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Environmental Transport and Fate Process Descriptors for Propellant Compounds

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Final report

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Abstract: Sustainable management of Army training ranges requires quantification of the distribution, transport, and fate of munitions constituents (propellants and explosives) in soil, surface and groundwater. Propellant formulations are mixtures consisting of energetic compounds, binders, stabilizers, and burning-rate modifiers. Factors that affect the transport and fate of these diverse compounds include dissolution, sorption, biotransformation, volatilization, and photochemical transformation. This report summarizes the current understanding of these processes, and provides process descriptors for propellant compounds. Results of leaching experiments on representative single-base, double-base, and triple-base propellant mixtures also are presented.

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Preface

The U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS, prepared this report. The research was sponsored by the U.S. Army Environmental Quality and Technology (EQT) Program, Hazard/Risk Thrust Area, Headquarters, U.S. Army Corps of Engineers (HQUSACE). The EQT Program Manager was Dr. M. John Cullinane, EL, ERDC.

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1 Introduction

Rationale

The release of uncombusted residues and transformation products of propellants on military training ranges may result in contaminated soils, surface water, and ground water, with the potential for off-site migration of munitions constituents (MC). Three general classes of solid propellants are considered here: single-base, double-base, and triple-base mixtures. Solid propellants are complex composite materials that consist of energetic compound mixtures infused in a nitrocellulose matrix. Additional compounds in this mixture serve to bind and stabilize the propellant during storage (Kirchner et al. 1993). When exposed to air, water, and sunlight, energetic compounds will leach from propellant pellets and flakes as the nitrocellulose matrix loses its integrity. Many of these compounds are subject to regulatory water-quality criteria (RDX, TNT, 2,4-dinitrotoluene, for example).

Objectives

The objectives of this report are three-fold. First, to survey solid propellant compositions. Second, to summarize the pathways that control transport and fate of propellant compounds in the environment. Third, to document textural and compositional changes that occur when propellant pellets and flakes are immersed in stirred aqueous solutions for 0 to 220 hours.

2 Propellants

Propellant composition

Propellants are energetic materials that react at a controlled rate to produce pressure (Kirchner et al. 1993). Propellant mixtures consist of five components (Table 1): an oxidizer or main propellant grain; a stabilizer, which reacts with nitrogen oxides to stabilize the propellant during storage (Bergens et al. 1985); a burning-rate modifier to slow the rate of deflagration; and binders and plasticizers, which enable loading and packing of propellant into the shell. Additional compounds can be added to reduce flash and smoke (e.g., K_2SO_4 , KNO_3 , or AlF_6Na_3 as cryolite), or to serve as an igniter or detonator (e.g., black powder, which consists of KNO_3 , charcoal, and sulfur). The latter compounds generally are not detrimental to the environment due to limited mass, so they will not be considered further. Propellants used in medium-to-large-caliber (60-mm to 155-mm) ammunition generally are solids, whereas propellants used in rockets are liquids. Only solid propellants are considered in this report.

Oxidizers (nitroguanidine and ammonium or potassium perchlorate) and their associated energetic binders (nitroglycerin and nitrocellulose) comprise the greatest mass of all propellant components, ranging between 60 and 90 percent by weight (Ase et al. 1985; Ross et al. 1988; Kirchner et al. 1993; Lieb and Heimerl 1994; Miller 1997; McDougal and Jepson 1998; Yazici et al. 1998; MIDAS 2003). Plasticizers and binders account for approximately 5 to 25 weight percent. Stabilizers and other compounds account for the remainder, typically at less than 5 weight percent each.

Solid propellants are classified into three categories based on oxidizer composition: single base, double base, and triple base. Single-base propellant consists primarily of nitrocellulose. Double-base propellant consists of nitrocellulose infused with nitroglycerin. Triple-base propellant consists of nitrocellulose, nitroglycerin, and nitroguanidine. Nitroguanidine has an explosive power similar to that of nitroglycerin, but burns at a lower temperature. Use of a triple-base propellant preserves the gun barrel and reduces flash.

Table 1. Propellant compounds and their transformation products.
 Propellant compounds in bold text, transformation products in normal text.

Compound	CAS Registry Number	Acronym
Oxidizers and their Transformation Products		
Nitroguanidine	556-88-7	NQ
Cyanamide	420-04-2	
Guanidine (as hydrochloride)	50-01-1	
Melamine	108-78-1	
n-Nitrosoguanidine	674-81-7	
Ammonium perchlorate	7790-98-9	
Potassium chlorate	3811-04-9	
Potassium perchlorate	7778-74-7	
Stabilizers and their Transformation Products		
Diphenylamine	122-39-4	DPA
N-Nitrosodiphenylamine	86-30-6	NNODPA
2,4-Dinitrodiphenylamine	961-68-2	2,4DNDPA
2-Nitrodiphenylamine	119-75-5	2NDPA
4-Nitrodiphenylamine	836-30-6	4NDPA
Methyl centralite 1,3-dimethyl-1,3-diphenylurea	611-92-7	
Ethyl centralite 1,3-diethyl-1,3-diphenylurea	85-98-3	
Burning-Rate Modifiers		
Lead salicylate	15748-73-9	
Lead resorcyate	20936-32-7	
Lead stearate	7428-48-0	
Plasticizers		
Dimethyl phthalate	131-11-3	DMP
Diethyl phthalate	84-66-2	DEP
Di-n-butyl phthalate	84-74-2	DNBP
Butylbenzyl phthalate	85-68-7	BBP
Bis(2-ethylhexyl)phthalate	117-81-7	DEHP
Energetic Plasticizers and Binders		
2,4-Dinitrotoluene	121-14-2	2,4DNT
Diethylene glycol dinitrate	693-21-0	DEGDN
Ethylene glycol dinitrate	628-96-6	EGDN
Nitrocellulose	9004-70-0	NC
Nitroglycerin	55-63-0	NG
Note: Shaded cells indicated "no data."		

Propellants are solid mixtures of compounds that exhibit a range of physical and chemical characteristics. Few investigators examine the transport and fate behavior of solid propellant mixtures (Dubois and Baytos 1991; Cannizzo et al. 1995; Adrian 1996; Morris 2002). Most transport and fate investigations focus on the behavior of individual compounds in the solid mixture. The latter approach is followed in this work.

Dissolution and hydrolysis of propellant compounds

Energetic compounds in propellant mixtures exhibit a range of aqueous solubilities (Table 2). Oxidizers generally are nitramine compounds or inorganic salts that have high aqueous solubilities measured in the parts-per-thousand range (grams per liter, g/L). Stabilizers are aliphatic nitramines that have low to moderate aqueous solubility, in the parts-per-million range (milligrams per liter, mg/L). Burning-rate modifiers cited here are lead-substituted aromatic and aliphatic compounds which are sparingly soluble. Plasticizer and binder compositions are diverse, including the phthalates (aromatic carboxylic acids), and alcohols that contain nitrogen (EGDN, DEGDN, nitroglycerin). Most plasticizers are moderately water-soluble. Major processes that control the transport and fate of energetic compounds and their transformation products are summarized below in the order presented in Table 2.

Nitroguanidine (NQ) and its transformation products

Nitroguanidine is a nitramine compound that serves as an oxidizer in triple-base propellants, and also reduces flash and temperature during deflagration (U.S. Army Armament Research and Development Command (USA-ARDEC) 1983). Nitroguanidine has high aqueous solubility, ranging between 2.6 and 5.0 g/L (Table 2). Once in aqueous solution, NQ concentration remains constant in heated, dilute hydrochloric acid, but will hydrolyze to NH_3 , N_2O , and CO_2 at pH greater than 10 (McKay 1952; Bissett and Levasseur 1976). Spanggord et al. (1985) quantified pH-dependent hydrolysis (25 °C; pH 7 to 13) with half-lives ranging from greater than 8 years to 7.5 hours, respectively. Haag et al. (1990) showed that nitroguanidine undergoes base-catalyzed hydrolysis (25 °C, pH 12), and also concluded that hydrolysis at environmental conditions (25 °C, pH less than 9) was slow, with half-lives greater than 100 days.

Table 2. Aqueous solubility of propellant compounds and their transformation products.
Propellant compounds in bold text, transformation products in normal text.

Compound	Aqueous Solubility		Reference
Oxidizers and their Transformation Products			
Nitroguanidine	3.6	g/L (20 °C)	Gibbs and Popolato (1980)
	2.6	g/L (25 °C)	Spanggord et al. (1985); Haag et al. (1990); Dave et al. (2000)
	4.4	g/L (25 °C)	Kenyon (1982); Van der Schalie (1985); Pal and Ryon (1986)
	4.2	g/L (25 °C)	CPIA (2000)
	5.0	g/L (28.2 °C)	USA-ARDEC (1983), Morris (2002)
Cyanamide	800	g/L (25 °C)	Shiu et al. (1990)
	775	g/L (15 °C)	Budavari et al. (1996)
Melamine	3,240	mg/L	Yalkowsky and He (2002); Hansch et al. (1995)
	<253	mg/L	Weber (1970)
n-Nitrosoguanidine	slightly soluble		USA-ARDEC (1983)
Ammonium perchlorate	200	g/L (25 °C)	Grayson (1985); Ashford (1994)
	217–220	g/L (20 °C)	Motzer (2001)
Potassium chlorate	70	g/L (25 °C)	Budavari et al. (1996)
Potassium perchlorate	15	g/L (25 °C)	Ashford (1994)
	7.5–16.8	g/L (20 °C)	Motzer (2001)
Stabilizers and their Transformation Products			
Diphenylamine	35–45	mg/L	Drzyzga (2003)
	52–54	mg/L (20 °C)	Dave et al. (2000)
	insoluble		Budavari et al. (1996)
	300	mg/L (25 °C)	Verschueren (1983)
	48–54	mg/L (20 °C)	Hashimoto et al. (1982)
	36	mg/L (25 °C)	Kitchens et al. (1978)
n-Nitrosodiphenylamine	35.1	mg/L (25 °C)	Yalkowsky and He (2002)
	113	mg/L (25 °C)	USEPA (1992)
2,4-Dinitrodiphenylamine	41.4	mg/L (25 °C)	Baughman and Perenich (1988)
2-Nitrodiphenylamine	<1	g/L (22 °C)	NTPCR (2002)
4-Nitrodiphenylamine	insoluble		Weast (1979)
Methyl centralite	insoluble		USA-ARDEC (1983)
Ethyl centralite	80	mg/L (20 °C)	USA-ARDEC (1983); CPIA (2000)
	insoluble		Kitchens et al. (1978)
Burning-Rate Modifiers			
Lead resorcyate	slightly soluble		Kitchens et al. (1978)
Lead salicylate	soluble in hot water		Kitchens et al. (1978)
Lead stearate	0.05	g/L (35 °C)	Kitchens et al. (1978)
	insoluble		Budavari et al. (1996)

