally and pharmacologically, PETN resembles nitroglycerin; thus, in the human health field it has been used medicinally in the treatment of angina. However, in cases of occupational exposure cycles of exposure and withdrawal associated with a 5-day workweek (exposure) followed by a 2-day weekend (withdrawal) contact with PETN can lead to the well-recognized "Monday-morning death" of munitions employees who are exposed to these substances on a regular basis. The phenomenon arises from cardiovascular events that are triggered by unrestrained compensatory vasoconstriction, as the normally high organic nitrate levels in the body become reduced during the weekend [14].

The importance of PETN as an environmental contaminant is related to its distribution at and around military sites and to its potential toxicity to wildlife and other ecological receptors. Current knowledge of the likely harmful impacts of PETN on wildlife emphasize threshold doses for the onset of toxicological effects, as described in reports of experimental studies of PETN. Surveying

the threshold dosimetry of the compound may point to the establishment of toxicity reference values that could serve as protective exposure standards for all wildlife ranging in the vicinity of affected sites.

20.5 EXAMPLE REGULATORY GUIDELINES FOR PETN

No information on regulatory limits of PETN exist to date.

20.6 DATA GAPS

Field studies on the fate and transport of explosive compounds have not produced much data on PETN; this is primarily due to the lack of detectable concentrations of PETN in soil or water samples at these field sites. This lack of data may be due to PETN not being used as often in test or training operations as TNT or RDX, degradation processes that dominate over transport processes, or both.

A. Fate and Transport

- **General Data Gaps**: Field tests specific to PETN, in which explosive samples containing PETN are detonated in the field, could be conducted to address the data gaps on PETN soil transport and fate routes of PETN in the environment. The data gained from this study may answer how PETN is dispersed into and subsequently transformed or removed from the environment.
- **Soil Transport**: Data comparing the effect of soil type of PETN sorption or transport are incomplete; this appears to be due to a lack of available field data for PETN, low use of PETN (and therefore less attention paid to it) in existing munitions, or both.
- **Hydrolysis and Photolysis**: Some data from laboratory studies on the hydrolysis and photolysis of PETN are available; however, neither of these processes appear to have been addressed in field studies due to the lack of detectable quantities of PETN in such studies. These data could also provide information on the fate of PETN in aqueous systems by providing information on whether or not PETN would be more likely to be subjected to degradation processes or settling at the bottom of such matrices, remaining relatively unchanged over time.

B. Toxicity. It has been reported that PETN may show potential toxicity to wildlife and other ecological receptors. However, studies on the toxic effects of this compound need to be developed.

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21. N-METHYL-PARANITROANILINE (MNA)

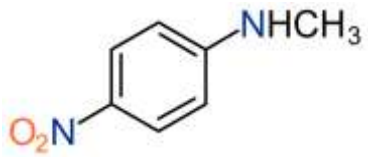

Figure 21-1. Chemical Structure of MNA

21.1 INTRODUCTION

Names: N-Methyl-paranitroaniline
Abbreviations and Other Names: MNA
CAS No.: 100-15-2
Chemical Formula: $C_7H_8N_2O_2$
Occurrence in Mixtures/Compositions: Used as an additive/plasticizer in insensitive munition formulations PAX-21, PAX-24, PAX-25, PAX-26, PAX-28, PAX-40, and PAX-41
Natural Occurrence: MNAs are not formed naturally and have been introduced into the environment in large quantities in the form of disinfectants, bleaching agents, and herbicides.
Physical/Chemical Properties: The physical/chemical properties of MNA are provided in Table 21-1.

Table 21-1. Physical and Chemical Properties of MNA [5, 6]

Property	Value	Units
Color	White	
Odor	None	
Physical state	Powder	
Melting temperature	60.96	°C
Vapor pressure (@ 20°C)	1.104E-6	atm
Specific gravity	1.16	None
Water solubility (@ 20°C)	85	mg/L
Dissolution rate in water	Unknown	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	2.10	None

21.2 FATE

N-methyl-paranitroaniline (MNA) is a chemical used in newer insensitive munition (IM) formulations as a processing aid or stabilizer [1, 2]. Its main function is to ease formulation synthesis by lowering the melting temperature of the primary energetic compound (e.g., DNAN) [3, 4]. Chemically, MNA is a nitroaromatic compound comprising a benzene ring. This causes some concern over the environmental fate of MNA because nitroaromatic compounds, in general, are known to be acutely toxic to humans and other life forms [1, 4]. However, the information on the specific environmental fate and transport of MNA appears to be lacking, perhaps due to the more recent introduction of this compound in explosive formulations.

The new IM formulations comprising MNA typically only contain small (i.e., single percentages or less) quantities of the compound. The impact of the potential release of these small amounts of MNA and the types of products formed through degradation processes and their toxicities need to be determined as the use of these new IM formulations become more widespread and manufacturing of MNA increases.

21.2.1 Relevant Properties

Properties that can be used to predict the fate and transport of MNA in the environment are provided in Table 21-1. The solubility of MNA (≈ 85 mg/L) is less than that of TNT (130 mg/L) and greater than that of RDX (≈ 4 mg/L), indicating that MNA will dissolve more readily in water than RDX and will be more mobile in the environment, but not to the extent of TNT. The octanol-water partition coefficient (log K_{ow} ≈ 2.10) is greater than that of RDX (≈ 0.87) and close to that of TNT (≈ 1.86), indicating that MNA will tend to partition more readily to the octanol phase.

21.2.2 Photolysis

Little data were found describing MNA photolysis or its associated rates of photolytic degradation. However, MNA is a nitroaromatic compound; these compounds (which include TNT and the DNTs) typically readily undergo photolysis.

21.2.3 Other Abiotic Reactions

No data were found on other abiotic routes for MNA with no reduction with iron compounds.

21.2.4 Biodegradation

Given MNA's poor solubility in water and its limited mobility in soil, interaction with biological systems may play an important role in its environmental fate and remediation. MNA is known to reduce to N-methyl-p-phenylenediamine (MPD) in an ethanol-amended anaerobic fluidized bed bioreactor where MNA was treated in a co-mixture with DNAN and perchlorate. Other than the bioreactor study, very little knowledge is available on the MNA biotic degradation. The proposed general MNA pathway for its anaerobic degradation is depicted in Figure 21-2.

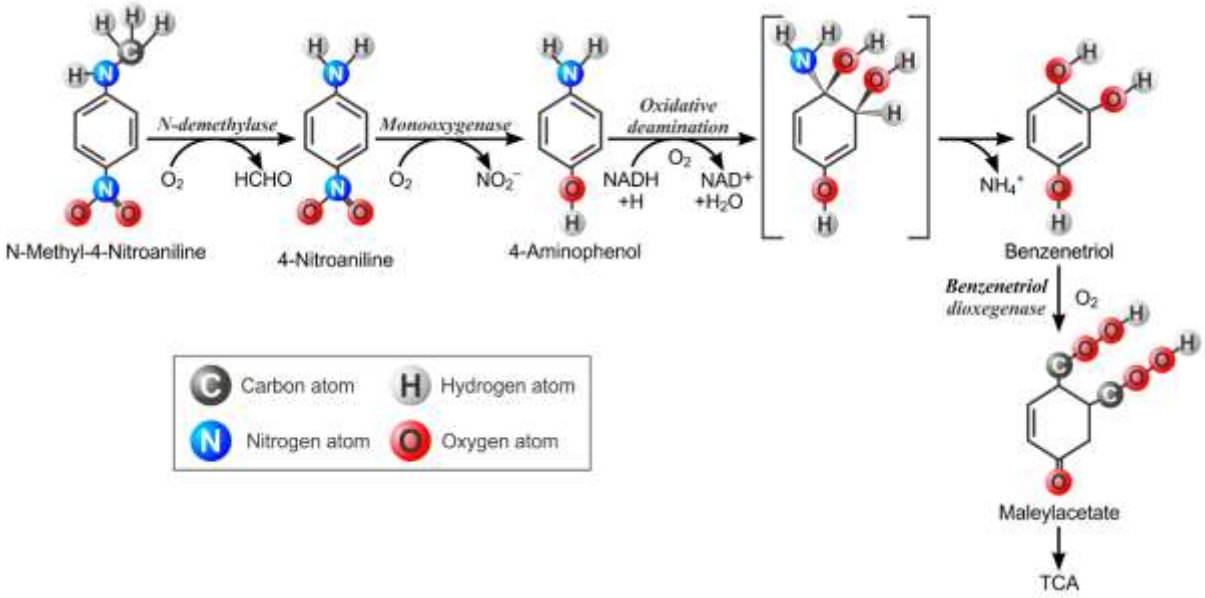

Figure 21-2. General Pathway for the Anaerobic Biotransformation of MNA [7]

MNA has been shown in laboratory studies to be degraded under aerobic conditions, with nitrogen-amended soils showing higher degradation rates compared to non-amended soils. A demethylation reaction results from this process, producing degradation intermediate products 4-nitroaniline (4-NA), 4-aminophenol (4-AP), and 1,2,4-benzenetriol (BT), with maleylacetate (MA) as the final end product from BT degradation [4].

21.2.5 Phytotransformation

No data were found regarding plant uptake and transformation of MNA.

21.2.6 Hydrolysis

No data were found on the hydrolysis of MNA. However, similar to what was stated for photolysis, nitroaromatic explosives can undergo hydrolysis in highly alkaline systems.

21.2.7 Key Degradation Products

Data from studies on MNA degradation have identified nitroaniline, aminophenol, benzenetriol, and maleylacetate as compounds formed during the degradation process. MNA is highly toxic and has been found to be harmful to aquatic organisms [8].

21.3 TRANSPORT

The release of MNA to the environment will likely result from waste stream discharges from manufacturing operations, or soil deposition from unexploded ordnance (UXO) or training operations [3, 9]. In either scenario, the concern with MNA transport is how easily it can reach groundwater systems; i.e., how mobile the substance is in a given matrix. The mobility of MNA will depend on its propensity to dissolve, undergo degradation reactions and bind to soils and sediments. Most of this information appears to be missing or, at best, incomplete for MNA.

With waste stream discharge, the transport of MNA to soil and aqueous systems can be somewhat controlled, given that parameters such as the quantity of MNA discharged and the discharge routes can be established in the manufacturing process. MNA discharge to soil systems can be a result of incomplete detonations [3], which, in contrast to waste stream discharge, introduces some level of uncertainty as to how susceptible groundwater is to MNA contamination. In this case, variables such as the amount of MNA dispersed into the soil following a UXO or training operation, the availability of water (e.g., rainwater) for transport; the soil composition, and proximity to groundwater will influence how readily MNA reaches groundwater. Identifying and understanding these variables along with the factors affecting MNA mobility in soil systems are therefore of particular importance to controlling environmental contamination.

21.3.1 Transport Process

The environmental impact of MNA has yet to be fully developed due to its more recent use in the new generation of IM formulations. However, some computer simulation work has been done to model and evaluate its environmental impact using known or predicted values for the octanol-water partition coefficient, Henry's law constant, vapor pressure, and other thermophysical

properties [6]. These properties have been used to assess how mobile MNA could be in a soil system.

21.3.2 Transport in Soil

The transport of MNA in soil has been evaluated in the available technical literature based on the properties that influence MNA mobility (e.g., water solubility and the octanol-water partition coefficient). Once dispersed into soil, the MNA must first come into contact with and dissolve into water to facilitate transport. The solubility of MNA (≈ 0.085 g/L) is low; therefore, the initial mobility in soil is expected to be limited [1]. Once MNA has dissolved into water, the octanol-water partition coefficient (log K_{ow} ≈ 2.10) and predicted Henry's Law constant (log H ≈ -3.88) suggest that MNA is not likely to bioaccumulate, will partition preferably to the aqueous phase, and therefore have the potential to be mobile in the soil and eventually reach groundwater [6].