Compound	Aqueous Solubility		Reference
Plasticizers			
Dimethyl phthalate	5,000	mg/L (20 °C)	Verschueren (1983)
	4,000+/-60	mg/L (20 °C)	Howard et al. (1985)
	4,320	mg/L (25 °C)	USEPA (1987a)
	4,290	mg/L (25 °C)	Zurmühl et al. (1991)
	4.3	g/L (25 °C)	CPIA (2000)
	4,300	mg/L	Shiu et al. (1990)
	4,200	mg/L	Staples et al. (1997)
Diethyl phthalate	120	mg/L	Kitchens et al. (1978)
	1,080+/-40	mg/L (20 °C)	Howard et al. (1985)
	680	mg/L (25 °C)	Russell and McDuffie (1986)
	896	mg/L (25 °C)	USEPA (1987a)
	928	mg/L (25 °C)	Zurmühl et al. (1991)
	1,100	mg/L	Staples et al. (1997)
	1,000	mg/L (25 °C)	Yalkowsky and He (2002)
Di-n-butyl phthalate	10	mg/L	Kitchens et al. (1978), Zurmühl et al. (1991)
	11.2+/-0.3	mg/L (20 °C)	Howard et al. (1985)
	9.2	mg/L (25 °C)	Russell and McDuffie (1986)
	13	mg/L (25 °C)	USEPA (1987a)
	4.5–11.1	mg/L (20 °C)	Shiu et al. (1990)
	13	mg/L (25 °C)	Shiu et al. (1990)
	11.2	mg/L	Staples et al. (1997)
Butylbenzyl phthalate	2.9+/-1.2	mg/L (20 °C)	Gledhill et al. (1980)
	2.82+/-1.2	mg/L (20 °C)	Leyder and Boulanger (1983)
	2.69	mg/L (25 °C)	Howard et al. (1985)
	2.0	mg/L (25 °C)	Russell and McDuffie (1986)
	2.8	mg/L (25 °C)	Zurmühl et al. (1991)
	0.71	mg/L (25 °C)	Yalkowsky and He (2002)
Bis(2-ethylhexyl) phthalate	0.34+/-0.4	mg/L (20 °C)	Howard et al. (1985)
	0.4	mg/L (25 °C)	Russell and McDuffie (1986)
	0.04–0.4	mg/L (25 °C)	Zurmühl et al. (1991)
	3	µg/L (20 °C)	Staples et al. (1997)
	0.285	mg/L (25 °C)	Yalkowsky and He (2002)
	0.19+/-0.21	µg/L (20 °C)	Letinski et al. (2002)
Energetic Plasticizers and Binders			
2,4-Dinitrotoluene	200	mg/L (22 °C)	Spanggord et al. (1980b)
	270	mg/L (22 °C)	Verscheuren (1983); Montgomery and Welkom (1989)
	280	mg/L (25 °C)	USA-ARDEC (1983), Burrows et al. (1989)
	166	mg/L	Dave et al. (2000)
	199+/-2.2	mg/L (25.2 °C)	Phelan and Barnett (2000)
DEGDN	4.0	g/L (20 °C)	Kitchens et al. (1978)
	3.90	g/L (25 °C)	Spanggord et al. (1985); Haag et al. (1991)
	4.0	g/L (25 °C)	Burrows et al. (1989); CPIA (2000)

Compound	Aqueous Solubility		Reference
EGDN	5.6	g/L (25 °C)	Burrows et al. (1989)
	5.2	g/L (25 °C)	Clayton and Clayton (1993)
	1.5	g/L (20 °C)	Yinon (1999)
Nitrocellulose	immiscible		Budavari et al. (1996)
Nitroglycerin	1,800	mg/L (20 °C)	Verscheuren (1983); Pal and Ryon (1986)
	1,950	mg/L (25 °C)	Burrows et al. (1989)
	1,380	mg/L (20 °C)	Seidell (1941)
	1,250	mg/L	Budavari et al. (1996)
	1.5	g/L (20 °C)	Yinon (1999)

Cyanamide, melamine, guanidine, and n-nitrosoguanidine are transformation products of nitroguanidine (Kaplan et al. 1982; Williams et al. 1989). Cyanamide and melamine have high aqueous solubilities, whereas n-nitrosoguanidine is insoluble (Table 2). Nitrourea was the only product identified from the hydrolysis of nitroguanidine (Spanggord et al. 1985). These transformation products have been identified in laboratory experiments, but have not been identified as contaminants of concern at any National Priorities List (Superfund) site (USEPA 2005a).

Perchlorate and chlorate salts

Ammonium and potassium perchlorate are inorganic salts that serve as oxidizers in propellant mixtures (Motzer 2001). For example, ammonium perchlorate is a major (70 percent by weight) constituent of Arcadene propellants used in MLRS (multiple launch rocket systems; MIDAS 2003). Potassium chlorate is a major constituent of primer mix used in the fuzes of various small-caliber ammunitions, hand grenades, and projectiles (MIDAS 2005). These salts have high aqueous solubilities in the parts-per-thousand range (Table 2). Dissolution of the salt yields the perchlorate (ClO_4^-) anion, which does not hydrolyze under environmental Eh and pH conditions (Motzer 2001).

Diphenylamine (DPA) and its nitro- and nitroso-substituted transformation compounds

Diphenylamine and 2-nitrodiphenylamine are used as stabilizers in many propellant mixtures (Kitchens et al. 1978; MIDAS 2003). Diphenylamine stabilizes single-base propellants, in which nitrocellulose is the primary energetic material; 2-nitrodiphenylamine stabilizes double- and triple-base propellants in which nitroglycerine gelatinizes the nitrocellulose

(IPI 2003). These compounds react with nitrogen oxides that form in situ from nitrocellulose degradation (Wentsel et al. 1979a; Bergens et al. 1985; Haberman 1986). Diphenylamine and related nitro-, dinitro-, and nitroso-substituted compounds show low to moderate aqueous solubility. A range of aqueous solubilities are reported in the literature for DPA, with values between 36 and 300 mg/L (Table 2). Hydrolysis of DPA was inferred from decreased *Daphnia* toxicity when aged (30-day) aqueous solutions of diphenylamine were used, although hydrolysis products were not quantified in these experiments (Dave et al. 2000).

N-nitrosodiphenylamine, 2-nitrodiphenylamine, 4-nitrodiphenylamine, and 2,4-dinitro-diphenylamine are transformation products of diphenylamine. During propellant storage, diphenylamine shows increasing nitrate-substitution as nitrogen oxides are consumed (Haberman 1986). N-nitroso-diphenylamine and 2-nitrodiphenylamine show low aqueous solubility, although the values are not well quantified (Table 2). These compounds also resist hydrolysis (Wentsel et al. 1979a; USEPA 1992). 4-Nitrodiphenylamine is effectively insoluble and is unlikely to hydrolyze.

Methyl and ethyl centralite

Methyl and ethyl centralite are diphenylurea (carbanilide) molecules with alkyl-group substituents. These compounds stabilize propellant mixtures and their ignition and detonator components in a variety of small- and large-caliber ammunition (MIDAS 2003). These compounds also reduce propellant temperature during deflagration, reduce flash, and act as a gelatinizer in propellants that contain nitroglycerine (USA-ARDEC 1983). Various nitrourea, aniline, and nitrosamine compounds form in situ as the propellant mixture ages (Wentsel et al. 1979b; Curtis 1987). Both methyl and ethyl centralite have low aqueous solubilities, although the quality of these solubility data may be equivocal (Table 2). If ethyl and methyl centralite are detected in soil, it is likely that they were dispersed as fine-grained solids, rather than as a solute. Ethyl centralite will hydrolyze to an aniline compound only under heated, acidic (100 °C, 60 percent sulfuric acid) conditions, (Wentsel et al. 1979b), and is resistant to base hydrolysis (Kitchens et al. 1978).

Burning-rate modifiers

Lead salicylate and resorcyate are mono- and di-hydroxybenzoic acids (respectively) in which lead complexes with two aromatic ring molecules. Lead stearate is a lead-substituted aliphatic carboxylic acid. Lead -resorcyate, -salicylate, and -stearate compounds slow deflagration in propellants. Only lead salicylate and stearate appear as propellant constituents in current ammunition inventories (MIDAS 2003). All three compounds have low aqueous solubilities (Table 2). During acidic or neutral pH dissolution, lead salicylate and resorcyate may hydrolyze, cleaving the metal complex to release the hydroxybenzoic acids and ultimately divalent lead (Kitchens et al. 1978).

Base hydrolysis results in soluble basic salts of these compounds (Kitchens et al. 1978). Stepwise hydrolysis of lead stearate will occur under acidic conditions, releasing a carboxy-lead complex and ultimately divalent lead (Kitchens et al. 1978).

Phthalate plasticizers

Non-energetic binders include esters of 1,2-benzenedicarboxylic (or phthalic) acids. These compounds are used widely in civilian and military applications. Dimethyl-, diethyl-, di-n-butyl-, butylbenzyl-, and bis(2-ethylhexyl)-phthalate are five phthalic acid esters found in non-energetic plasticizers for military applications (MIDAS 2003). Butylbenzyl- and di-n-butyl-phthalate are endocrine-disrupting compounds (Jobling et al. 1995; National Academy of Sciences 1999; Kim et al. 2002). Generally, aqueous solubility decreases with increasing length of the alkyl ester chain (Table 2), until the chain length exceeds eight carbons (Ellington 1999). Aqueous solubility values for high molecular weight phthalate esters may be too high owing to experimental difficulties with the measurement of these hydrophobic compounds (Staples et al. 1997).

Hydrolysis rates estimated from linear free energies are slow, especially for high molecular weight phthalate esters (Wolfe et al. 1980). A slow (abiotic) hydrolysis rate (less than 5 percent hydrolysis in 28 days) was observed for butylbenzyl phthalate (Gledhill et al. 1980).

2,4-Dinitrotoluene

2,4-Dinitrotoluene (2,4-DNT) is an energetic binder in some propellant and high explosives formulations (MIDAS 2003). Although 2,4-DNT has moderate aqueous solubility (Table 2), hydrolysis is not an important transformation reaction. Spanggord et al. (1980b) conclude that 2,4-DNT will not hydrolyze under environmental conditions because the molecule lacks readily hydrolysable substituent groups.

DEGDN and EGDN

Diethylene- and ethylene-glycol dinitrate (DEGDN and EGDN, respectively) are energetic plasticizers that are liquids at room temperature. DEGDN is a less-sensitive gelatinizer of nitrocellulose than nitroglycerine (USA-ARDEC 1983). DEGDN is a component of JA2 propellant (MIDAS 2003). EGDN also is a gelatinizer and is a major constituent of some liquid rocket propellants (MIDAS 2003). Both DEGDN and EGDN have moderate aqueous solubility (Table 2). DEGDN has been observed to solubilize in JA2 propellant grains stored in high humidity conditions (Pesce-Rodriguez et al. 1997). Neither DEGDN or EGDN hydrolyze readily. Spanggord et al. (1985) inferred slow hydrolysis rates (25 °C) for DEGDN in aqueous solutions, characterized by half-lives ranging between 440 days (pH 7) and 130 days (pH 12.8). Haag et al. (1991) calculated slow hydrolysis rates for DEGDN in aqueous solutions having pH values between 7 and 10, resulting in a half-life greater than 400 days.

Nitrocellulose (NC)

Nitrocellulose is a non-volatile, fibrous, white colloid consisting of polymerized glucoside (aliphatic) units in which substituent hydroxyl groups have reacted to form nitrate esters (Boudeau 1993). Nitrocellulose is mixed with nitroglycerine to form a gelatinized energetic binder. The nitrogen content of nitrocellulose typically ranges between 12.6 and 13.25 weight percent (Pal and Ryon 1986; Ross et al. 1988; Palmer et al. 1996; Miller 1997). In its solid fibrous form, nitrocellulose is insoluble in water (Table 2). Nitrocellulose will not dissolve or hydrolyze in aqueous solutions except with strong base (NaOH or NH₃) and high temperatures (50 to 80 °C; Cannizzo et al. 1995; 30 to 90 °C; Christodoulatos et al. 2001). Nitrocellulose fines will flocculate from aqueous suspension when pH is raised to 11.6 through the addition of lime (Smith et al. 1983).

Nitroglycerine (NG)

Nitroglycerine is an aliphatic nitrate ester, which will gelatinize nitrocellulose for use in double- and triple-base propellants. Nitroglycerine is a viscous liquid at room temperature, and has moderate aqueous solubility (Table 2). Spanggord et al. (1980b) inferred second-order, base-catalyzed hydrolysis rates, characterized by half-lives ranging between 96 and 37 days (18 and 25 °C, respectively), at pH 9. Alkaline hydrolysis of nitroglycerine will proceed at temperatures between 10 and 25 °C, and pH between 11.9 and 12.5. The predominant products of alkaline hydrolysis of NG by calcium hydroxide are calcium nitrate and calcium nitrite (Capellos et al. 1984). Nitroglycerine disappeared within one week in sterile, anoxic solutions with mineral salts, presumably by an abiotic, aqueous reaction (Adrian 1996).

Sorption of propellant compounds

Sorption processes involve the association of a solute with a solid at the solid-solution interface. The specific reaction and the rate at which it occurs depend on the nature of the molecule in solution (hydrophobic or hydrophilic; ionic or neutral) and the nature of the surface (organic, mineral, oxide). The general mechanisms of sorption of energetic compounds are discussed in Ainsworth et al. (1993), McGrath (1995), and Pennington and Brannon (2002). A good general discussion of distribution coefficients can be found in Fetter (1999).

The following discussion considers only linear descriptors of sorption behavior using the distribution coefficient (K_d), the distribution coefficient normalized for soil organic carbon (K_{oc}), and the octanol-water partition coefficient (K_{ow}), and their net effect on the mobility of propellant solutes. Briefly, the K_d value ($K_d = [X]_{\text{sorbed}}/[X]_{\text{solution}}$; where $[X]$ is the concentration of solute, K_d in units of L/kg) is a measure of a solute's tendency to partition to the solid phase. Greater K_d values indicate a greater tendency for partitioning out of solution. K_d values are determined experimentally, using a site-specific soil or sediment that ideally has well-defined physicochemical characteristics. Implicit in the K_d sorption model are the assumptions of isothermal conditions, equilibrium, and reversibility. The K_{oc} value is the distribution coefficient normalized by the fraction (in weight percent) of soil organic carbon ($K_{oc} = K_d/f_{oc}$). Greater K_{oc} values indicate the tendency for a hydrophobic organic solute to partition into the non-polar

soil organic carbon fraction. K_{oc} values can be measured experimentally, estimated from aqueous solubility and K_{ow} values, or estimated using molecular structure-activity relationships (e.g., Meylan and Howard 1991; Meylan et al. 1992). The K_{ow} value ($K_{ow} = [X]_{octanol}/[X]_{water}$ where $[X]$ is the solute concentration) is a measure of hydrophobicity, or tendency for an organic solute to dissolve in a non-polar solvent. K_{ow} values are measured experimentally, or are estimated using molecular structure-activity relationships (e.g., Hansch et al. 1995).

Nitroguanidine and its transformation products

Nitroguanidine, cyanamide, and melamine are mobile in soil environments. Mobility is indicated by high aqueous solubility and low K_d values (Table 3). Low K_{oc} values indicate limited sorption. Nitroguanidine, cyanamide, and melamine are hydrophilic, as indicated by low values of K_{ow} . Although soluble, melamine has a maximum extent of sorption on montmorillonite at pH 4, but no K_d value was calculated (Weber 1970). No partition coefficients were found in the literature for nitrosoguanidine.

Perchlorate and chlorate salts

No sediment distribution or partition coefficients were found in the literature for perchlorate and the chlorate salts. Because these salts have high aqueous solubility and form oxyanions on dissolution, sorption is unlikely to be a significant process affecting transport in soil and aquifer environments, except in low pH soils that have high anion exchange capacity. Column experiments support this conclusion (Kim and Logan 2001; Tipton et al. 2003). Perchlorate can be reduced to chloride during combined sorption-electron transfer reactions under anoxic conditions at the surface of zero-valent iron (Gurol and Kim 2000; Moore et al. 2003). This complex reaction requires a solid iron phase (presumably as a catalyst), and reduced ferrous iron as an electron donor. Perchlorate associates with the ferrous iron-ferric hydroxide solid surface, and is reduced ultimately to chloride (Moore et al. 2003). Optimum conditions for this reaction are neutral pH values, and low background chloride concentrations (Gurol and Kim 2000). Reaction rates are generally slow, which may limit the application of this reaction to remediation strategies (Moore et al. 2003).

Table 3. Distribution coefficients (K_d), soil organic carbon distribution coefficients (K_{oc}), and octanol-water partition coefficients (K_{ow}) for propellant compounds and their transformation products.

Compound	K_d	Soil Type	Reference	$\log K_{oc}^1$	Reference	$\log K_{ow}$	Reference
Oxidizers and their Transformation Products							
Nitroguanidine	<0.1	EPA-6, -12	Haag et al. (1990)	0.356 ² 1.41 ³	Burrows et al. (1989) SRC (2003)	-0.83 0.156 0.148 -0.89 ⁴	Dave et al. (2000); Burrows et al. (1989) Spanggord et al. (1985) Haag et al. (1990) Hansch et al. (1995); McDougall and Jepson (1998)
Cyanamide				0.398 ²	SRC (2003)		
Melamine						-1.37 ⁴	Hansch et al. (1995)
n-Nitrosoguanidine							
Ammonium perchlorate							
Potassium chlorate							
Potassium perchlorate							
Stabilizers and their Transformation Products							
Diphenylamine				2.78 3.28 ³	Meylan et al. (1992) Meylan et al. (1992)	3.50 ⁴ 3.62 3.42	Hansch et al. (1995); McDougal and Jepson (1998) Dave et al. (2000) Drzyzga (2003)
n-Nitrosodiphenylamine				3.08 ²	SRC (2003)	3.13 ⁴	Hansch et al. (1995)
2-Nitrodiphenylamine						3.07 ⁴ 3.66 ⁴	Wentzel et al. (1979a) Hansch et al. (1995)
4-Nitrodiphenylamine							
2,4-Dinitrodiphenylamine				2.40	Rosenblatt (1986)	4.55	Baughman and Perenich (1988)
Methyl centralite							
Ethyl centralite						4.37 to 5.88 4.2	Wentzel et al. (1979b) McDougal and Jepson (1998)
Burning-Rate Modifiers							
Lead salicylate							
Lead resorcyate							
Lead stearate							