However, the ability of MNA to move within the soil is ultimately dependent on the effects or influences of absorption or degradation processes present in the soil. Mobility may be higher in some soils than others, for example, anilines, in general, bind strongly to humus or organic matter [5].

21.3.3 Transport in Water

As the need for larger quantities of new IM formulations such as PAX-21 increase, the demand and production of MNA at explosive production facilities is also expected to increase [9]. This has led to planned research on the transport and degradation of MNA in waste streams [2]. As of now, data on the transport of MNA in water are lacking or difficult to access. MNA directly discharged to aqueous systems is likely to remain in water (i.e., not sorb to sediment) based on the value of the octanol-water partitioning coefficient; the MNA may also be present in aqueous systems as solid particles, given its low solubility in water. MNA will likely persist in water, unless the degradation processes of photolysis, hydrolysis, and biodegradation can occur at significant rates. More data are needed on these specific degradation processes before a complete evaluation of the transport of MNA in water can be made.

21.4 TOXICITY DATA OF MNA

Little to no information on MNA toxicity is documented to date. Regarding the inhibitory potential of MNA, there are no dedicated studies on its cytotoxicity. MNA has been suggested to be mutagenic based on Ames test results and mutagenicity prediction models.

21.5 EXAMPLE REGULATORY GUIDELINES FOR MNA

No regulatory limits for MNA exist to date.

21.6 DATA GAPS

MNA is a relatively new compound that undergoes laboratory studies and testing. Little information is known on its degradation compounds and specific treatment technologies as well as its toxicity. Several data gaps pertaining to MNA are presented below.

A. Fate and transport. Fate and transport processes and/or reactions are not fully known or understood due to MNA not being used in explosives until recently.

- **Photolysis and abiotic degradation processes.** Data on photolysis, hydrolysis, plant uptake, and soil absorption (iron reduction) are lacking or incomplete.
- An assessment on the possible or potential effects of MNA waste streams on MNA fate and transport is needed, as domestic MNA production begins to increase with new IM formulation production.

B. Toxicity. Data gaps need to be closed on the specific toxicity of MNA and its degradation compounds. Existing data show that nitroaromatic compounds tend to have significant toxicity concerns.

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22. NITROCELLULOSE

22.1 INTRODUCTION

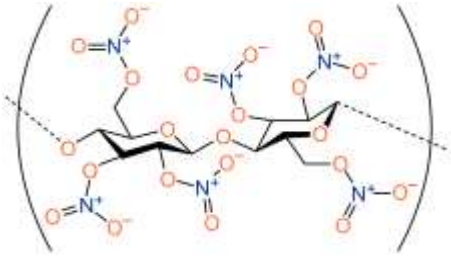

Figure 22-1. Chemical Structure of Nitrocellulose

Names: Nitrocellulose
Abbreviations and Other Names: Pyroxylin, gun cotton, collodion
CAS No.: 9004-70-0
Chemical Formula: Varies; e.g., $C_{24}H_{36}N_8O_{38}$
Occurrence in Mixtures/Compositions: Single-, double-, and triple-based smokeless gun propellants
Natural Occurrence: Does not occur naturally; requires the nitrification of cellulose
Physical/Chemical Properties: The physical/chemical properties of nitrocellulose are provided in Table 22-1.

Table 22-1. Physical and Chemical Properties of Nitrocellulose [5]

Property	Value	Units
Color	White	
Odor	Ether-Like	
Physical state	Fibrous	
Melting temperature	160 – 170	°C
Vapor pressure (@ 20°C)	1.32e-8	atm
Specific gravity	1.3	None
Water solubility (@ 20°C)	<1	g/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partitioning coefficient (Log K_{ow})	NA	None

Nitrocellulose, as an explosive material, is primarily used in smokeless gun propellants (single-, double-, and triple-based). In single-based propellant formulations (e.g., M1, M6, and M10), it is the main explosive ingredient and will contain additives for improved chemical stability (dry nitrocellulose is ignition-sensitive) and performance (e.g., 2,4-DNT). In double-based propellants (e.g., M2, M5, and M8), nitrocellulose and nitroglycerin are the explosive ingredients. Triple-based propellants (e.g., M30 and M31) comprise nitrocellulose, nitroglycerin, and nitroguanidine. Nitrocellulose is classified as an aliphatic nitrate ester explosive [1].

22.2 FATE

The fate of nitrocellulose in the environment is not considered to be a significant area of concern compared to other explosives such as TNT, RDX, HMX, PETN, etc. This is mostly due to its low level of toxicity [2] and insolubility; the latter property results in high resistance to mobility in the environment (i.e., nitrocellulose will remain where deposited and persist or be subjected to degradation or weathering effects [2, 3]). This insolubility of nitrocellulose can, however, have a significant effect on the transport and subsequent soil and water contamination from the other, water-soluble explosive ingredients comprising gun propellants. In a double-based propellant, for

example, nitroglycerin is combined with nitrocellulose, resulting in the water-soluble nitroglycerin contained within the water-insoluble nitrocellulose. The insolubility of the nitrocellulose can prevent immediate dissolution of nitroglycerin into rainwater, leaving significant quantities of nitroglycerin at the soil surface while providing a prolonged, slow release of nitroglycerin into the environment [4].

22.2.1 Relevant Properties

Relevant properties for nitroglycerin are provided in Table 22-1. Data are not available for properties related to environmental transport and fate, such as the octanol-water partitioning coefficient and dissolution rate due to the insolubility of nitrocellulose in water and subsequent reluctance to mobility and transport.

22.2.2 Photolysis

Data from laboratory studies with nitrocellulose-based propellants suggest that only very slight nitrocellulose degradation (≈ 1% over a 30-day period) upon exposure to UV rays is possible [4, 6], likely releasing nitrates (NO_3^-) and nitrites (NO_2^-) in the process.

22.2.3 Other Abiotic Reactions

No data were found on the abiotic reduction of nitrocellulose. However, laboratory studies on other aliphatic nitrate ester explosives such as PETN [7] and nitroglycerin [8] have shown that iron can reduce these compounds. In the case of nitroglycerin, ferrous iron (Fe^{2+}) reduction removed nitrite (NO_2^-) from the nitroglycerin.

22.2.4 Biodegradation

Most studies have concluded that nitrocellulose is resistant to biodegradation. Microorganisms are able to degrade nitrocellulose by two pathways: 1) cleavage of b-1,4-glucoside bonds that produce nitrooligosaccharides of various length, normally carried out by fungi [9], and 2) degradation by methanogenic or sulfate-reducing bacteria under anaerobic conditions [9].

Reports on nitrocellulose degradation with use of various fungi for composting purposes have been published [10, 11]. Duran et al. [12] examined the biodegradability of nitrocellulose under methanogenic conditions using a sewage sludge inoculum. Total gas production was monitored during batch tests with a primary substrate (e.g., cellulose or acetate) and 36 to 54 g/L of nitrcellulose. NC inhibited total gas production initially, but complete recovery occurred at the lower concentrations. An increase in gas output from NC was observed when cellulose served as the primary substrate, particularly in systems that were configured with an acid phase reactor preceding a methanogenic reactor. However, no measurements were made of changes in the composition of NC following digestion to determine if biotransformation of the NC altered its reactivity [12].

22.2.5 Phytotransformation

No data were found on the phytotransformation of nitrocellulose.

22.2.6 Hydrolysis

Limited data are available on the hydrolysis of nitrocellulose. Nitrocellulose has been shown in laboratory studies to undergo hydrolysis in alkaline (pH > 7) solutions (containing sodium hydroxide [NaOH]) at 70°C over a 35-minute test duration [3]. Nitrates (NO_3^-) and nitrites (NO_2) were formed directly from a single-step cleavage process. Concentrations of nitrates and nitrites increased with increasing sodium hydroxide content. At the end of the 35-minute test, for example, nitrate production was ≈ 20 mg/L in a 0.2% NaOH solution and ≈ 275 mg/L in a 2.0% NaOH solution.

22.2.7 Key Degradation Products

Nitrocellulose is expected to be immobile and very persistent in the environment. Degradation may occur over time due to hydrolysis or photolysis (if conditions for either are favorable). Should nitrocellulose degradation occur, the likely degradation products are nitrates and nitrites. This could lead to higher nitrate and nitrite levels in the environment, but only if the presence and rates of nitrocellulose degradation reactions are significant enough to produce higher-than-normal levels of these contaminants.

22.3 TRANSPORT

Nitrocellulose is not expected to be mobile in the environment due to its insolubility with water and its size and morphology (i.e., larger, fibrous solid particles which are physically difficult to transport via water advection) [13, 14]. It is often used at training ranges for operations in which single-, double-, and triple-based propellants are used. Nitrocellulose contamination at training ranges has been documented; it is often found on soil surfaces at gun, mortar, and tank artillery firing positions [13].

While nitrocellulose is often used at training ranges, specific data on the quantities of nitrocellulose deposited onto soils are often not reported [15, 16], whereas quantity data for the other explosive compounds present in gun propellants (e.g., nitroglycerin) are sometimes provided. This may be a result of its poor mobility of nitrocellulose (i.e., there is little to no concern over nitrocellulose reaching groundwater) and its low toxicity levels. However, one report [6] did suggest that presence of nitrocellulose in soil may need to be known since it could pose a danger to building demolition activities on formerly used ammunition facilities.

22.3.1 Transport Process

Nitrocellulose transport in the environment does not appear to be a concern in the area of range contamination due to explosive compounds. The compound is highly resistant to water, the main driver for environmental transport. Thus, nitrocellulose will remain relatively unchanged in the environment and subjected to weathering effects or degradation process, if the conditions for these processes are available.

22.3.2 Transport in Soil

Nitrocellulose will persist on soil surface and resist transport. Degradation processes, if available, could drive denitration reactions that would leave cellulose in the environment, which is not expected to be an environmental or toxicity concern.

22.3.3 Transport in Water

Nitrocellulose is not expected to reach groundwater supplies through soil migration. Transport in water is likely to be a result of direct deposition of nitrocellulose into water systems. Once deposited into water, nitrocellulose is expected to persist as a solid particle due to its insolubility with water. Its specific gravity is higher than that of water, so settling of the nitrocellulose particles is expected to occur. If the conditions are favorable for hydrolysis or photolysis, nitrate and nitrite ions could be liberated with particles of cellulose remaining and persisting in the aqueous environment.

22.4 TOXICITY DATA OF NITROCELLULOSE

Studies with nitrocellulose indicate no toxicity at concentrations up to 975 µmoles/L when tested with freshwater fish species, invertebrates and microalgae. The overall lack of toxicity of nitrocellulose is likely a result of its insolubility in water.

Available data on human health effects and mammalian toxicity suggest nitrocellulose is virtually nontoxic. The LD50 values were in excess of 5,000 mg/kg. Chronic toxicity studies in mice demonstrated only physical effects (fiber impaction) in the digestive tract (presumably because of the small size of the mouse digestive tract). Genotoxicity and developmental toxicity studies did not demonstrate any other significant toxic effects. Carcinogenicity data generated by an epidemiology study of occupational exposure during production of nitrocellulose suggest some association between nitrocellulose and rectal/digestive tract cancers; this should be researched further. Metabolism data in rats indicate no absorption from the gastrointestinal tract. However, nitrocellulose does appear to produce significant abiotic environmental effects. Because of its fibrous nature, it blankets benthic habitats (limiting available oxygen) and fills in interstitial spaces used as cover for benthic organisms. This habitat alteration is compounded by the resistance of nitrocellulose to environmental degradation. Habitat alteration becomes a significant aspect of regulatory control.

22.5 EXAMPLE REGULATORY GUIDELINES FOR NITROCELLULOSE

The Health Advisory Program, sponsored by the EPA's Office of Water, defines nitrocellulose as relatively nontoxic so no regulatory limits exist for nitrocellulose to date.

22.6 DATA GAPS

Some data gaps pertaining to the fate and transport of NC as well as treatment technologies of NC-containing formulations exist. Several of the data gaps are listed below:

A. Fate and Transport.

- **Fate and Transport (General):** For formulations comprising NC with other energetic materials (e.g., NG), the effects of the insoluble NC matrix on the fate and transport of the other explosives should be studied. Some work has been done to show the effects of dissolution for NC-based formulations.

- **Transport:** Data on the amount of nitrocellulose typically found on training range soils or former ammunition sites may be needed to help qualify the risk and contamination concern.
- **Degradation:** Studies concerning phytotransformation, abiotic reduction, and photolysis are non-existent or limited. Therefore, further studies should be considered to examine the fate of NC with these mechanisms.

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23. 2,4,6-TRIAMINO-1,3,5-TRINITROBENZENE (TATB)

Figure 23-1. Chemical Structure of TATB

23.1 INTRODUCTION

Names: 2,4,6-triamino-1,3,5-trinitrobenzene
Abbreviations and Other Names: TATB
CAS No.: 67539-61-1
Chemical Formula: $C_6H_6N_6O_6$
Occurrence in Mixtures/Compositions: Used in insensitive high explosives (IHE) including PAX-34, PBX-9502, LX-17-0, and PBX-9503
Natural Occurrence: TATB is not formed naturally.
Physical/Chemical Properties: The physical/chemical properties of TATB are provided in Table 23-1.

Table 23-1. Physical and Chemical Properties of TATB [5, 6]

Property	Value	Units
Color	Light yellow	
Odor	sweet	
Physical state	Crystals	
Melting temperature	350	^oC
Vapor pressure (@ 20^{o}C)	1.76E-14	atm
Specific gravity	1.93	None
Water solubility (@ 20^{o}C)	32	mg/L
Dissolution rate in water	NA	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient (Log K_{ow})	0.7	None

TATB is an explosive belonging to the class of aromatic nitrates. It exhibits high thermal stability, good shock resistance, and low solubility [1, 2]. It is primarily used in nuclear weapons systems due to its high degree of reaction insensitivity, which makes the explosive safer to handle by lowering the risk of inadvertent detonation [3, 4].

23.2 FATE

In comparison to an explosive such as TNT and RDX, which are used in significant quantities and in several different explosive formulations and munitions, not much data are available on the fate of TATB. The lack of studies on degradation processes of TATB could be a result of its limited use: TATB is primarily only used in nuclear warheads. Its excellent thermal stability and insensitivity make it ideal for storage and use; however, it is also significantly more expensive to manufacture. Less expensive, but sufficiently stable compounds such as TNT or RDX are more commonly used in high-production munitions. The available data on fate are typically resulting from or derived from studies performed on TATB to assess its stability.

23.2.1 Relevant Properties

The value for the melting point of TATB is provided in Table 23-1, although most thermal decomposition studies with TATB have shown that TATB will decompose to gas directly from the solid state unless heated at very high rates [1]. Most technical reports on TATB do not report a melting temperature. The solubility of TATB (≈ 32 mg/L) is greater than that of PETN (≈ 1.5 mg/L) and comparable to that of RDX (≈ 47 mg/L), signifying that TATB is only slightly soluble in water. The octanol-water partition coefficient for TATB (≈ 0.7) is also close to that of RDX (≈ 0.9), which indicates that partitioning to water is more likely than sorption to soil and TATB will be more mobile in the environment once dissolved than a compound with a higher octanol-water partition coefficient (e.g., TNT).

23.2.2 Photolysis

TATB will undergo photolysis, changing in color from light yellow to green under light irradiation. This color change is believed to be due to free radical formation on the surface of TATB [2, 7].

TATB photolysis appears to be a complex process. The initial photolysis-driven decomposition step has yet to be fully characterized but it is thought to involve depletion of the $-NO_2$ group via $C-NO_2$ bond cleavage following UV or visible light irradiation [2, 7]. The main product of TATB photolysis is reported to be a "free radical" that can persist for up to two years at room temperature, the presence of which may be the source of the green color change. The mechanism for photolysis involves the formation of mono-nitroso derivatives due to a loss of oxygen from a TATB molecule [2]. Rates appear to not be available for this reaction.

23.2.3 Other Abiotic Reactions

Not much data on additional abiotic processes of TATB pertinent to its environmental fate were found. However, one early report on TATB [8] discovered that iron can accelerate the thermal decomposition of TATB, such that it occurs 50 to 75°C lower than its typical decomposition temperature of 350°C. The products of this reaction include carbon dioxide and cyanogen $(CN)_2$ gases. Specific information on the iron used in these experiments (for example, zero valent, etc.) was not disclosed.

23.2.4 Biodegradation

No reports on biotic TATB degradation were found.

23.2.5 Phytotransformation

No data were found on the uptake and transformation of TATB by plants.

23.2.6 Hydrolysis

Hydrolysis of TATB has been shown to occur via base catalyzed hydrolysis (0.1 N NaOH), converting the TATB to the weak acid 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB). In this process, TATB is fully transformed with production of three NH_2 groups, which are step-wise replaced by HO^- with the liberation of ammonia (NH_3) [9]. Data on hydrolysis rates were not provided.

23.2.7 Key Degradation Products

TATB degradation products include THTNB, NH_3, and mono-nitroso derivatives. Little data on the toxicity of THTNB appear to be available. Cyanogen has been produced in thermal degradation studies that examined the effect of metal catalysts on the reaction rate; it is not clear at this point if this product would be regularly encountered in environmental fate processes.

23.3 TRANSPORT

23.3.1 Transport Process

Similar to information on the fate of TATB in the environment, not as much data on the transport of TATB have been reported. Field reports by subject matter experts on military range contamination [5, 10] do not report any data on TATB contamination. Similar to what was noted for the fate of TATB, the dearth of TATB transport data could be a result of its primary use in nuclear warheads, as well as its lack of use on training ranges or in unexploded ordnance (UXO) removal operations. It is estimated that in terms of general quantities of TATB, the Department of Energy maintains a 5-year supply for its Stockpile and Stewardship Management Program [4]. The high cost to produce TATB has also been an impediment to its widespread use in explosive formulations [4].

Because its use on training ranges is extremely limited or non-existent, releases of TATB to the environment are more likely to result from manufacturing activities, producing waste stream discharges. Leaching out of existing stockpiled munitions is also a common contamination source for most military explosives; however, the stability of TATB is such that leaching should not be considered a significant concern. New insensitive munition (IM) formulations that contain TATB as an ingredient, such as PAX-34, are also being developed. The use of these new IM formulations may become more widespread with time, such that the use of TATB may increase at training ranges. This places an added emphasis on understanding the transport of TATB in the environment.

The transport of TATB in the environment needs to be understood to assess how easily it can reach groundwater systems, i.e., how mobile this explosive is in the environment. Little to no specific data on the transport of TATB (and transformation products) were found in the open literature. In this section, most of the transport processes for TATB are based on an analysis of properties related to transport, such as the octanol-water partitioning coefficient, vapor pressure, and water solubility. These properties are taken into consideration with the transformation or degradation processes for TATB to establish an assumed, preliminary transport model.

23.3.2 Transport in Soil

TATB exhibits excellent chemical stability as shown by its vapor pressure value (1.76E-14 atm), thus it will not volatize into the air upon environmental release. Once dispersed onto soil, TATB must first come into contact with and dissolve into water to facilitate transport. The solubility of TATB ($\approx$ 32 mg/L) is comparable to RDX and higher than the more insoluble explosive materials such as PETN, suggesting that TATB will exhibit slight mobility in soil, comparable to RDX, which is thought to be continuously released to the environment over an extended period of time

when deposited onto soil. The octanol-water partitioning coefficient for TATB (≈ 0.7) indicates that partitioning to water is more likely than sorption to soil.

Thus, when TATB dissolves into water, it is expected to be slightly mobile, less likely to sorb to soil, and could have the potential to reach the groundwater only if it is not subjected to transformation degradation processes. However, some data suggest that processes such as photolysis and hydrolysis may affect the available amount of TATB for transport; however, data on the specific rates of these reactions need to be identified and understood to better assess this balance between soil mobility and TATB degradation and transformation.

23.3.3 Transport in Water

No data were found specific to the transport of TATB in water. Based on the value of the octanol-water partitioning coefficient and only slight solubility with water, TATB directly deposited to water systems is expected to remain in water (i.e., not sorbed to sediment), perhaps present as solid particles that only slowly dissolve into the water over time. However, similar to what was provided for soil transport, the effects of degradation and transformation processes need to be better understood to fully assess the transport of TATB in water. The persistence, fate, and toxicity of TATB reaction products are especially critical to identify and understand if any of these products feature mobility and toxicity values more severe than its parent compound.

23.4 TOXICITY DATA OF TATB

No toxicity information on TATB was found.

23.5 EXAMPLE REGULATORY GUIDELINES FOR TATB

No regulatory information on TATB was found.

23.6 DATA GAPS

TATB is a relatively new compound and a variety of knowledge gaps pertaining to its basic chemical and physical characteristics exist. Moreover, data on TATB toxicity, transport and environmental fate are as well incomplete and require further research efforts. Main gaps identified for TATB are listed below.

A. Fate and Transport

- **Fate:** TATB degradation processes need to be better understood to evaluate the transport of TATB in the environment. For example, processes such as photolysis could have a significant influence on TATB degradation and transport; however, reaction rates are not known. In addition, no information was found for biodegradation and phytotransformation and limited information on hydrolysis and abiotic reactions.
- **Transport:** TATB use is limited to nuclear weapons systems. If there are plans to increase its use, for example in new IM formulations, more data on its transport may be needed to assess toxicity and environmental risk.

B. Toxicity. Basic toxicity data including human and ecotoxicity, reference dose and exposure risk information are missing for TATB.

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24. COPPER (I) 5-NITROTETRAZOLATE (DBX-1)

24.1 INTRODUCTION

Names: Copper(I) 5-Nitrotetrazolate
Abbreviations and Other Names: DBX-1
CAS No.: 957133-97-0
Chemical Formula: $C_2Cu_2N_{10}O_4$
Occurrence in Mixtures/Compositions: Used in detonators (e.g., M55 stab detonators) as a drop-in replacement for lead azide
Natural Occurrence: DBX-1 is not formed naturally.
Physical/Chemical Properties: The physical/chemical properties of DBX-1 are provided in Table 24-1.

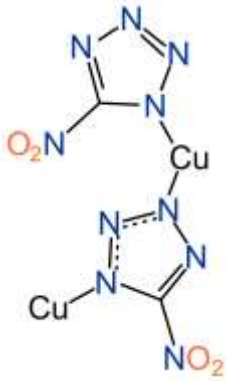

Figure 24-1. Chemical Structure of DBX-1

Table 24-1. Physical and Chemical Properties of DBX-1 [3-6]

Property	MNA	Units
Color	Brown	
Odor	Not Reported	
Physical state	Monoclinic Crystals	
Melting temperature	NA; decomposes	^oC
Vapor pressure (@ 20^{o}C)	Extremely low	atm
Specific gravity	2.59	None
Water solubility (@ 20^{o}C)	Not Reported	g/L
Dissolution rate in water	Not Reported	$\mu g\text{-}cm^{-2}\text{-}s^{-1}$
Octanol-water partition coefficient	Not Reported	None

Copper (I) 5-nitrotetrazolate (DBX-1) is a primary explosive, recently developed as an environmentally-friendly replacement for lead azide, a chemical widely used in detonators [1, 2]. DBX-1 has high thermal stability, and ignition sensitivity and energy output comparable to that of lead azide; it eliminates the use of lead, a heavy metal with significant toxicity concerns [2]. DBX-1 has also been shown to be more stable than lead azide in non-hermetic systems [1, 2]..