Compound	K _d	Soil Type	Reference	log K _{oc} ¹	Reference	log K _{ow}	Reference
Plasticizers							
Dimethyl phthalate	0.189	Oakville A	Altfelder et al. (2001)	2.18 - 2.86	Banerjee et al. (1985)	1.53	Leyder and Boulanger (1983)
	0.519	Oakville B	Altfelder et al. (2001)	1.3 - 1.8 ²	Ritsema et al. (1989)	1.47 +/- 0.212	Howard et al. (1985)
				>5.2	Ritsema et al. (1989)	1.53 - 2.1 ⁵	Zurmühl et al. (1991)
				1.88, 1.89	Zurmühl et al. (1991)	1.56 ⁴	Hansch et al. (1995)
				4.70-5.20	SRC (2003)	1.46 - 1.90 ⁵	Staples et al. (1997)
Diethyl phthalate	8.81	Alfisol	Von Oepen et al. (1991)	1.84, 2.65 ²	Russell & McDuffie (1986)	1.60 +/- 0.04	Ellington (1999)
	83.70	Podzol	Von Oepen et al. (1991)	2.0 - 2.2 ²	Ritsema et al. (1989)	2.35	Leyder and Boulanger (1983)
	15.86	Sediment	Von Oepen et al. (1991)	1.94, 1.99	Zurmühl et al. (1991)	2.24 +/- 0.086	Howard et al. (1985)
	1.1	Broome Co. NY soil	Russell & McDuffie (1986)	2.85-3.24	Von Oepen et al. (1991)	2.96	Parker et al. (1994)
						2.47 ⁴	Hansch et al. (1995)
Di-n-butyl phthalate	22	Broome Co. NY soil	Russell & McDuffie (1986)	3.14, 3.81	Russell & McDuffie (1986)	2.21 - 3.00 ⁵	Staples et al. (1997)
	17.46	Tsinghua garden	Wang et al. (1997)	3.5 - 4.02	Ritsema et al. (1989)	2.42 +/- 0.04	Ellington (1999);
				3.06	Zurmühl et al. (1991)		Parker et al. (1994)
Butylbenzyl phthalate	270	Broome Co. NY soil	Russell & McDuffie (1986)	4.23	Russell & McDuffie (1986)	4.77	Gledhill et al. (1980)
				4.02	Ritsema et al. (1989)	4.57	Leyder and Boulanger (1983)
						4.79 +/- 0.234	Howard et al. (1985)
						5.2	Parker et al. (1994)
						4.724	Hansch et al. (1995)
Bis (2-ethylhexyl) phthalate	1,390	Broome Co. NY soil	Russell & McDuffie (1986)	4.94, 4.282	Russell & McDuffie (1986)	3.74 - 5.155	Staples et al. (1997)
				5.7	Ritsema et al. (1989)	4.50 +/- 0.03	Ellington (1999)
Energetic Plasticizers and Binders							
2,4-Dinitrotoluene	12	sediment	Spanggord et al. (1980b)	1.95 ²	Spanggord et al. (1980a)	1.98	Layton et al. (1987); Burrows et al. (1989); Hansch et al. (1995)
				2.41	Layton et al. (1987)		
				2.56 ³	SRC (2003)		

Compound	K _d	Soil Type	Reference	log K _{oc} ¹	Reference	log K _{ow}	Reference
Diethylene glycol dinitrate	2.3 +/- 2.8	EPA-5	Haag et al. (1991)	2.03	Spanggord et al. (1985)	0.96-0.99	Spanggord et al. (1985)
	0.8 +/- 0.9	EPA-18	Haag et al. (1991)	2.00, 2.08	Haag et al. (1991)	1.13 ⁴ 0.98	Burrows et al. (1989) Haag et al. (1991)
Ethylene glycol dinitrate				1.28 ³ 2.00 ²	Burrows et al. (1989) SRC (2003)	2.11 ⁴ 1.16	Burrows et al. (1989) Hansch et al. (1995)
Nitrocellulose							
Nitroglycerin				2.77 1.6 ³	Spanggord et al. (1980b) Burrows et al. (1989)	1.77 2.81 ⁴ 1.62 ⁴	Jenkins (1989) Burrows et al. (1989) Hansch et al. (1995); McDougal and Jepson (1998)

Note: Shaded cells indicate "no data."

¹ log K_{oc} values were measured experimentally unless noted otherwise.

² log K_{oc} values were estimated from K_{ow} and aqueous solubility.

³ log K_{oc} values were estimated from molecular structure activity relationships.

⁴ log K_{ow} values were estimated from molecular structure activity relationships.

⁵ Ranges of log K_{ow} values were determined by several methods.

Diphenylamine and nitro- and nitroso-substituted transformation products

Few data describe the partitioning behavior of diphenylamine and its transformation products. Most abundant are K_{ow} values (Table 3), which suggest hydrophobic behavior for DPA, n-nitrosodiphenylamine, 2- and 4-nitrodiphenylamine, and 2,4-dinitrodiphenylamine.

Methyl and ethyl centralite

Few data describe the partitioning behavior of methyl and ethyl centralite. High K_{ow} values (Table 3) suggest hydrophobic behavior for ethyl centralite, should this compound be released into the environment as a solute.

Burning-rate modifiers

No distribution or partition coefficients were found in the literature for lead salicylate, lead resorcyate, or lead stearate. These compounds are sparingly soluble in water. However, once in solution, these compounds will hydrolyze to form complex cations of divalent lead. Cations tend to sorb on sediment and soil due to a prevalence of cation exchange mineral phases.

Phthalate plasticizers

Experimental data that define the partitioning behavior of phthalate esters are abundant, but variable (Table 3). Phthalate esters tend toward hydrophobicity, and have increasing K_{ow} values with increasing length of the alkyl ester side chain. There is a positive linear relationship between $\log K_{ow}$ and chain length up to eight carbons (Ellington 1999). Partition coefficients vary considerably for some phthalate esters. For example, published experimental $\log K_{oc}$ values for dimethylphthalate vary over three orders of magnitude (Table 3). Generally, phthalates having longer alkyl side chains have greater $\log K_{oc}$ and K_d values, although this trend is qualitative.

2,4-Dinitrotoluene

Few experimental data are available to interpret sorption behavior of 2,4-DNT (Table 3). Estimated $\log K_{ow}$ and K_{oc} values suggest moderately hydrophilic behavior and limited sorption, respectively. Batch sorption experiments (Spanggord et al. 1980b) yielded low K_d values, suggesting limited partitioning of 2,4-DNT into sediment.

DEGDN and EGDN

Both compounds have $\log K_{ow}$ values that suggest hydrophilic behavior, and low $\log K_{oc}$ values that indicate limited sorption. Low K_d values from batch sorption experiments using USEPA standard soils (Haag et al. 1991) confirm that DEGDN and EGDN are mobile in soil environments.

Nitrocellulose

Because nitrocellulose exists as a fibrous solid, it serves as a sorbent rather than a sorbed species. Nitrocellulose fibers have long been known to sorb biological molecules (Tew and Jaffe 1973), and similarly could sorb organic molecules in the environment. Double- and triple-base propellant formulations consist of nitrocellulose gelatinized with EGDN, DEGDN, and/or nitroglycerin, and is stabilized with methyl or ethyl centralite. All of these compounds could coexist with nitrocellulose in the environment.

Nitroglycerine

Nitroglycerine has low log K_{ow} values that suggest hydrophilic behavior, and low log K_{oc} values that indicate limited sorption (Table 3). Nitroglycerine is mobile in soil environments.

Biotransformation of propellant compounds

Microbe-mediated transformation reactions can reduce some propellant compound concentrations in soil and subsurface environments. Microbes facilitate electron transfer reactions between carbon-rich electron donors and electron acceptors such as oxygen, nitrate, sulfate, or ferric iron to obtain energy. Some propellant compounds can serve as carbon-rich substrates, or are co-metabolized with other carbon molecules in the environment. Microbe-mediated transformation reactions can occur in virtually all environments, though the specific reaction mechanism and microbial population affecting the reactions will vary.

Nitroguanidine and its transformation products

Nitroguanidine is biotransformed in aquatic environments under both aerobic and anaerobic conditions. Apparently, NQ biotransformation in soils occurs under both aerobic and anaerobic conditions; however, biotransformation rate is affected by the presence of nutrients or organic carbon, and the condition of microbial adaptation to NQ. Without amendments, nitroguanidine in solution did not degrade under aerobic, nitrate-reducing, sulfate-reducing, or methanogenic conditions (Adrian 1996).

Nitroguanidine was co-metabolized under aerobic conditions in natural water samples. Aerobic biotransformation rate was accelerated with the addition of nutrient broth or yeast extract – from 85 days (nutrient-poor) to 30 hours (nutrient-enriched) (Spanggord et al. 1985; Haag et al. 1990). Microorganisms that facilitated these aerobic reactions were isolated from pond water at Sunflower Army Ammunition Plant, and experiments were conducted in sterile Kansas River water. Cyanamide was the only aerobic biotransformation product reported (Haag et al. 1990).

Column studies were performed to quantify aerobic biotransformation of NQ in soil environments (Kaplan and Kaplan 1985; Williams et al. 1989).

Kaplan and Kaplan (1985) showed NQ reduction, with ammonia as the only product. Williams et al. (1989) also performed column experiments to optimize nutrient concentrations for aerobic bioremediation of NQ in soil. Incomplete transformation of nitroguanidine (to nitrosoguanidine and ammonia) was observed, possibly due to locally reducing conditions in the column. This biotransformation process is significant due to the potential carcinogenicity of nitrosoguanidine. Nitroguanidine was co-metabolized under anaerobic conditions in activated sludge amended with nutrients and glucose (Kaplan et al. 1982). Nitrosoguanidine was the primary biotransformation product – melamine, cyanamide, and cyanoguanidine appear as products that likely resulted from abiotic transformation of nitrosoguanidine (Kaplan et al. 1982). Biotransformation processes probably accounted for nitroguanidine degradation in spiked, moist unsaturated soils that were incubated in the dark (Mulherin et al. 2005). Half-lives reported for nitroguanidine biotransformation ranged between 15 and 56 days, and may be affected by the soil organic carbon content.

Perchlorate and chlorate salts

Perchlorate and chlorate anion concentrations are diminished by microbe-mediated reactions or during plant uptake. A growing body of literature documents optimum conditions for microbe-mediated and phytoremediation reactions.

Many aerobic and anaerobic microbes can reduce perchlorate and chlorate compounds to chloride in soil environments, sludge, and wastewaters (Logan 1998). Although perchlorate reduction to chloride has been observed under aerobic conditions (Coates et al. 2000), it is likely that these microbes (for example, *Dechlorimonas* and *Dechloridsoma* groups; Michaelidou et al. 2000) function as facultative anaerobes. Much more attention is focused on the use of these (and other) microbes to reduce perchlorate and chlorate under anaerobic conditions.

Microbe-mediated perchlorate and chlorate reduction proceeds readily under anaerobic conditions, although the addition of nutrients and a carbon source may be required (Chaudhuri et al. 2002). Typically, a carbon source (electron donor) is required to facilitate perchlorate reduction, either as soil organic carbon (Tipton et al. 2003), carbon dioxide (Zheng et al. 2002), a carboxylic acid (e.g., acetate; Herman and

Frankenberger 1999; Giblin et al. 2000; Logan et al. 2001; Kim and Logan 2001), or even the co-contaminant nitroglycerin (Attaway 1994). Perchlorate reduction requires molybdenum in some microbe strains (Chaudhuri et al. 2002). Many studies report sequential or simultaneous reduction of nitrate and perchlorate under anaerobic conditions by different microbe strains or communities (Herman and Frankenberger 1999; Giblin et al. 2000; Okeke et al. 2002; Chaudhuri et al. 2002; Tipton et al. 2003). Anaerobic perchlorate reduction is inhibited by nitrite, which appears as a nitroglycerin transformation product during propellant manufacture (Attaway 1994). Salt-tolerant microbes are capable of perchlorate reduction under anaerobic conditions, which may be applied to the remediation of ion-exchange waste products (Logan et al. 2001; Okeke et al. 2002).

Biochemical reactions that occur during phyto- and rhizo-transformation also reduce aqueous perchlorate concentrations (Sursala et al. 1999; Nzungu et al. 1999; Nzungu and Wang 2000). Perchlorate accumulation has been measured in leaves and stems of eucalypts and willows grown in hydroponic bioreactors (Nzungu et al. 1999). French tarragon and spinach showed declining perchlorate concentrations in leaf tissue over time, suggesting enzyme-catalyzed transformation (Nzungu and Wang 2000). During rhizotransformation, perchlorate reduction in solution occurs faster than transpiration. Rhizotransformation of perchlorate has been confirmed in willow roots (Nzungu et al. 2000).

Diphenylamine and nitro- and nitroso-substituted transformation products

Microbe-mediated transformation of diphenylamine occurs under both aerobic (Gardner et al. 1982; McCormick et al. 1985) and anaerobic conditions (Christodoulatos et al. 1997a; Drzyzga and Blotevogel 1997). One hundred percent of C¹⁴-labelled DPA was transformed under aerobic conditions within 24 hours, with aniline, indole, and 4-hydroxy-diphenylamine appearing as transformation products (Gardner et al. 1982). Aerobic batch-culture experiments conducted with nutrients and methanol as carbon source (without sediment) showed rapid loss of DPA (DPA below detection after 7 days) with a corresponding increase of two unidentified transformation products (McCormick et al. 1985). Aerobic pure and mixed activated sludge cultures utilized diphenylamine as the sole carbon source, with a half-life of 1.40 days (Christodoulatos et al.

1997a). Anaerobic sediment-water batch culture experiments conducted under methanogenic conditions with acetone as carbon source showed slower loss of DPA (60 percent DPA loss after 6 weeks) with the appearance of a transformation product tentatively identified as an aniline compound (Drzyzga and Blotevogel 1997).

Microbe-mediated transformation of the nitro-substituted DPA compounds (2-nitrodiphenylamine, 4-nitrodiphenylamine, and 2,4-dinitrodiphenylamine) proceeds most readily under anaerobic conditions (McCormick et al. 1985; Drzyzga et al. 1995; Powell et al. 1998) by sulfate-reducing bacteria (Drzyzga et al. 1996). Transformation proceeds by successive amination, forming 2-amino-4-nitrodiphenylamine and 2,4-diaminodiphenylamine (from 2,4-DNDPA), 2-aminodiphenylamine (from 2-NDPA), and 4-aminodiphenylamine (from 4-NDPA; Drzyzga et al. 1995). Phenazine and N-phenylbenzimidazole also were identified as anaerobic transformation products of 2-NDPA (McCormick et al. 1985). Anaerobic transformation of 2-NDPA as a component of Otto fuel proceeded only when a glucose carbon source was provided (Powell et al. 1998). Although 2-NDPA was completely transformed, the products were not identified in these experiments.

Microbe-mediated reduction of 2-nitrodiphenylamine also proceeds in aerobic batch cultures, but only to about 60 percent of initial concentration unless high concentrations of nutrient were used (McCormick et al. 1985). Nutrient-enriched aerobic cultures degraded 90 percent of 2-NDPA. Although 2-NDPA was transformed, the products were not identified in these experiments (McCormick et al. 1985).

Microbe-mediated reduction of nitrosodiphenylamine proceeds in aerobic batch cultures. One hundred percent of nitrosodiphenylamine was transformed within 10 days in aerobic sediment-water batch cultures amended with wheat straw as a carbon source (Mallick and Tesfai 1981). Eighty-seven percent of nitrosodiphenylamine (initial concentrations 5 or 10 mg/L) was transformed within 7 days in aerobic aqueous cultures amended with yeast extract (Tabak et al. 1981). Transformation products were not identified in any of these studies.

Methyl and ethyl centralite

Few experiments have examined the microbe-mediated transformation reactions of methyl and ethyl centralite. Centralite (without methyl- and ethyl-substituent groups) was reduced under aerobic conditions to approximately 35 percent of initial concentration after 5 days (McCormick et al. 1985). N-ethylaniline and ethyldiphenylurea were identified as transformation products. Negligible transformation of centralite was observed under anaerobic conditions (McCormick et al. 1985).

Burning-rate modifiers

No data or experiments were found to define microbe-mediated transformation of lead resorcyate, lead salicylate, and lead stearate. When not complexed to lead, the carboxylic acids resorcyate, salicylate, and stearate can serve as carbon sources for microbe-mediated transformation under a variety of conditions (e.g., Beeder et al. 1995; Gallus and Schink 1998).

Phthalate plasticizers

Discussion of microbe-mediated transformation reactions of phthalates is restricted to those five compounds used currently in military propellants (Table 1). Phthalate transformation reactions proceed under both aerobic and anaerobic conditions (Staples et al. 1997), with faster rates reported for aerobic transformation reactions (Yuan et al. 2002). The rate and extent to which phthalates are biotransformed depends on the length and structure of the alkyl side-chain, presence of nutrients, and temperature (Johnson et al. 1984; Zeng et al. 2004).

Microbe-mediated transformation of dimethyl phthalate (DMP) proceeds under both aerobic (Tabak et al. 1981; Ribbons et al. 1984; Vega and Bastide 2003; Zeng et al. 2004) and anaerobic (Kleezerbezem et al. 1999a; Wang et al. 2000) conditions. Biotransformation by an aerobic consortium to the monomethyl isomer, then to phthalic acid, involves cleavage of the ester bond (Niazi et al. 2001; Vega and Bastide 2003). Rapid aerobic transformation of DMP (100 percent in 7 days) occurred using domestic wastewater inocula amended with yeast extract in batch cultures (Tabak et al. 1981). Anaerobic biotransformation also proceeds by cleavage of the ester bond to the monomethyl isomer (Kleerebezem et al. 1999b). Anaerobic (methanogenic) transformation reduced initial DMP

concentrations by 50 percent after 16 to 38 +/- 2 days (Kleerebezem et al. 1999b), and 24 days (Wang et al. 2000) by different sludge microbes.

Microbe-mediated transformation of diethyl phthalate (DEP) proceeds under both aerobic (Tabak et al. 1981; Hashizume et al. 2002; Yuan et al. 2002; Chang et al. 2004; Zeng et al. 2004) and anaerobic (Parker et al. 1994), specifically methanogenic (Ejlertsson et al. 1996), conditions. Aerobic transformation of DEP is faster than anaerobic transformation. An average half-life of 2.5 days was reported for aerobic transformation by Yuan et al. (2002). Aerobic transformation proceeds to the monoethyl isomer then phthalic acid, analogous to that of DMP transformation (Karegoudar and Pujar 1984). Anaerobic transformation of DEP apparently requires methanogenic conditions, resulting in production of the corresponding monoethyl isomer and phthalic acid, as observed in simulated landfill conditions (Ejlertsson et al. 1996). Half-lives reported for anaerobic transformation of DEP are 33.6 days (Yuan et al. 2002), and 8.6 and 10.9 days (Gavala et al. 2003).

Microbe-mediated transformation of di-n-butyl phthalate (DNBP) proceeds under both aerobic (Tabak et al. 1981; Englehardt and Walln  ffer 1978; Wang et al. 1997; Hashizume et al. 2002; Yuan et al. 2002; Chang et al. 2004; Zeng et al. 2004) and anaerobic (Benckiser and Ottow 1982; Parker et al. 1994; Ejlertsson et al. 1996; Scholz et al. 1997; Angelidaki et al. 2000; Wang et al. 2000; Gavala et al. 2003) conditions in a variety of aqueous and soil environments. Biotransformation of DBP as the sole carbon source occurs with nitrate as the electron acceptor (Wang et al. 1999). The average half-life of DNBP under aerobic conditions is 2.9 days (Yuan et al. 2002). The pathway of aerobic transformation of DNBP in a microbial consortium begins with production of the monobutyl isomer, dealkylation to the phthalic acid, and subsequent mineralization (Englehardt and Walln  ffer 1978). Anaerobic transformation of DNBP occurs under denitrifying and methanogenic conditions. Under denitrifying conditions, DNBP is transformed to phthalic acid as an end product (Benckiser and Ottow 1982). Under methanogenic conditions, almost 100 percent of DNBP is transformed, although the products were not identified (Wang et al. 2000). Half-lives reported for anaerobic transformation of DNBP are 32.1 hours (under methanogenic conditions; Wang et al. 2000); 0.4 day (anaerobic conditions; Yuan et al. 2002), and 5.1 and 6.2 days (under methanogenic conditions; Gavala et al. 2003). Generally, ease of

anaerobic transformation is correlated positively with higher aqueous solubility (Ejlertsson et al. 1997) and shorter ester side-chains on the phthalic acid molecule (Wang et al. 2000).

Microbe-mediated transformation of butylbenzyl phthalate (BBP) occurs under both aerobic (Tabak et al. 1981; Yuan et al. 2002; Chang et al. 2004) and anaerobic (Parker et al. 1994; Jonsson et al. 2003) conditions. Enzyme-catalyzed transformation of BBP also occurs by *Fusarium* and yeast (Kim et al. 2002). Aerobic transformation of BBP occurs in batch cultures, but apparently requires prior acclimation to phthalates (Tabak et al. 1981; Yuan et al. 2002). A half-life reported for aerobic transformation of BBP is 3.1 days (Yuan et al. 2002). Anaerobic transformation of BBP occurs with the production of the monobenzyl ester and phthalic acid (Jonsson et al. 2003). A half-life reported for anaerobic transformation is 19.3 days (Yuan et al. 2002). Approximately 60 percent of BBP is transformed within 8 hours by esterase and cutinase enzymes (Kim et al. 2002). Transformation products include butylmethyl phthalate, dimethyl phthalate, benzene methanol, and benzofurandione; of these, butylmethyl phthalate may be toxic (Kim et al. 2002).