24.2 FATE

Data on the environmental fate of DBX-1 and likely degradation processes are lacking, primarily due to its more recent development. It appears from the surveyed literature that DBX-1 may still be in the characterization phase.

24.2.1 Relevant Properties

Values for the properties shown in Table 24-1 have yet to be widely reported in the open literature. It has been shown [4] that DBX-1 is capable of dissolving into water and decomposing; however, specific data on the water solubility limit at temperature were not found. Several of these

properties, such as water solubility and the octanol-water portioning coefficient, can be used at the to predict the environmental fate of a given compound. These data are lacking for DBX-1, presenting significant challenges to assessing its fate.

24.2.2 Photolysis

No data were found specific to photolysis of DBX-1.

24.2.3 Abiotic Reduction

No data were found on abiotic reduction processes of DBX-1.

24.2.4 Biodegradation

No data were found on biotic degradation of DBX-1.

24.2.5 Phytotransformation

No data were found on plant uptake and phytotransformation of DBX-1. However, data on copper (i.e., the element likely to persist following DBX-1 detonation) uptake in plants are available [7], though the process is not well understood. Copper can be taken up by plant roots and transported to every portion of the plant, including stems and leaves. Data were not provided for transport rates.

24.2.6 Hydrolysis

DBX-1 can dissolve very slowly in water and decomposes to a copper (II) complex of 5-nitrotetrazolate [1, 3]. Specific rate data for this reaction were not provided.

24.2.7 Key Degradation Products

The key degradation product from DBX-1 use appears to be copper.

24.2.8 Transport

Little data on the environmental transport of DBX-1 are available, primarily due to it being a more recently developed explosive material that has yet to be integrated into munitions and used in significant quantities. DBX-1 is being vetted as a replacement for lead azide; for an estimate of how much DBX-1 could be used by the military, current lead azide use is approximately 1 ton/year [3].

The use of DBX-1 eliminates all use of lead and any associated lead contamination; however, the metal replacement for lead (i.e., copper) may be an aquatic environmental issue if enough of the material is discharged to the environment [8]. The use of DBX-1 in non-hermetic systems may have the potential to directly release copper to aquatic systems, particularly if this explosive is used in Naval ordnance [8].

24.3 TRANSPORT PROCESS

No data were found on the transport of DBX-1 in soil and water systems and it is difficult to make predictions on the anticipated transport behavior due to the lack of chemical and physical property data (i.e., Table 24-1) that are relevant to transport. For now, data on the environmental transport of copper can be used as a starting point until data more specific to DBX-1 become available.

24.3.1 Transport in Soil

Copper is naturally present in the earth's crust, with levels typically in the range of 5 to 70 mg/kg; most of it is bound to organic matter [9]. Copper deposited into soil systems will tend to not be very mobile in soils with significant levels of organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides [9]. Adsorption to these soils is expected to keep copper concentrated within the upper 5 to 10 centimeters of soil with little to no propensity for mobility [9]. Copper deposited into sandy soils with low pH can show some leaching capabilities. Laboratory experiments have demonstrated copper bound to sand becoming remobilized after the pH was reduced from a pH of 9 to 4 [9].

24.3.2 Transport in Water

Copper directly deposited into water systems is expected to settle out as particular matter and adsorb to organic matter, hydrous iron, manganese oxides, and clay [9]. This adsorption rate is anticipated to be rather fast, with a significant fraction of copper adsorbed within the first hour in a water column, and equilibrium obtained within 24 hours [9].

24.4 TOXICITY DATA OF DBX-1

No data were found on toxicity of DBX-1.

24.5 EXAMPLE REGULATORY GUIDELINES FOR DBX-1

No data were found on regulatory limits for DBX-1.

24.6 DATA GAPS

DBX-1 is a new compound and a variety of knowledge gaps pertaining to its basic chemical and physical characteristics exist. Moreover, data on DBX-1 toxicity, transport and environmental fate are incomplete and require further research efforts. Main data gaps identified for DBX-1 are listed below.

A. Fate and Transport

- **Fate and Transport (General):** Data from laboratory and field studies on fate and transport of DBX-1 are needed, particularly if energetic material replacement efforts accelerate or become more realistic. Such information will be needed prior to DBX-1 use on training ranges.
- **Transport and Fate in Water:** A better understanding of the risks of copper discharge to aquatic environments is needed, particularly since DBX-1 could be used in Naval ordnance.

- **Fate (General):** Data on the fate of DBX-1, which degradation processes are significant and their rates, are needed. Little to no data are available for the typical fate processes (e.g., photolysis, hydrolysis).

B. Toxicity. Basic toxicity data including human and ecotoxicity, reference dose and exposure risk information are missing for DBX-1.

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APPENDIX B

Constituent Name		Perchlorate	Ammonium Perchlorate	Potassium Perchlorate	Potassium Chlorate	Potassium Chlorite	Potassium Chloride
Chemical Name		Perchlorate	Ammonium Perchlorate	Potassium Perchlorate	Potassium Chlorate	Potassium Chlorite	Potassium Chloride
CAS #	None	14797-33-0	7790-98-9	7778-74-7	38110-04-9	14314-27-3	7447-40-7
Constituent Class	None	Propellant	Propellant	Propellant	Propellant	Propellant	Propellant
Chemical Formula	None	ClO_4	NH_4ClO_4	$KClO_4$	$KClO_3$	$KClO_2$	KCl
Parent or Byproduct	None	Parent	Parent	Parent	Parent or Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	99.4503	117.49	138.55	83.447	106.55	74.5513
Solubility in Water	mg/L	2.45E+05	2.00E+03	1.68E+04	7.00E+04	ND	2.54E+04
Vapor Pressure	atm	25	low	low	low	low	low
Odor		None	None	None	None	None	None
Physical State	None	ND	Orthorhombic Crystal	Orthorhombic Crystal or Crystalline Powder	Solid, monoclinic Crystal	ND	White Crystalline Solid
Specific Gravity	None	ND	1.95	2.53	2.3	ND	1.99
Melting Temperature	°C	ND	>200	400 - 525	368	ND	770
log Kow	None	ND	-5.84	-7.18	ND	ND	-0.46
Reference Dose (RfD)	mg/kg/day	7.00E-04			0.03	ND	ND
MCL:							
MCL (California)	µg/L	1	1	1	800	ND	ND
MCL (Massachusetts)	µg/L	2	2	2	ND	ND	ND
Animal Toxicity:							
LD50	mg/kg/day	3621 (human)	3621 (human)	3621 (human)	1870 (rat)	ND	1500 (mouse)
Ecotoxicity:		ND	ND	ND	Nontoxic for freshwater and marine species	ND	Chronic toxicity to aquatic invertebrates
Acute Toxicity:		ND	ND	ND	> 100 mg/L	ND	Acute toxicity to plants, aquatic invertebrates, and fish
DOT Classification:	None	ND	Class 5.1 Oxidizing Material	Class 5.1 Oxidizing Material	Class 5.1 Oxidizing Material	ND	Not a DOT Controlled Material

ND - not detected

Constituent Name		TNT	2-ADNT	4-ADNT	2,4-DANT	2,6-DANT
Chemical Name		2,4,6-Trinitrotoluene	2-amino-2,6-dinitrotoluene	4-amino-2,6-dinitrotoluene	2,4-diamino-6-nitroluene	2,6-diamino-6-nitroluene
CAS #	None	118-96-7	35572-78-2	19406-51-0	6629-29-4	59229-75-3
Constituent Class	None	Explosive	ND	ND	ND	ND
Chemical Formula	None	$C_7H_5N_3O_6$	$C_7H_7N_3$	$C_7H_7N_3$	$C_7H_9N_3O_2$	$C_7H_9N_3O_2$
Parent or Byproduct	None	Parent	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	227.13	197.148	197.148	167.165	167.165
Solubility in Water	mg/L	130 mg/L	0.498	0.498	ND	ND
Vapor Pressure	atm	7.20E-09	ND	ND	ND	ND
Odor		Strong almond scent	ND	ND	ND	ND
Physical State	None	Flakes, needles, column shaped crystals; several crystalline structures including orthorhombic and monoclinic	ND	ND	Liquid at room temperatures	ND
Specific Gravity	None	1.654 (solid); 1.47 (molten)	ND	ND	ND	1.369
Melting Temperature	°C	80 - 82	168 - 169	171	-45.7	
log Kow	None	1.86	2.8	2.62	ND	ND
Reference Dose (RfD)	mg/kg/day	5.00E-04	6.00E-05	ND	ND	ND
MCL:						
MCL (California)	µg/L	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND
Animal Toxicity:						
LD50	mg/kg/day	660 - 1320 (rat)	1394 (female rat); 2240 (male rat)	939 (female rat); 1360 (male rat)	ND	ND
Ecotoxicity:		Lethal toxicity values available for freshwater species, for example, mussels, algae, and fish	Amphibian toxicity data available	Amphibian toxicity data available	ND	ND
Acute Toxicity:		ND	ND	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	Not DOT dangerous good	Not DOT dangerous good	Class 3 Flammable Liquid	Class 3 Flammable Liquid

ND - not detected

Constituent Name		HMX
Chemical Name		octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
CAS #	None	2691-41-0
Constituent Class	None	Explosive
Chemical Formula	None	$C_4H_8N_8O_8$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	296.155
Solubility in Water	mg/L	4.5
Vapor Pressure	atm	< 1.0e-16
Odor		None
Physical State	None	White crystalline solid
Specific Gravity	None	1.91
Melting Temperature	^{o}C	279.5 - 280
log Kow	None	0.545
Reference Dose (RfD)	mg/kg/day	400 µg/L health advisory level for drinking water
MCL:	µg/L	
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		ND
Acute Toxicity:		ND
DOT Classification:	None	Class 1.1D Explosive

ND - not detected

Constituent Name		RDX	MNX	DNX	TNX	MEDINA	NDAB
Chemical Name		1,3,5-trinitroperhydro-1,3,5-triazine	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine	hexahydro-1,3-dinitroso-5-nitro-1,3,5- triazine	hexahydro-1,3,5-trinitroso-1,3,5-triazine	methylenedinitramine	4-nitro-2,4,-diazabutanal
CAS #	None	121-82-4	91-78-1	80251-29-2	13980-04-6	14168-44-6	
Constituent Class	None	Explosive	Explosive	Explosive	Explosive	Explosive	Explosive
Chemical Formula	None	$C_3H_6N_6O_6$	$C_3H_5O_7N_5$	$C_3H_6N_6O_5$	$C_3H_6N_6O_7$	$CH_4N_4O_4$	$C_2H_5N_3$
Parent or Byproduct	None	Parent	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	222.12	206.118	190.119	174.118	136.067	119.079
Solubility in Water	mg/L	47	ND	ND	ND	ND	ND
Vapor Pressure	atm	< 5e-12	ND	ND	ND	ND	ND
Odor		None	ND	ND	ND	ND	ND
Physical State	None	White crystalline solid	ND	ND	ND	ND	ND
Specific Gravity	None	1.81	ND	ND	ND	ND	ND
Melting Temperature	°C	203.3 - 205	190-192	ND	ND	ND	ND
log Kow	None	7.41	ND	ND	ND	ND	ND
Reference Dose (RfD)	mg/kg/day	3.00E-03	ND	ND	ND	ND	ND
MCL:							
MCL (California)	µg/L	ND	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND	ND
Animal Toxicity:							
LD50	mg/kg/day	20 (rat)	575 (deer mice)	ND	338 (deer mice)	ND	ND
Ecotoxicity:		Toxicity data is available for marine freshwater species	ND	ND	ND	ND	ND
Acute Toxicity:		ND	ND	ND	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	ND	ND	ND	ND	ND