Microbe-mediated transformation of di-(2-ethylhexyl) phthalate (DEHP) occurs under aerobic (Tabak et al. 1981; Roslev et al. 1998; Banat et al. 1999; Madsen et al. 1999; Zeng et al. 2004; Change et al. 2004; DiGennaro et al. 2005) and anaerobic (Parker et al. 1994; Madsen et al. 1999; Angelidaki et al. 2000), specifically methanogenic conditions (Gavala et al. 2003) in soils and sludges. DEHP was not transformed in other trials under anaerobic conditions (Ejlertsson et al. 1996). The low aqueous solubility (Ejlertsson et al. 1997) and/or irreversible sorption (Roslev et al. 1998) of DEHP likely inhibit biotransformation and explain in part the persistence of DEHP in the environment. Aerobic transformation of DEHP occurs in sludge-amended batch cultures (Roslev et al. 1998; Banat et al. 1999; Madsen et al. 1999; DiGennaro et al. 2005) and river sediments (Yuan et al. 2002). Half-lives for aerobic transformation of DEHP are 14.8 days (Yuan et al. 2002), and 37 to 120 days for aerobic inocula of sludges and soils at 20 °C (Madsen et al. 1999; DiGennaro et al. 2005). Aerobic transformation of DEHP occurs more rapidly at higher temperatures (20 to 63 °C; Banat et al. 1999; Madsen et al. 1999). Although aerobic transformation frequently is interpreted as a first-order reaction, detailed studies suggest more complex reaction kinetics (Roslev et al.

1998; Madsen et al. 1999). Anaerobic transformation of DEHP occurs more slowly compared to aerobic transformation (Madsen et al. 1999; Gavala et al. 2003; Yuan et al. 2002). Half-lives for anaerobic transformation of DEHP are 34.7 days (Yuan et al. 2002), 173 to 198 days (Gavala et al. 2003), and 301 to greater than 365 days (Madsen et al. 1999). Anaerobic transformation rates have also been interpreted as first-order (Gavala et al. 2003), and more complex (Madsen et al. 1999) kinetic models.

Energetic plasticizers and binders

These compounds have diverse chemical structures, so biotransformation reactions are likewise dissimilar. Microbe-mediated reactions will be considered in the context of each individual compound. Compounds include 2,4-dinitrotoluene, DEGDN, EGDN, nitrocellulose, and nitroglycerin.

2,4-Dinitrotoluene

Microbe-mediated transformation of 2,4-dinitrotoluene (2,4-DNT) is important because this compound is a suspected human carcinogen. Aerobic transformation of 2,4-DNT to carbon dioxide and nitrite has been documented in soil slurries and munitions plant wastewater inoculated with known DNT-degrading microbes (Spanggord et al. 1991; Spain 1995; Nishino et al. 1999; Nishino et al. 2000; Christopher et al. 2000; Zhang et al. 2000; Snellinx et al. 2003), and by native microbes in DNT-contaminated soil and aquifer material (Bradley et al. 1994; Bradley et al. 1997). However, the persistence of 2,4-DNT in soils colonized by DNT-degrading microbes suggests slow rates of mineralization, possibly due to inhibition by 2,6-DNT (Nishino et al. 2000) or nitrite (Smets and Mueller 2001; Fortner et al. 2003). Unstable dihydroxylaminonitrotoluene intermediates, and aminonitrotoluene end-products result from biotransformation under certain aerobic conditions, suggesting that only a fraction of 2,4-DNT is mineralized to CO₂ (McCormick et al. 1978; Bradley et al. 1994; Spain 1995; Bradley et al. 1997; Hughes et al. 1999). Nearly complete mineralization of 2,4-DNT in solution (10 to 50 mg/L) was observed when mixed with non-sterile poultry litter leachate (Gupta et al. 2004). Two fungal species have been shown to transform 2,4-DNT by different pathways, resulting in complex sequences of intermediate compounds (McCormick et al. 1978; Valli et al. 1992). 2,4-DNT has been transformed in plant-soil systems by a genetically modified soil bacterium (Dutta et al.

2003). Microbe mediated biotransformation of 2,4-DNT under anaerobic conditions was studied using different electron-acceptor conditions in a fluidized-bed bioreactor (Vanderloop et al. 1999) and in culture solutions (Cheng et al. 1998). 2,4-DNT was transformed stoichiometrically to 2,4-diaminonitrotoluene under methanogenic conditions (Vanderloop et al. 1999) with different carbon substrates (Cheng et al. 1998). Further mineralization of 2,4-diaminonitrotoluene was not observed, so anaerobic biotransformation probably will serve only as a wastewater pre-treatment method.

DEGDN and EGDN

Little is known at present about microbe-mediated transformation of DEGDN and EGDN. Because these compounds are used as gelatinizers of nitroglycerin, NG would be a co-contaminant in most matrices. Microbe-mediated aerobic transformation of DEGDN and EGDN does occur in sediment, aqueous (river water), and sludge-amended batch cultures (Cornell et al. 1981; Haag et al. 1991). Biotransformation results in the production of mononitrate intermediates, followed by removal of the nitro-group to form ethylene- and diethylene-glycols (Ramos et al. 1996; Cornell et al. 1981). Subsequent mineralization of glycol products has been reported for EGDN (Ramos et al. 1996); however, Kaplan et al. (1981) infer that abiotic processes are responsible for DEGDN mineralization. A half-life reported for aerobic biotransformation of DEGDN is approximately 2 years (Haag et al. 1991). Anaerobic biotransformation of EGDN and DEGDN has not been reported in the literature.

Nitrocellulose

Quantification of microbe-mediated transformation of nitrocellulose (NC) is limited by the difficult measurement of nitrocellulose mass, especially in complex matrices. Nitrocellulose mass is quantified indirectly, by dissolving NC and measuring nitrate or nitrite substituent concentrations by titration or HPLC. Variation in the percent nitrogen of nitrocellulose among propellant formulations also complicates quantitative analysis. Despite these issues, microbe-mediated transformation of nitrocellulose fines has been reported under nitrate-reducing (Freedman et al. 2002), sulfate-reducing (Freedman et al. 2002; Petrova et al. 2002), and methanogenic (Freeman et al. 1996) conditions. Under nitrate-, sulfate-, and methanogenic reducing conditions, nitrate ester groups on NC are

reduced to nitrogen gas in the presence of methanol, concurrent with decreased percent nitrogen in the remaining nitrocellulose (Freedman et al. 1996; Freedman et al. 2002). However, it seems that the decrease in percent nitrogen that leads to non-reactive nitrocellulose occurs only under methanogenic conditions. Fungus-mediated transformation of nitrocellulose fines has also been reported, although the mechanism was not identified (Sundaram et al. 1995).

Nitroglycerin

Microbe-mediated transformation of nitroglycerine (NG; or glycerol trinitrate) has been documented under aerobic (Bhaumik et al. 1997; Accashian et al. 1998; Accashian et al. 2000; White et al. 1996; Marshall and White 2001) and anaerobic (Wendt et al. 1978; Christodoulatos et al. 1997b; Bhaumik et al. 1997) conditions, by pure and mixed microbe cultures and cell extracts (Ducrocq et al. 1989; Meng et al. 1995; Blehert et al. 1997; Accashian et al. 1998), and fungal cell cultures and extracts (Zhang et al. 1997). Both aerobic and anaerobic transformation pathways are described as successive denitrification reactions, from glycerol-trinitrate, to -dinitrate, then -mononitrate isomer intermediates, ultimately to form glycerol. Four major differences can be defined among biotransformation pathways: 1) the extent to which dinitrate and mononitrate isomer intermediates accumulate and are consumed; 2) whether the transformation pathway stops at the mononitrate compound, or proceeds to glycerol and ultimately to CO₂; 3) whether nitrate and nitrite, as denitrification byproducts, serve as electron acceptors during subsequent steps of the pathway; and 4) identifying the maximum concentration of nitroglycerin or intermediate products that is non-toxic to microbial populations. Typically, transformation of nitroglycerin to glycerol proceeds most readily with a mixed microbial culture under either aerobic (Meng et al. 1995; Accashian et al. 2000) or anaerobic conditions (Christodoulatos et al. 1997b). Transformation of nitroglycerin to glycerol was shown by single cultures of the microbe *Rhodococcus* sp. (Marshall and White 2001), and fungus *Penicillium* (Zhang et al. 1997).

Volatilization of propellant compounds

Vapor pressure and the Henry's law constant are two parameters to quantify the volatility of a compound. The pressure of a gas in equilibrium with pure liquid at a known temperature is its vapor pressure. The Henry's law

constant for a compound is the ratio of dissolved gas concentration (solution) divided by gas partial pressure (vapor). Greater volatility from dry surfaces is suggested by larger vapor pressure values. More extensive partitioning from water or moist soil to gas is indicated by greater Henry's law constant values. Compounds that are volatile have a greater likelihood of photochemical reactions, which will be discussed in the following section. Literature values for vapor pressure and Henry's law constant are listed in Table 4.

Table 4. Henry's law constants and vapor pressures of propellant compounds and their transformation products.