ND - not detected

Constituent Name		2,4-DNT	2,6-DNT	2A4NT	4A2NT	aniline	DAT	2A4NBA	2,4-DNBOH	2,4-DNBCHO
Chemical Name		1-methyl-2,4-dinitrobenzene	1-methyl-2,6-dinitrotolene	2-amino-4-nitrotoluene	4-amino-2-nitrotoluene	aniline	2,4-diaminotoluene	2-amino-4-nitrobenzoic acid	2,4-dinitrobenzyl alcohol	2,4-dinitrobenzaldehyde
CAS #	None	121-14-2	606-20-2	99-55-8	199-32-4	62-53-3	95-80-7	619-17-0	4836-66-2	528-75-6
Constituent Class	None	explosive	explosive	explosive	organic compound	organic compound	organic compound	organic compound	organic compound	organic compound
Chemical Formula	None	$C_7H_6N_2O_4$	$C_7H_6N_2O_4$	$C_7H_6N_2O_2$	$C_7H_6N_2O_2$	$C_6H_5NH_2$	$C_7H_{10}N_2$	$C_7H_6N_2O_4$	$C_7H_6N_2O_5$	$C_7H_4N_2O_5$
Parent or Byproduct	None	Parent and Byproduct	Parent and Byproduct	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	182.134	182.134	152.1506	152.153	93.129	122.17	182.135	198.134	196.118
Solubility in Water	mg/L	270	180	<1.0	insoluble	10 to 50	1 to 5	<0.1	4.057x10-2	1.72x10-2
Vapor Pressure	atm	6.70E-06	6.57E-03	3.5x10-5	7.8x10-4	6.67x10-1	1	ND	1.89x10-5	9.20x10-5
Odor		ND	ND	ND	ND	amine-like	ND	ND	ND	ND
Physical State	None	Solid	Solid	Solid	Solid	Liquid	Solid	Solid	Solid	Solid
Specific Gravity	None	1.32	1.28	1	ND	1.022	1.05	ND	ND	ND
Melting Temperature	°C	71	66	80-90	172-174	-6	97-99	97-99	114-118	68.3
log Kow	None	1.98	1.98	1.26	ND	0.9	0.14	ND	7.75	1.44
Reference Dose (RfD)	mg/kg/day	2.00E-03	3.00E-04	ND	ND	ND	ND	ND	ND	ND
MCL:	µg/L									
MCL (California)	µg/L	ND	ND	ND	ND	1.6x10-6 inhalation unit risk estimate	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND
Animal Toxicity:										
LD50	mg/kg/day	268 - 650	177 - 795	143- 246	ND	1290 guinea pig	ND	ND	ND	ND
Ecotoxicity:		Lethal and sub-lethal toxicity to marine invertebrates	ND	ND	ND	Lethal and sub-lethal toxicity to marine invertebrates	ND	ND	ND	ND
Acute Toxicity:		No toxicity data for marine freshwater invertebrates	ND	ND	ND	Very toxic to humans	ND	ND	ND	ND
DOT Classification:	None	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous

ND - not detected

Constituent Name		2-NT	3-NT	4-NT
Chemical Name		2-nitrotoluene	3-nitrotoluene	4-nitrotoluene
CAS #	None	88-72-2	99-08-1	99-99-0
Constituent Class	None	explosive	explosive	explosive
Chemical Formula	None	$C_7H_7NO_2$	$C_7H_7NO_2$	$C_7H_7NO_2$
Parent or Byproduct	None	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	137.138	137.138	137.138
Solubility in Water	mg/L	609	450	288
Vapor Pressure	atm	2.40E-04	1.40E-04	1.40E-04
Odor		ND	ND	ND
Physical State	None	Liquid	Liquid (typ.)	Solid
Specific Gravity	None	1.16	1.16	1.16
Melting Temperature	^oC	-10.4	15.5	51.6
log Kow	None	2.3	2.42	2.4
Reference Dose (RfD)	mg/kg/day	ND	ND	ND
MCL:				
MCL (California)	µg/L	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND
Animal Toxicity:				
LD50	mg/kg/day	891 (rat)	1072 - 2400 (rat)	975 (rat)
Ecotoxicity:		ND	ND	ND
Acute Toxicity:		ND	ND	ND
DOT Classification:	None	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous

ND - not detected

Constituent Name		Nitrobenzene	Nitrophenols	Nitrohydroquinone	Nitrocatechol	Catechol	Nitrosobenzene
Chemical Name		Nitrobenzene	Nitrophenols	Nitrohydroquinone	Nitrocatechol	Catechol	Nitrosobenzene
CAS #	**None**	98-95-3		16090-33-8	3316-09-4	120-80-9	586-96-9
Constituent Class	**None**	Explosive	Explosive	Explosive	Explosive	Explosive	Explosive
Chemical Formula	**None**	$C_6H_5NO_2$	$HOC_6H_4NO_2$	$C_6H_5NO_4$	$C_6H_5NO_4$	$C_6H_4(OH)_2$	C_6H_5NO
Parent or Byproduct	**None**	Parent and byproduct	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	**g/mole**	123.06	NR	155.108	155.09	110.1	107.11
Solubility in Water	**mg/L**	2.10E+03	NR	2.00x10-2	9.45x10-2	4.19	2.52x10-2
Vapor Pressure	**atm**	3.70E-04	NR	3.26x10-4	6.04x10-6	1.89x10-5	1.34
Odor		ND	NR	phenolic	phenolic	phenolic	
Physical State	**None**	Liquid	NR	Solid	Solid	Solid	Solid
Specific Gravity	**None**	1.2	NR	NR	NR	NR	NR
Melting Temperature	**°C**	-5.6	NR	120	175	105	68.5
log Kow	**None**	1.85	NR	1.43	1.53	1.01	2.01
Reference Dose (RfD)	**mg/kg/day**	5.00E-04	NR	ND	ND	ND	ND
MCL:							
MCL (California)	**µg/L**	ND	NR	ND	ND	ND	ND
MCL (Massachusetts)	**µg/L**	ND	NR	ND	ND	ND	ND
Animal Toxicity:							
LD50	**mg/kg/day**	780 (rat)	NR	ND	ND	300	ND
Ecotoxicity:		ND	NR	ND	ND	ND	ND
Acute Toxicity:		ND	NR	ND	ND	ND	ND
DOT Classification:	**None**	Class 6.1 Poisonous	Class 6.1 Poisonous	Class 6.1 Poisonous	ND	ND	ND

ND - not detected

Constituent Name		Nitroglycerin	1,2-Dinitroglycerol	1,3-Dinitroglycerol	2-Mononitroglycerol	1-Mononitroglycerol
Chemical Name		Nitroglycerin	1,2-Dinitroglycerol	1,3-Dinitroglycerol	2-Mononitroglycerol	1-Mononitroglycerol
CAS #	None	55-63-0	621-65-8	623-87-0	620-12-2	624-43-1
Constituent Class	None	Explosive	Explosive	Explosive	Explosive	Explosive
Chemical Formula	None	$C_3H_4N_3O_9$	$C_3H_6N_2O_7$	$C_3H_6N_2O_7$	$C_3H_7NO_5$	$C_3H_7NO_5$
Parent or Byproduct	None	Parent	Byprodct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	227.0865	182.088	182.088	137.091	137.091
Solubility in Water	mg/L	173	3.14x10-1	ND	2.74	ND
Vapor Pressure	atm	2.33E-06	1.02x10-2	ND	3.43x10-1	ND
Odor		ND	ND	ND	ND	ND
Physical State	None	Liquid	Liquid	Liquid	Liquid	Liquid
Specific Gravity	None	1.596	ND	ND	ND	ND
Melting Temperature	°C	13.5	53.9	ND	54	ND
log Kow	None	1.62	0.83	ND	-0.356	ND
Reference Dose (RfD)	mg/kg/day	ND	ND	ND	ND	ND
MCL:						
MCL (California)	µg/L	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND
Animal Toxicity:						
LD50	mg/kg/day	822 (rat)	ND	ND	ND	ND
Ecotoxicity:		Data is available for aquatic organisms	ND	ND	ND	ND
Acute Toxicity:		Not toxic to aquatic invertebrates and freshwater fish	ND	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	Class 3 Flammable	Class 3 Flammable	Class 3 Flammable	Class 3 Flammable

ND - not detected

Constituent Name		Nitroguanidine	Nitrosoguanidine	Cyanamide	Guanidine	Cyanoguanidine	Melamine	Nitrosamide
Chemical Name		Nitroguanidine	Nitrosoguanidine	Cynamide	Guanidine	Cyanoguanidine	Melamine	Nitrosamide
CAS #	None	556-88-7	674-81-7	420-04-2	113-00-8	461-58-5	108-78-1	35576-91-1
Constituent Class	None	Explosive	Explosive	Explosive	Explosive	Explosive		
Chemical Formula	None	$CH_4N_4O_2$	CH_4N_4O	CN_2H_2	$HNC(NH_2)_2$	$C_2H_4N_4$	$C_3H_6N_6$	H_2N_2O
Parent or Byproduct	None	Parent	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	104.07	88.07	42.04	59.07	84.08	126.12	46.029
Solubility in Water	mg/L	5.00E+03	2.55	11.9	3.11x10-2	4.91x10-1	2.56x10-2	ND
Vapor Pressure	atm	3.95E-05	3.43x10-2	3.75x10-3	2.89	1.82	3.59x10-10	ND
Odor		odorless	odorless	odorless	odorless	odorless	odorless	odorless
Physical State	None	Solid crystals	Solid crystals	Solid crystals	Solid crystals	Solid crystals	Solid crystals	Solid crystals
Specific Gravity	None	1.5	ND	1.28	ND	1.404	ND	ND
Melting Temperature	°c	225 - 250	129	44	50	209	348	198
log Kow	None	-0.89	-0.983	-0.82	-1.45	-1.15	-1.37	-1.32
Reference Dose (RfD)	mg/kg/day	Not toxic to aquatic invertebrates and freshwater fish	ND	ND	ND	ND	ND	ND
MCL:								
MCL (California)	µg/L	ND	ND	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND	ND	ND
Animal Toxicity:								
LD50	mg/kg/day	10,200	90	125	150	>30,000	ND	ND
Ecotoxicity:		ND	ND	ND	ND	ND	ND	ND
Acute Toxicity:		Acute toxicity low; toxicity increases upon photolysis	Toxic if ingested and inhaled	Hazardous in skin contact	Hazardous in skin contact	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	Class 4.1 Flammable solid, Class 6.1 toxic material	Class 6.1 toxic material	Class 5.1 oxidizing material	Class 1.1D Explosive	Class 1.1D Explosive	Class 1.1D Explosive

ND - not detected

Constituent Name		NTO
Chemical Name		3-nitro-1,2,4-triazole-5-one
CAS #	None	24807-55-4
Constituent Class	None	Explosive
Chemical Formula	None	$C_2N_4O_3$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	130.063
Solubility in Water	mg/L	1.280E+03 - 2.000E+03
Vapor Pressure	atm	low
Odor		ND
Physical State	None	Crystalline powder
Specific Gravity	None	1.93
Melting Temperature	^{o}C	268 - 271
log Kow	None	0.85
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	> 5000 mg/kg
Ecotoxicity:		NTO ecotoxicity data exists for invertebrates and freshwater fish
Acute Toxicity:		Under development
DOT Classification:	None	Class 1.1D Explosive