Compound	Henry's Law Constant	Reference	Vapor Pressure	Reference
Oxidizers and their Transformation Products				
Nitroguanidine	$4.67 \times 10^{-16} \text{ atm}\cdot\text{m}^3/\text{mol}^1$	Burrows et al. (1989)	$1.43 \times 10^{-11} \text{ mm Hg}(25^\circ\text{C})$ ⁵	Burrows et al. (1989)
	$<7 \times 10^{-6}$ (dimensionless) ²	Haag et al. (1990)	$<0.04 \text{ mm Hg}(25^\circ\text{C})$	Dave et al. (2000)
	3.1×10^{-14} (dimensionless) ¹	Palmer et al. (1996)	$0.03 \text{ mm Hg}(25^\circ\text{C})$	SRC (2003)
	$4.5 \times 10^{-12} \text{ atm}\cdot\text{m}^3/\text{mol}^3$	SRC (2003)		
Cyanamide	$2.6 \times 10^{-10} \text{ atm}\cdot\text{m}^3/\text{mol}^3$	Swann et al. (1983)	$3.75 \times 10^{-3} \text{ mm Hg}(20^\circ\text{C})$	SRC (2003)
Guanidine HCl				
Melamine	$1.8 \times 10^{-14} \text{ atm}\cdot\text{m}^3/\text{mol}^1$	Weber (1970)	$3.6 \times 10^{-10} \text{ mm Hg}(20^\circ\text{C})$	SRC (2003)
N-nitrosoguanidine				
Ammonium perchlorate				
Potassium chlorate				
Potassium perchlorate				
Stabilizers and their Transformation Products				
Diphenylamine	$2.8 \times 10^{-6} \text{ atm}\cdot\text{m}^3/\text{mol}^1$	Meylan & Howard (1991)	$1 \text{ mm Hg}(108.3^\circ\text{C})$ $6.39 \times 10^{-4} \text{ mm Hg}$	Sax (1979) Drzyzga (2003)
N-nitrosodiphenylamine	$6.4 \times 10^{-4} \text{ atm m}^3/\text{mol}^4$ $1.21 \times 10^{-6} \text{ atm}\cdot\text{m}^3/\text{mol}^1$	USEPA (1987b) Meylan & Howard (1991)	$0.1 \text{ mm Hg}(25^\circ\text{C})$	SRC (2003)
2,4-dinitrodiphenylamine				
2-nitrodiphenylamine				
4-nitrodiphenylamine				
Methyl centralite				
Ethyl centralite				
Burning-Rate Modifiers				
Lead resorcyate				
Lead salicylate				

Compound	Henry's Law Constant	Reference	Vapor Pressure	Reference
Lead stearate				
Plasticizers				
Dimethyl phthalate	$2.0 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	Banerjee et al. (1985)	$1.65 \times 10^{-3} \text{ mm Hg (25 }^\circ\text{C)}$	Howard et al. (1985)
	$2.5 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	USEPA (1987a)	$2.0 \times 10^{-3} \text{ mm Hg (25 }^\circ\text{C)}$	Staples et al. (1997)
			$3.08 \times 10^{-3} \text{ mm Hg (20 }^\circ\text{C)}$	SRC (2003)
Diethyl phthalate	$6.1 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	Hinckley et al. (1990)	$1.65 \times 10^{-3} \text{ mm Hg (25 }^\circ\text{C)}$	Howard et al. (1985)
	$7.8 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	USEPA (1987a)	$1.0 \times 10^{-3} \text{ mm Hg (25 }^\circ\text{C)}$	Staples et al. (1997)
			$2.1 \times 10^{-3} \text{ mm Hg (25 }^\circ\text{C)}$	SRC (2003)
Di-n-butyl phthalate	$4.5 \times 10^{-6} \text{ atm-m}^3/\text{mol}$	Roy (1995)	$7.3 \times 10^{-5} \text{ mm Hg (25 }^\circ\text{C)}$	Howard et al. (1985)
	$2.2 \times 10^{-6} \text{ atm-m}^3/\text{mol}^1$	USEPA (1987a)	$2.7 \times 10^{-5} \text{ mm Hg (25 }^\circ\text{C)}$	Staples et al. (1997)
			$1 \times 10^{-4} \text{ mm Hg (25 }^\circ\text{C)}$	CPIA (2000)
			$2.01 \times 10^{-5} \text{ mm Hg (25 }^\circ\text{C)}$	SRC (2003)
Butylbenzyl phthalate	$1.2 \times 10^{-6} \text{ atm-m}^3/\text{mol}^1$	USEPA (1987a)	$5.0 \times 10^{-6} \text{ mm Hg (25 }^\circ\text{C)}$	Howard et al. (1985)
	$4.78 \times 10^{-6} \text{ atm-m}^3/\text{mol}^1$	SRC (2003)	$6.5 \times 10^{-5} \text{ mm Hg (25 }^\circ\text{C)}$	Staples et al. (1997)
			$8.25 \times 10^{-6} \text{ mm Hg (25 }^\circ\text{C)}$	SRC (2003)
Bis (2-ethylhexyl) phthalate	$1.1 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	USEPA (1987a)	$6.5 \times 10^{-5} \text{ mm Hg (25 }^\circ\text{C)}$	Howard et al. (1985)
	$1.50 \times 10^{-5} \text{ atm-m}^3/\text{mol}^3$	Meylan & Howard (1991)	$7.23 \times 10^{-8} \text{ mm Hg (25 }^\circ\text{C)}$	SRC (2003)
	$1.3 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	SRC (2003)		
Energetic Plasticizers and Binders				
2,4-Dinitrotoluene	3.4 torr /M ¹	Spanggord et al. (1980a)	$1.1 \times 10^{-4} \text{ mm Hg (20 }^\circ\text{C)}$	Pella (1977)
	$8.7 \times 10^{-2} \text{ torr /M}^1$	Layton et al. (1987)	0.08 mm Hg	Dave et al. (2000)
	$1.86 \times 10^{-7} \text{ atm-m}^3/\text{mole}^1$	Burrows et al. (1989)	$2.17 \times 10^{-4} \text{ mm Hg (25 }^\circ\text{C)}$ ⁵	Burrows et al. (1989)
	$1.8 \times 10^{-4} \text{ (dimensionless)}^1$	Palmer et al. (1996)	$5.1 \times 10^{-3} \text{ mm Hg (20 }^\circ\text{C)}$	Spanggord et al. (1980a)
	$1.3 \times 10^{-7} \text{ atm-m}^3/\text{mole}^4$	SRC (2003)		
DEGDN	0.018 torr-L/mol (25°C) ¹	Spanggord et al. (1985)	0.0036 mm Hg (20 °C)	Kitchens et al. (1978)
	$3.83 \times 10^{-7} \text{ atm-m}^3/\text{mol}^1$	Burrows et al. (1989)	0.00593 mm Hg (25 °C)	Holleman et al. (1983)
	0.30 torr/M ¹	Haag et al. (1990)	0.0059 mm Hg (25 °C)	Haag et al. (1991)

Compound	Henry's Law Constant	Reference	Vapor Pressure	Reference
	9.7×10^{-6} (dimensionless) ¹	Palmer et al. (1996)		
Energetic Plasticizers and Binders (continued)				
EGDN	2.8×10^{-6} atm-m ³ /mol ³ 2.52×10^{-6} atm-m ³ /mol ¹ 1.3×10^{-4} (dimensionless)	SRC (2003) Burrows et al. (1989) Palmer et al. (1996)	0.0490 mm Hg (20 °C) 0.0565 mm Hg (22 °C) 0.07059 mm Hg (25 °C) 0.05 mm Hg (20 °C) 0.07043 mm Hg (25 °C) 0.0706 mm Hg (25 °C) 0.045 mm Hg	USA-ARDEC (1983) Verschuren (1983) Holleman et al. (1983) Burrows et al. (1989) Clayton and Clayton (1993)
Nitrocellulose				
Nitroglycerin	0.06 – 3.3 torr/M 2.71×10^{-6} atm-m ³ /mol ¹ 1×10^{-6} (dimensionless) ¹	Spanggord et al. (1980a) Burrows et al. (1989) Palmer et al. (1996)	2.0×10^{-2} mm Hg (20 °C) 3.8×10^{-4} mm Hg (20 °C) 1.8×10^{-3} mm Hg (25 °C) 1.77×10^{-3} mm Hg (25 °C) 2.5×10^{-3} mm Hg	Kemp et al. (1957) Spanggord et al. (1980a) Holleman et al. (1983) Pal and Ryon (1986) Clayton and Clayton (1993)
Note: Shaded cells indicate "no data." ¹ Estimated from vapor pressure and aqueous solubility. ² Estimated from the method of Mackay et al. (1979). ³ Estimated from the structure-activity relationship method of Meylan and Howard (1991). ⁴ Estimated from the method of Lyman et al. (1990). ⁵ Extrapolated from lower or higher temperature data.				

Volatilization from dry surfaces is an important transport pathway for the following compounds: nitroguanidine, EGDN, dimethylphthalate, and nitroglycerin. Volatility is indicated by large vapor pressures generally greater than 10^{-3} torr (equal to 10^{-3} mm Hg at 0 °C, or 0.13328 Pascals (SI), or 1.3168×10^{-6} atmospheres). Significant partitioning to the atmosphere is indicated by larger Henry's law constants (greater than 10^{-6} atm•m²/mol). Partitioning from water or moist soil surfaces to air is an important transport pathway for diphenylamine, nitrosodiphenylamine, EGDN, two of the phthalate compounds (dibutyl phthalate and butylbenzyl phthalate), and nitroglycerin.

Photochemical transformations of propellant compounds

Photochemical transformations may be one of the most important influences on propellant fate in surface and ground water environments. Many propellant compounds are photosensitive, with absorption maxima in the UV-visible range (240 to 290 nm). Products of photochemical transformations of energetic compounds in aqueous solution can be pink or black in color.

Nitroguanidine and its transformation products

Nitroguanidine is transformed readily by photochemical reaction in the ultraviolet spectrum, and under natural sunlight conditions. Nitroguanidine dissolved in solution (5 to 50 mg/L concentration) reacts to form nitrosoguanidine, hydroxyguanidine, and/or cyanoguanidine intermediates, and end-products of guanidine, nitrite, nitrate, and ammonia (Kaplan et al. 1982; Burrows et al. 1988; Haag et al. 1990). Nitrosoguanidine transforms readily to cyanamide under UV light (Kaplan et al. 1982). Cyanamide is not photosensitive (SRC 2003). These products of nitroguanidine photochemical transformation are more toxic than NQ (Van der Schalie 1985; Burrows et al. 1988). No reports of photosensitivity were found for ammonium perchlorate, potassium perchlorate, or potassium chlorate.

Diphenylamine and nitro- and nitroso-substituted transformation products

Diphenylamine and nitrosodiphenylamine in aqueous solution both undergo photochemical transformation to carbazole and tetrahydrocarbazole (Shizuka et al. 1970; Sur et al. 2000; Drzyzga 2003). Photochemical transformation of 2-nitrodiphenylamine in aqueous solution is not reported in the literature, but photo-induced isomerism is hypothesized by Kitchens et al. (1978).

Methyl and ethyl centralite

No references were found that describe phototransformation reactions of methyl and ethyl centralite.

Burning-rate modifiers

No references were found that describe phototransformation of lead salicylate, lead resorcyate, or lead stearate.