ND - not detected

Constituent Name		DNAN	2-ANDN	4-ANDN	DAAN	2,4-DNP
Chemical Name		2,4-dinitroanisole	2-amino-4-nitroanisole	4-amino-2-nitroanisole	diaminoanisole	2,4-dinitrophenol
CAS #	None	119-27-7	99-59-2	577-72-0	615-05-4	51-28-5
Constituent Class	None	Explosive	Explosive	Explosive	Explosive	Explosive
Chemical Formula	None	$C_7H_6N_2O_5$	$C_7H_8N_2O_3$	$C_7H_8N_2O_3$	$C_7H_{10}N_2O$	$HOC_6H_3(NO_2)_2$
Parent or Byproduct	None	Parent	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	198.134	184.17	168.152	138.17	184.107
Solubility in Water	mg/L	1.28E+03 - 2.00E+03	ND	ND	ND	ND
Vapor Pressure	atm	ND	ND	ND	ND	3.9x10-4
Odor		ND	ND	ND	ND	ND
Physical State	None	Crystalline powder	Crystalline powder	Crystalline powder	Crystalline powder	Crystalline powder
Specific Gravity	None	1.93	ND	ND	ND	ND
Melting Temperature	°C	268 - 271	117-120	44.5	67.5	110
log Kow	None	0.858	ND	ND	ND	1.67
Reference Dose (RfD)	mg/kg/day	ND	ND	ND	ND	ND
MCL:						
MCL (California)	µg/L	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND
Animal Toxicity:						
LD50	mg/kg/day	199 (rat)	ND	ND	ND	ND
Ecotoxicity:		Data available for invertebrates and freshwater fish	ND	ND	ND	ND
Acute Toxicity:		ND	ND	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	Class 1.1D Explosive	Class 1.1D Explosive	Class 1.1D Explosive	Class 1.1D Explosive

ND - not detected

Constituent Name		Tetrazene
Chemical Name		Tetrazene
CAS #	None	31330-63-9
Constituent Class	None	Explosive
Chemical Formula	None	$C_2H_6N_{10}$-H_2O
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	188.15
Solubility in Water	mg/L	insoluble
Vapor Pressure	atm	low
Odor		ND
Physical State	None	Crystals
Specific Gravity	None	1.7
Melting Temperature	°C	140 - 160 (decomposes)
log Kow	None	ND
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		ND
Acute Toxicity:		ND
DOT Classification:	None	Explosive 1.1A

ND - not detected

Constituent Name		Tetryl	Picric Acid	N-methylpicramide
Chemical Name		Tetryl	Picric Acid	N-methylpicramide
CAS #	None	479-45-8	88-89-1	1022-07-7
Constituent Class	None	Explosive	Explosive	Explosive
Chemical Formula	None	$C_7H_5N_5O_8$	$C_6H_3N_3O_7$	$C_7H_6N_4O_6$
Parent or Byproduct	None	Parent	Byproduct	Byproduct
Molecular Weight	g/mole	287.15	229.1	242.147
Solubility in Water	mg/L	75	13.1	1.66x10-3
Vapor Pressure	atm	5.30E-13	9.87E-10	3.88x10-6
Odor		ND	ND	ND
Physical State	None	Solid Crystals	Crystals	Crystals
Specific Gravity	None	1.57	1.77	ND
Melting Temperature	°C	130 - 132	121.8	147
log Kow	None	2.4	1.33	2.1
Reference Dose (RfD)	mg/kg/day	ND	ND	ND
MCL:				
MCL (California)	µg/L	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND
Animal Toxicity:				
LD50	mg/kg/day	> 2,000 (rabbit)	ND	ND
Ecotoxicity:		ND	ND	ND
Acute Toxicity:		ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	Class 1.1D Explosive	Class 1.1D Explosive

ND - not detected

Constituent Name		Lead Azide
Chemical Name		Lead Azide
CAS #	None	13424-46-9
Constituent Class	None	Explosive
Chemical Formula	None	$Pb(N_3)_2$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	291.24
Solubility in Water	mg/L	2.3
Vapor Pressure	atm	Extremely low
Odor		ND
Physical State	None	Needle-like crystals
Specific Gravity	None	4.8
Melting Temperature	^{o}C	245 - 250
log Kow	None	ND
Reference Dose (RfD)	mg/kg/day	action level for drinking water limit 0.015 mg/L
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		ND
Acute Toxicity:		ND
DOT Classification:	None	Explosive 1.1A

ND - not detected

Constituent Name		Lead Styphnate
Chemical Name		Lead Styphnate
CAS #	None	15245-44-0
Constituent Class	None	Explosive
Chemical Formula	None	$C_6HN_3O_8Pb$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	450.288
Solubility in Water	mg/L	8
Vapor Pressure	atm	low
Odor		ND
Physical State	None	Solid crystals
Specific Gravity	None	3
Melting Temperature	^{o}C	190
log Kow	None	0.006
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		Marine pollutant; reported cases of development toxicity
Acute Toxicity:		ND
DOT Classification:	None	Explosive 1.1A

ND - not detected

Constituent Name		Ammonium Picrate
Chemical Name		Ammonium Picrate
CAS #	None	131-74-8
Constituent Class	None	Explosive
Chemical Formula	None	$C_6H_6N_4O_7$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	246.13
Solubility in Water	mg/L	1.00E+04
Vapor Pressure	atm	4.43E-12
Odor		ND
Physical State	None	Crystals
Specific Gravity	None	1.72
Melting Temperature	^{o}C	280
log Kow	None	0.02
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		ND
Acute Toxicity:		ND
DOT Classification:	None	Class 1.1D Explosive

ND - not detected

Constituent Name		Picric Acid	Picramic Acid	2,4-Dinitrophenol
Chemical Name		Picric Acid	Picramic Acid	2,4-Dinitrophenol
CAS #	**None**	88-89-1	96-97-3	51-28-5
Constituent Class	**None**	Explosive	Explosive	Explosive
Chemical Formula	**None**	$C_6H_3N_3O_7$	$C_6H_5N_3O_5$	$C_6H_4N_2O_5$
Parent or Byproduct	**None**	Parent	Byproduct	Byproduct
Molecular Weight	**g/mole**	229.1	199.12	184.16
Solubility in Water	**mg/L**	13.1	ND	ND
Vapor Pressure	**atm**	9.87E-10	ND	3.9x10-4
Odor		ND	ND	ND
Physical State	**None**	Crystals	Crystals	Crystals
Specific Gravity	**None**	1.77	ND	ND
Melting Temperature	**°C**	121.8	169	110
log Kow	**None**	1.33	ND	1.67
Reference Dose (RfD)	**mg/kg/day**	ND	ND	ND
MCL:				
MCL (California)	**µg/L**	ND	ND	ND
MCL (Massachusetts)	**µg/L**	ND	ND	ND
Animal Toxicity:				
LD50	**mg/kg/day**	ND	ND	ND
Ecotoxicity:		ND	ND	ND
Acute Toxicity:		ND	ND	ND
DOT Classification:	**None**	Class 1.1D Explosive	Class 4.1 Flammable solid	Class 4.1 Flammable solid

ND - not detected

Constituent Name		PETN	PeTriN	PEDN	PEMN	PE
Chemical Name		Pentaerythritol Tetranitrate	Pentaerythritol Trinitrate	Pentaerythritol dinitrate	Pentaerythritol mononitrate	Pentaerythritol
CAS #	None	78-11-5	1607-17-6	1607-01-8	1607-00-7	115-77-5
Constituent Class	None	Explosive	ND	ND	ND	ND
Chemical Formula	None	$C_5H_8N_4O_{12}$	$C_5H_9N_3O_{10}$	$C_5H_{10}N_2O_8$	$C_5H_{11}NO_6$	$C_5H_{12}O_4$
Parent or Byproduct	None	Parent	Byproduct	Byproduct	Byproduct	Byproduct
Molecular Weight	g/mole	316.135	271.138	ND	181.144	ND
Solubility in Water	mg/L	1.5	2.6x10-2	ND	ND	ND
Vapor Pressure	atm	7.10E-12	ND	ND	ND	ND
Odor		ND	ND	ND	ND	ND
Physical State	None	Crystalline solid	Crystalline solid	Crystalline solid	Crystalline solid	Crystalline solid
Specific Gravity	None	1.76	ND	ND	ND	ND
Melting Temperature	°C	143.3	ND	ND	ND	ND
log Kow	None	1.33	ND	ND	ND	ND
Reference Dose (RfD)	mg/kg/day	ND	ND	ND	ND	ND
MCL:						
MCL (California)	µg/L	ND	ND	ND	ND	ND
MCL (Massachusetts)	µg/L	ND	ND	ND	ND	ND
Animal Toxicity:						
LD50	mg/kg/day	ND	ND	ND	ND	ND
Ecotoxicity:		Potential toxicity	ND	ND	ND	ND
Acute Toxicity:		ND	ND	ND	ND	ND
DOT Classification:	None	Class 1.1D Explosive	ND	ND	ND	ND

ND - not detected

Constituent Name		MNA	MPD
Chemical Name		n-methyl-paranitroaniline	n-methly-p-phenylenediamine
CAS #	**None**	100-15-2	4760-34-3
Constituent Class	**None**	Stabilizer	Stabilizer
Chemical Formula	**None**	$C_7H_8N_2O_2$	$CH_3NHC_8H_4NH_2$
Parent or Byproduct	**None**	Parent	Byproduct
Molecular Weight	**g/mole**	152.153	122.171
Solubility in Water	**mg/L**	85	2.15x10-1
Vapor Pressure	**atm**	1.10E-06	8.55x10-3
Odor		ND	ND
Physical State	**None**	Powder	Powder
Specific Gravity	**None**	1.16	1.19
Melting Temperature	**°C**	60.96	48.9
log Kow	**None**	2.1	7.64x10-1
Reference Dose (RfD)	**mg/kg/day**	ND	ND
MCL:			
MCL (California)	**µg/L**	ND	ND
MCL (Massachusetts)	**µg/L**	ND	ND
Animal Toxicity:			
LD50	**mg/kg/day**	ND	ND
Ecotoxicity:		ND	ND
Acute Toxicity:		ND	ND
DOT Classification:	**None**	Class 6.1 Poisonous	Class 6.1 Poisonous

ND - not detected

Constituent Name		Nitrocellulose
Chemical Name		Nitrocellulose
CAS #	None	9004-70-0
Constituent Class	None	Propellant
Chemical Formula	None	C18H21N11O38
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	999.405
Solubility in Water	mg/L	insoluble
Vapor Pressure	atm	1.32E-08
Odor		ND
Physical State	None	Fibrous
Specific Gravity	None	1.3
Melting Temperature	°C	160 - 170
log Kow	None	ND
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	> 5,000 mg/kg
Ecotoxicity:		No significant ecotoxicity
Acute Toxicity:		
DOT Classification:	None	Class 4.1 Flammable Solid

ND - not detected

Constituent Name		TATB	THTNB
Chemical Name		2,4,6-triamino-1,3,5-trinitrobenzene	1,3,5-trihydroxy-2,4,6-trinitrobenzene
CAS #	None	67539-61-1	4328-17-0
Constituent Class	None	Explosive	Explosive
Chemical Formula	None	C6H6N6O6	$C_6H_3N_3O_9$
Parent or Byproduct	None	Parent	Byproduct
Molecular Weight	g/mole	258.15	262.102
Solubility in Water	mg/L	32	1.58x10-2
Vapor Pressure	atm	1.76E-14	3.00x10-4
Odor		ND	ND
Physical State	None	Crystals	Cyrstals
Specific Gravity	None	1.93	ND
Melting Temperature	°C	350	177
log Kow	None	0.7	2.2
Reference Dose (RfD)	mg/kg/day	ND	ND
MCL:			
MCL (California)	µg/L	ND	ND
MCL (Massachusetts)	µg/L	ND	ND
Animal Toxicity:			
LD50	mg/kg/day	ND	ND
Ecotoxicity:		ND	ND
Acute Toxicity:		ND	ND
DOT Classification:	None	Class 1.1D Explosive	Class 1.1D Explosive

ND - not detected

Constituent Name		DBX-1
Chemical Name		copper(I)5-nitrotetrazolate
CAS #	None	957133-97-0
Constituent Class	None	explosive
Chemical Formula	None	$C_2Cu_2N_{10}O_4$
Parent or Byproduct	None	Parent
Molecular Weight	g/mole	355
Solubility in Water	mg/L	ND
Vapor Pressure	atm	extremely low
Odor		ND
Physical State	None	Monoclinic crystals
Specific Gravity	None	2.59
Melting Temperature	^{o}C	ND; decomposes
log Kow	None	ND
Reference Dose (RfD)	mg/kg/day	ND
MCL:		
MCL (California)	µg/L	ND
MCL (Massachusetts)	µg/L	ND
Animal Toxicity:		
LD50	mg/kg/day	ND
Ecotoxicity:		ND
Acute Toxicity:		ND
DOT Classification:	None	ND

ND - not detected

APPENDIX C

Contaminant		Toxicity and Chemical-specific Information								Human Health Risk Based Concentrations (EPA, RSLs, May 2016)										ATSDR MRL				ARARs		
Analyte	CAS No.	SFO (mg/kg-day)$^{-1}$	key	IUR (ug/m^3)$^{-1}$	key	RfD_o (mg/kg-day)	key	RfC_i (mg/m^3)	key	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Resident Air (ug/m^3)	key	Industrial Air (ug/m^3)	key	Tapwater (ug/L)	key	Inhalation - acute (mg/kg/day)	Inhalation - chronic (mg/kg/day)	Oral - acute	Oral - chronic	Federal MCL (ug/L)	State MCL	Primary Drinking Water MCLs ug/L1,2,3
~Perchlorate and Perchlorate Salts	14797-73-0					7.0E-04	I			5.5E+00	n	8.2E+01	n					1.4E+00	n							15Interim Health Advisory; OSWER
~Potassium Perchlorate	7778-74-7					7.0E-04	I			5.5E+00	n	8.2E+01	n					1.4E+00	n							
~Sodium Perchlorate	7601-89-0					7.0E-04	I			5.5E+00	n	8.2E+01	n					1.4E+00	n							
~Ammonium Perchlorate	7790-98-9					7.0E-04	I			5.5E+01	n	8.2E+02	n					1.4E+01	n							
potassium chlorate	3811-04-9																									
Trinitrotoluene, 2,4,6- (TNT)	118-96-7	3.0E-02	I			5.0E-04	I			2.1E+01	c**	9.6E+01	c**					2.5E+00	c**							
tetrazocine (HMX)	2691-41-0					5.0E-02	I			3.9E+03	n	5.7E+04	n					1.0E+03	n			0.1	0.05			
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	1.1E-01	I			3.0E-03	I			6.1E+00	c*	2.8E+01	c					7.0E-01	c*			0.2	0.1			
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2	3.1E-01	C	8.9E-05	C	2.0E-03	I			1.7E+00	c*	7.4E+00	c	3.2E-02	c	1.4E-01	c	2.4E-01	c			0.05	0.001			0.11 76
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2	1.5E+00	P			3.0E-04	X			3.6E-01	c*	1.5E+00	c					4.9E-02	c			0.09	0.004			
Nitrotoluene, o-	88-72-2	2.2E-01	P			9.0E-04	P			3.2E+00	c**	1.5E+01	c**					3.1E-01	c**							
Nitrotoluene, m-	99-08-1					1.0E-04	X			6.3E-01	n	8.2E+00	n					1.7E-01	n							
Nitrotoluene, p-	99-99-0	1.6E-02	P			4.0E-03	P			2.5E+01	n	1.4E+02	c**					4.3E+00	c**							
Nitrobenzene	98-95-3			4.0E-05	I	2.0E-03	I	9.0E-03	I	5.1E+00	c**	2.2E+01	c**	7.0E-02	c*	3.1E-01	c*	1.4E-01	c**							
Nitroglycerin (NG)	55-63-0	1.7E-02	P			1.0E-04	P			6.3E+00	n	8.2E+01	n					2.0E+00	n							
Nitroguanidine (NQ)	556-88-7					1.0E-01	I			6.3E+03	n	8.2E+04	n					2.0E+03	n							
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																									
2,4-dinitroanisole (DNAN)	119-27-7																									
tetrazene explosive	31330-63-9																									
Tetryl (Trinitrophenylmethylnitramine)	479-45-8					2.0E-03	P			1.6E+02	n	2.3E+03	n					3.9E+01	n							
~Lead Chromate	7758-97-6	5.0E-01	C	1.5E-01	C	2.0E-02	C	2.0E-04	C	3.0E-01	c	6.2E+00	c	6.8E-06	c	8.2E-05	c	4.1E-02	c							
~Lead Phosphate	7446-27-7	8.5E-03	C	1.2E-05	C					8.2E+01	c	3.8E+02	c	2.3E-01	c	1.0E+00	c	9.1E+00	c							
~Lead acetate	301-04-2	8.5E-03	C	1.2E-05	C					6.4E+01	c	2.7E+02	c	2.3E-01	c	1.0E+00	c	9.2E+00	c							
~Lead and Compounds	7439-92-1									4.0E+02	L	8.0E+02	L	1.5E-01	L			1.5E+01	L							
~Lead subacetate	1335-32-6	8.5E-03	C	1.2E-05	C					6.4E+01	c	2.7E+02	c	2.3E-01	c	1.0E+00	c	9.2E+00	c							
~Tetraethyl Lead	78-00-2					1.0E-07	I			7.8E-04	n	1.2E-02	n					1.3E-04	n							
lead azide	13424-46-9																									
lead styphnate	15245-44-0																									
ammonium picrate	31-74-8																									
Picric Acid (2,4,6-Trinitrophenol)	88-89-1					9.0E-04	X			5.7E+00	n	7.4E+01	n					1.8E+00	n							
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3					1.0E-04	X			6.3E-01	n	8.2E+00	n					2.0E-01	n							
Pentaerythritol tetranitrate (PETN)	78-11-5	4.0E-03	X			2.0E-03	P			1.3E+02	n	5.7E+02	c**					1.9E+01	c**							
N-Methyl-paranitroaniline (MNA)	100-15-2																									
Nitrocellulose	9004-70-0					3.0E+03	P			1.9E+08	nm	2.5E+09	nm					6.0E+07	n							
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																									
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																									

Key: I = IRIS; P = PPRTV; A = ATSDR; C = Cal EPA; X = APPENDIX PPRTV SCREEN (See FAQ #27); H = HEAST; F = See FAQ; J = New Jersey; O = EPA Office of Water; E = see user guide Section 2.3.5; L = see user guide on lead; M = mutagen; S = see user guide Section 5; V = volatile; R = RBA ap
SL; ** = where n SL < 10X c SL; SSL values are based on DAF=1; m = Concentration may exceed ceiling limit (See User Guide); s = Concentration may exceed Csat (See User Guide)

Contaminant						Biota Benchmarks															
Analyte	CAS No.	Proposed Primary Drinking Water MCLs ug/L3,13	Secondary Drinking Water SMCLs ug/L24, 25	Human Health WQC for Aquatic Organisms and Drinking Water ug/L	Human Health WQC for Aquatic Organisms Only ug/L	BCMOELP 1998 Fish Screening Benchmark mg/kg1	CCME 1999 Piscivorous Wildlife Screening Benchmark mg/kg2	CCME Piscivorous Wildlife Screening Benchmark mg/kg2	CEC 1988 Fish Screening Benchmark mg/kg3	ECW Avian Blood Screening Benchmark mg/kg4	ECW Avian Bone Screening Benchmark mg/kg5	ECW Avian Brain Screening Benchmark mg/kg6	ECW Avian Carcass Screening Benchmark mg/kg7	ECW Avian Diet Screening Benchmark mg/kg8	ECW Avian Egg Screening Benchmark mg/kg9	ECW Avian Kidney Screening Benchmark mg/kg10	ECW Avian Liver Screening Benchmark mg/kg11	ECW Fish Brain Screening Benchmark mg/kg12	ECW Fish Egg Screening Benchmark mg/kg13	ECW Fish Muscle Screening Benchmark mg/kg14	ECW Fish Whole Body Screening Benchmark mg/kg15
~Perchlorate and Perchlorate Salts	14797-73-0																				
~Potassium Perchlorate	7778-74-7																				
~Sodium Perchlorate	7601-89-0																				
~Ammonium Perchlorate	7790-98-9																				
potassium chlorate	3811-04-9																				
Trinitrotoluene, 2,4,6- (TNT)	118-96-7																				
tetrazocine (HMX)	2691-41-0																				
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4																				
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2	3.4 76																			
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2																				
Nitrotoluene, o-	88-72-2																				
Nitrotoluene, m-	99-08-1																				
Nitrotoluene, p-	99-99-0																				
Nitrobenzene	98-95-3																				
Nitroglycerin (NG)	55-63-0																				
Nitroguanidine (NQ)	556-88-7																				
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																				
2,4-dinitroanisole (DNAN)	119-27-7																				
tetrazene explosive	31330-63-9																				
Tetryl (Trinitrophenylmethylnitramine)	479-45-8																				
~Lead Chromate	7758-97-6																				
~Lead Phosphate	7446-27-7																				
~Lead acetate	301-04-2																				
~Lead and Compounds	7439-92-1																				
~Lead subacetate	1335-32-6																				
~Tetraethyl Lead	78-00-2																				
lead azide	13424-46-9																				
lead styphnate	15245-44-0																				
ammonium picrate	31-74-8																				
Picric Acid (2,4,6-Trinitrophenol)	88-89-1																				
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3																				
Pentaerythritol tetranitrate (PETN)	78-11-5																				
N-Methyl-paranitroaniline (MNA)	100-15-2																				
Nitrocellulose	9004-70-0																				
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																				
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																				

Key: I = IRIS; P = PPRTV; A = ATSDR; C = Cal EPA; pplied (See User Guide for Arsenic notice) ; c = cancer; n = noncancer; * = where: n SL < 100X SL; ** = where n SL < 10X c SL; SSL values are base

Contaminant																					
Analyte	CAS No.	ECW Mammal Blood Screening Benchmark mg/kg16	ECW Mammal Fat Screening Benchmark mg/kg17	ECW Mammal Kidney Screening Benchmark mg/kg18	ECW Mammal Liver Screening Benchmark mg/kg19	Environment Ontario 1984 Piscivorous Wildlife Screening Benchmark mg/kg20	New York State DEC Cancer Piscivorous Wildlife Screening Benchmark mg/kg21	New York State DEC Noncancer Piscivorous Wildlife Screening Benchmark mg/kg22	Swain and Holms 1985 Fish Screening Benchmark mg/kg23	ARCS NEC Sediment Screening Benchmark mg/kg24	ARCS PEC Sediment Screening Benchmark mg/kg25	ARCS TEC Sediment Screening Benchmark mg/kg26	Canadian ISQG Sediment Screening Benchmark mg/kg27	Canadian PEL Sediment Screening Benchmark mg/kg28	Consensus PEC Sediment Screening Benchmark mg/kg29	Consensus TEC Sediment Screening Benchmark mg/kg30	FDEP PEL Sediment Screening Benchmark mg/kg31	FDEP TEL Sediment Screening Benchmark mg/kg32	NOAA ERL Sediment Screening Benchmark mg/kg33	NOAA ERM Sediment Screening Benchmark mg/kg34
~Perchlorate and Perchlorate Salts	14797-73-0																				
~Potassium Perchlorate	7778-74-7																				
~Sodium Perchlorate	7601-89-0																				
~Ammonium Perchlorate	7790-98-9																				
potassium chlorate	3811-04-9																				
Trinitrotoluene, 2,4,6- (TNT)	118-96-7																				
tetrazocine (HMX)	2691-41-0																				
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4																				
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2																				
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2																				
Nitrotoluene, o-	88-72-2																				
Nitrotoluene, m-	99-08-1																				
Nitrotoluene, p-	99-99-0																				
Nitrobenzene	98-95-3																				
Nitroglycerin (NG)	55-63-0																				
Nitroguanidine (NQ)	556-88-7																				
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																				
2,4-dinitroanisole (DNAN)	119-27-7																				
tetrazene explosive	31330-63-9																				
Tetryl (Trinitrophenylmethylnitramine)	479-45-8																				
~Lead Chromate	7758-97-6																				
~Lead Phosphate	7446-27-7																				
~Lead acetate	301-04-2																				
~Lead and Compounds	7439-92-1																				
~Lead subacetate	1335-32-6																				
~Tetraethyl Lead	78-00-2																				
lead azide	13424-46-9																				
lead styphnate	15245-44-0																				
ammonium picrate	31-74-8																				
Picric Acid (2,4,6-Trinitrophenol)	88-89-1																				
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3																				
Pentaerythritol tetranitrate (PETN)	78-11-5																				
N-Methyl-paranitroaniline (MNA)	100-15-2																				
Nitrocellulose	9004-70-0																				
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																				
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																				

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Contaminant		Sediment Benchmarks																		
Analyte	CAS No.	Ontario Low Sediment Screening Benchmark mg/kg35	Ontario Severe Sediment Screening Benchmark mg/kg36	ORNL Lowest Chronic Value Daphnids Equilibrium Partitioning EqP Benchmark mg/kg37	ORNL Lowest Chronic Value Fish EqP Sediment Screening Benchmark mg/kg38	ORNL Lowest Chronic Value Nondaphnid InvertsEqP Sediment Screening Benchmark mg/kg39	ORNL Secondary Chronic Value EqP Sediment Screening Benchmark mg/kg40	OSWER Ecotox Thresholds Sediment Screening Benchmark mg/kg41	OSWER ET Benchmark Identifier mg/kg42	SD EPA R4 Sediment Screening Benchmark mg/kg43	EPA R4 benchmark Identifier mg/kg44	SD EPA R5 ESL Sediment Screening Benchmark mg/kg45	SD EPA R6 FW Sediment Screening Benchmark mg/kg46	SD EPA R6 Mar Sediment Screening Benchmark mg/kg47	Washington MAEL Sediment Screening Benchmark mg/kg48	Washington NEL Sediment Screening Benchmark mg/kg49	EPA R3 BTAG Freshwater Sediment Screening Benchmark mg/kg86	EPA R3 BTAG Marine Sediment Screening Benchmark mg/kg88	Dutch Intervention Soil Screening Benchmark mg/kg50	Dutch HC50 Soil Screening Benchmark mg/kg90
~Perchlorate and Perchlorate Salts	14797-73-0																			
~Potassium Perchlorate	7778-74-7																			
~Sodium Perchlorate	7601-89-0																			
~Ammonium Perchlorate	7790-98-9																			
potassium chlorate	3811-04-9																			
Trinitrotoluene, 2,4,6- (TNT)	118-96-7																0.092			
tetrazocine (HMX)	2691-41-0																			
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4																0.013			
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2											0.0144					0.0416			
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2											0.0398								
Nitrotoluene, o-	88-72-2																			
Nitrotoluene, m-	99-08-1																			
Nitrotoluene, p-	99-99-0																4.06			
Nitrobenzene	98-95-3											0.145								
Nitroglycerin (NG)	55-63-0																			
Nitroguanidine (NQ)	556-88-7																			
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																			
2,4-dinitroanisole (DNAN)	119-27-7																			
tetrazene explosive	31330-63-9																			
Tetryl (Trinitrophenylmethylnitramine)	479-45-8																			
~Lead Chromate	7758-97-6																			
~Lead Phosphate	7446-27-7																			
~Lead acetate	301-04-2																			
~Lead and Compounds	7439-92-1																			
~Lead subacetate	1335-32-6																			
~Tetraethyl Lead	78-00-2																			
lead azide	13424-46-9																			
lead styphnate	15245-44-0																			
ammonium picrate	31-74-8																			
Picric Acid (2,4,6-Trinitrophenol)	88-89-1																			
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3																			
Pentaerythritol tetranitrate (PETN)	78-11-5																			
N-Methyl-paranitroaniline (MNA)	100-15-2																			
Nitrocellulose	9004-70-0																			
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																			
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																			

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Contaminant		Soil Benchmarks												Surface Water Benchmarks						
Analyte	CAS No.	Dutch Target Soil Screening Benchmark mg/kg51	Eco-SSL Avian Soil Screening Benchmark mg/kg52	Eco-SSL Inverts Soil Screening Benchmark mg/kg53	Eco-SSL Mammalian Soil Screening Benchmark mg/kg54	Eco-SSL Plants Soil Screening Benchmark mg/kg55	EPA R6 Earthworms Surface Soil Screening Benchmark mg/kg56	EPA R6 Plants Surface Soil Screening Benchmark mg/kg57	ORNL Invertebrates Soil Screening Benchmark mg/kg58	ORNL Microbes Soil Screening Benchmark mg/kg59	ORNL Plants Screening Benchmark mg/kg60	SO EPA R4 Soil Screening Benchmark mg/kg61	SO EPA R5 ESL Soil Screening Benchmark mg/kg62	Australian and New Zealand Surface Water Screening Benchmark mg/L88	British Columbia Surface Water Screening Benchmark mg/L89	Canadian WQG Surface Water Screening Benchmark mg/L63	EC20 Daphnids Surface Water Screening Benchmark mg/L64	EC20 Fish Surface Water Screening Benchmark mg/L65	EC20 Sensitive Species Surface Water Screening Benchmark mg/L66	EC25 Bass Population Surface Water Screening Benchmark mg/L67
~Perchlorate and Perchlorate Salts	14797-73-0																			
~Potassium Perchlorate	7778-74-7																			
~Sodium Perchlorate	7601-89-0																			
~Ammonium Perchlorate	7790-98-9																			
potassium chlorate	3811-04-9																			
Trinitrotoluene, 2,4,6- (TNT)	118-96-7													0.14						
tetrazocine (HMX)	2691-41-0																			
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4																			
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2												1.28	0.065						
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2												0.0328							
Nitrotoluene, o-	88-72-2																			
Nitrotoluene, m-	99-08-1																			
Nitrotoluene, p-	99-99-0																			
Nitrobenzene	98-95-3						40		40	1000		40	1.31	0.55						
Nitroglycerin (NG)	55-63-0																			
Nitroguanidine (NQ)	556-88-7																			
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																			
2,4-dinitroanisole (DNAN)	119-27-7																			
tetrazene explosive	31330-63-9																			
Tetryl (Trinitrophenylmethylnitramine)	479-45-8																			
~Lead Chromate	7758-97-6																			
~Lead Phosphate	7446-27-7																			
~Lead acetate	301-04-2																			
~Lead and Compounds	7439-92-1																			
~Lead subacetate	1335-32-6																			
~Tetraethyl Lead	78-00-2																			
lead azide	13424-46-9																			
lead styphnate	15245-44-0																			
ammonium picrate	31-74-8																			
Picric Acid (2,4,6-Trinitrophenol)	88-89-1																			
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3																			
Pentaerythritol tetranitrate (PETN)	78-11-5																			
N-Methyl-paranitroaniline (MNA)	100-15-2																			
Nitrocellulose	9004-70-0																			
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																			
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																			

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Contaminant		Surface Water Benchmarks																		
Analyte	CAS No.	EPA R4 Acute Surface Water Screening Benchmark mg/L68	EPA R4 Chronic Surface Water Screening Benchmark mg/L69	LCV Aquatic Plants Surface Water Screening Benchmark mg/L70	LCV Daphnids Surface Water Screening Benchmark mg/L71	LCV Fish Surface Water Screening Benchmark mg/L72	LCV Non-Daphnid Inverts Surface Water Screening Benchmark mg/L73	NAWQC Acute Surface Water Screening Benchmark mg/L74	NAWQC Chronic Surface Water Screening Benchmark mg/L75	OSWER Ambient Water Quality Criteria mg/L76	OSWER Tier II Secondary Surface Water Screening Benchmark mg/L77	SW EPA R5 ESL Surface Water Screening Benchmark mg/L78	SW EPA R6 FW Surface Water Screening Benchmark mg/L79	SW EPA R6 Mar Surface Water Screening Benchmark mg/L80	Tier II SAV Surface Water Screening Benchmark mg/L81	Tier II SCV Surface Water Screening Benchmark mg/L82	EPA R4 Acute Salt Water Screening Benchmark mg/L83	EPA R4 Chronic Salt Water Screening Benchmark mg/L84	EPA R3 BTAG Freshwater Screening Benchmark mg/L85	EPA R3 BTAG Marine Screening Benchmark mg/L87
~Perchlorate and Perchlorate Salts	14797-73-0																			
~Potassium Perchlorate	7778-74-7																			
~Sodium Perchlorate	7601-89-0																			
~Ammonium Perchlorate	7790-98-9																			
potassium chlorate	3811-04-9																			
Trinitrotoluene, 2,4,6- (TNT)	118-96-7												0.1	0.1	0.57	0.13			0.1	0.1
tetrazocine (HMX)	2691-41-0												0.15		1.9	0.33			0.15	
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4												0.36		1.4	0.19			0.36	
Dinitrotoluene, 2,4- (2,4-DNT)	121-14-2	3.1	0.31					0.33				0.044	2.43						0.044	
Dinitrotoluene, 2,6- (2,6-DNT)	606-20-2											0.081							0.081	
Nitrotoluene, o-	88-72-2												0.88							
Nitrotoluene, m-	99-08-1												0.75						0.75	
Nitrotoluene, p-	99-99-0												1.9						1.9	
Nitrobenzene	98-95-3	2.7	0.27					27				0.22	0.27	0.0668			0.668	0.0668		0.0668
Nitroglycerin (NG)	55-63-0												0.138						0.138	
Nitroguanidine (NQ)	556-88-7																			
3-nitro-1,2,4-triazole-5-one (NTO)	24807-55-4																			
2,4-dinitroanisole (DNAN)	119-27-7																			
tetrazene explosive	31330-63-9																			
Tetryl (Trinitrophenylmethylnitramine)	479-45-8																			
~Lead Chromate	7758-97-6																			
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~Lead and Compounds	7439-92-1																			
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Picric Acid (2,4,6-Trinitrophenol)	88-89-1																			
Picramic Acid (2-Amino-4,6-dinitrophenol)	96-91-3																			
Pentaerythritol tetranitrate (PETN)	78-11-5												85						85	
N-Methyl-paranitroaniline (MNA)	100-15-2																			
Nitrocellulose	9004-70-0																			
2,4,6-triamino-1,3,5-trinitrobenzene (TATB)	67539-61-1																			
Copper(I) 5-Nitrotetrazolate (DBX-1)	957133-97-0																			

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