Phthalate plasticizers

Few references described photochemical transformation reactions of the phthalate plasticizers. However, where tested, phthalate esters in water degrade within hours of exposure to UV radiation. UV irradiation (254 nm) degraded 90 percent of DNBP in water between pH 3 and 11 to aromatic carboxylic derivatives within 1 hour (Lau et al. 2005). Photo-oxidation (UV/hydrogen peroxide/ferrous iron) degraded 81 percent of DMP within 2 hours (Zhao et al. 2004).

Energetic plasticizers and binders

These compounds (2,4-DNT, EGDN, DEGDN, nitrocellulose, NG) react in sunlight to produce a variety of transformation products, many of which impart color to aqueous solutions.

2,4-Dinitrotoluene

2,4-DNT reacts rapidly by photolysis (wavelengths greater than 290 nm), particularly in alkaline pH solutions. Fifty percent of 2,4-DNT photo-transformed after 5 hours of irradiation at pH of 10.8, resulting in new nitroaromatic compound products (Spanggord et al. 1980). Photolysis rates of 2,4-DNT are enhanced 2 to 5 times in natural waters with humic acids (366 nm; Simmons and Zepp 1986) and aqueous solutions with surfactant (254 nm; Diehl et al. 2002).

EGDN and DEGDN

EGDN as a gas will react with photochemically produced hydroxyl radicals in the atmosphere, with a half-life of 22 days (estimated using the method of Meylan and Howard 1993). DEGDN undergoes photolysis under natural sunlight and in natural, oligotrophic waters to yield nitrate, nitrite, and 2-hydroxyethyl nitrate, and ultimately nitrate and short-chain organic acids (Haag et al. 1991). Half-lives for phototransformation reactions range from 15 to 59 days, depending on season.

Nitrocellulose

Nitrocellulose fibers show color change from white to yellow to brown after exposure to ultraviolet radiation (Selwitz 1988). Apparently, this macroscopic textural change results from changing ratios of carbon, nitrogen, and oxygen, and reduced cross-linking among nitrate esters (Clark and Stephenson 1982).

Nitroglycerin

No references were found that describe phototransformation reactions induced by natural environmental (UV-visible) wavelengths. UV-photocatalytic oxidation technologies can reduce nitroglycerin concentrations in aqueous waste streams (Kempe and Lateulere 1999), but these reactions involve titanium surfaces and wavelengths up to 400 nm.

3 Results of Propellant Leaching Experiments

Experimental methods

Leaching experiments were conducted to determine the sequence and composition of compounds that would leach from single-base (M10, pellet), double-base (M9 grain), and triple-base (M30 pellet) propellants. The external surfaces of propellant grains and pellets were examined by scanning electron microscopy (SEM) to examine textural changes that occurred after 220 hours of stirred immersion in aqueous solution.

Leaching experiments were conducted in stirred flask reactors at room temperature (25 °C). In a 250-mL Erlenmeyer flask, one gram (weighed to ± 0.001 g) of propellant grains (M9) or one pellet (M10, M30) was immersed in 200 mL distilled, deionized water. The solution in the flask was bubbled with N₂ to degas dissolved oxygen, a stir bar was inserted, then the flask was capped (stopper and parafilm). Flasks were wrapped in aluminum foil to prevent phototransformation reactions. Flask reactors were prepared in triplicate to be sampled at time intervals of 0, 6, 24, 48, 72, 120, 144, 168, 192, and 216 hours (long-term experiments; Appendix A). In the case of the M9, nitroglycerin leached from the propellant matrix so rapidly that an additional experiment was performed to sample triplicate reactors intensively during the time period from 0 to 48 hours. For the short-duration leaching experiment using M9 propellant, sampling times occurred at 0, 1, 2, 4, 8, 12, 24, 32, and 48 hours in addition to the long-term experiment (Table A2).

After stirring, each reactor solution was processed for analysis by gas chromatography-mass spectroscopy (GC/MS). Solution was decanted from remaining propellant solid, then spiked with 0.5 mL of 100 µg/L solution of 3,4-DNT to calculate percent recovery during sample processing. Solutions were spiked after propellant solids were removed because sorption of 3,4-DNT to propellant solids resulted in poor percent recoveries. Spiked aqueous solutions (approximately 220 mL) were extracted using Waters

brand Oasis HLB solid-phase extraction cartridges, then eluted with 5 mL HPLC-grade acetonitrile into ultraclean crimp-top crimped vials.

All propellant compound concentrations (except nitroguanidine) were quantified using GC/MS, following a modified USEPA method 8270 (USEPA 2005b; semi-volatile organic compounds). Analyses were performed on a Hewlett Packard model 5890 GC equipped with an Agilent DB5M5 column. The mass spectrometer is an Agilent model 5971 Mass selective detector run in selective ion monitoring mode. The GC/MS has a calibrated range of 0.25 to 40 parts per million. Percent recoveries of 3,4-DNT and propellant compound concentrations (n = 3) at each time interval are reported for M9, M10, and M30 propellant matrices (Appendix A).

Nitroguanidine was analyzed by reverse-phase high performance liquid chromatography (RP-HPLC) following a modified method of Bissett and Levasseur (1976). The RP-HPLC configuration included a 5-micron particle size cyano-propyl HPLC column. The mobile phase was water (71 percent), acetonitrile (21 percent), and methanol (8 percent) at a flow rate of 1.2 mL/min. The RP-HPLC used a mercury lamp UV detector at 254 nm. The calibration range was 0.2 to 19.2 parts per million with a reporting level of 0.2 ppm.

M10 (single-base) propellant leaching results

M10 propellant consists primarily of nitrocellulose (84.2 to 97.8 weight percent of pellet mass; MIDAS 2005), with minor percentages of diphenylamine (1 to 2.9 weight percent,) and (in one formulation) 2,4-DNT (9.9 weight percent; MIL-P-63194). This propellant material is formulated as small pellets. M10 propellant is used in a variety of small caliber (0.50-cal and 40-mm), and large caliber (90-mm, 120-mm, 155-mm, and 8-inch) ammunitions (MIDAS 2005).

Two compounds appeared in aqueous solution containing single M10 pellets after 216 hours of stirring: 2,4-DNT and DPA (Figure 1). The maximum mass of energetic compounds available per pellet is 98 mg (2,4-DNT) and 10 mg (DPA; maximum mass equals total pellet mass x weight percent for each compound). The maximum mass that leached from an M10 pellet after 216 hours was 0.39 mg (2,4-DNT) and 0.03 mg

(DPA). Therefore, significant energetic residues remained in the propellant pellet after 216 hours of stirring. It is not clear that equilibrium between solid and solution was attained because concentrations of 2,4-DNT (and to a lesser extent DPA) increased toward the end of the experiment. The solutions are undersaturated with respect to 2,4-DNT and DPA (Table 2). The aqueous solubility of 2,4-DNT is approximately four times greater than DPA (Table 2). Greater mass and solubility indicate that 2,4-DNT should preferentially leach from M10 propellant pellets, consistent with results shown in Figure 1.

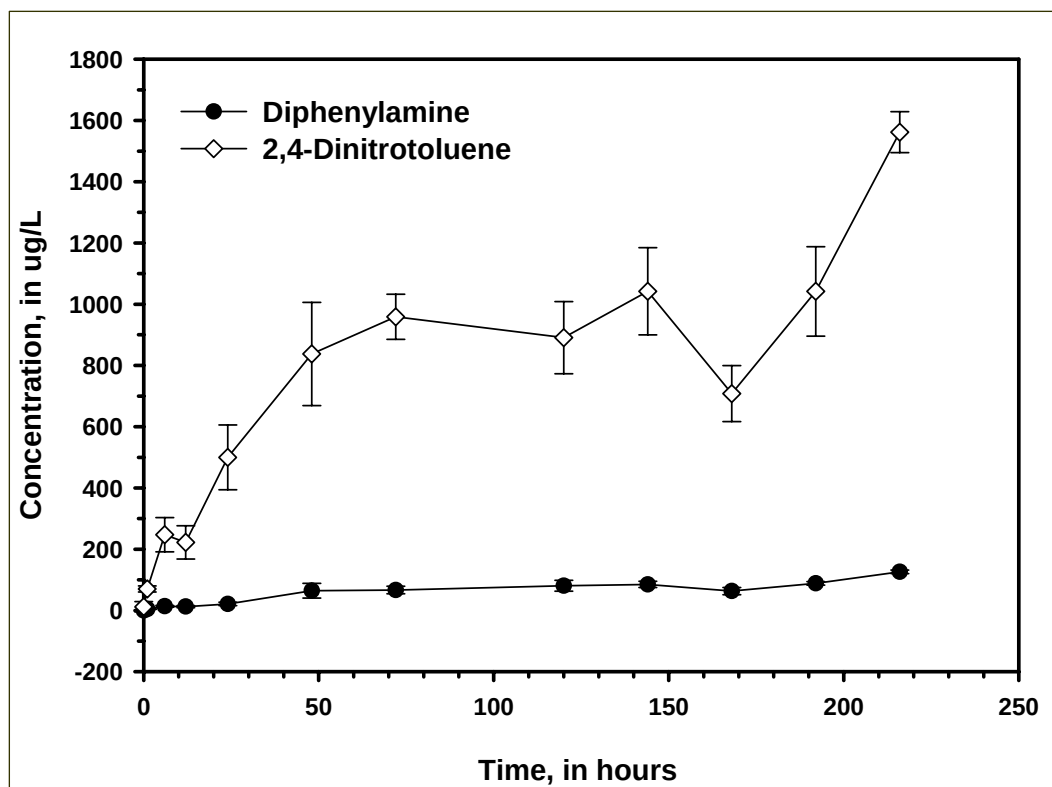


Figure 1. Results of M10 propellant leaching experiment. Concentrations are well below saturation with respect to 2,4-DNT (approximately 200 mg/L; Table 2) and DPA (approximately 40 mg/L). Circles represent the mean of triplicate analyses $\pm$ standard deviation.

SEM of M10 pellet surfaces before and after the experiment show only a subtle “smoother” textural change in the latter (Figure 2). A comparison of textures suggests that the nitrocellulose framework remains mostly intact after 216 hours of stirring, and thus retains most of the energetic compound mass. It is likely that aqueous solubility is not the only control of energetic compound release from M10 propellant pellets into the environment.

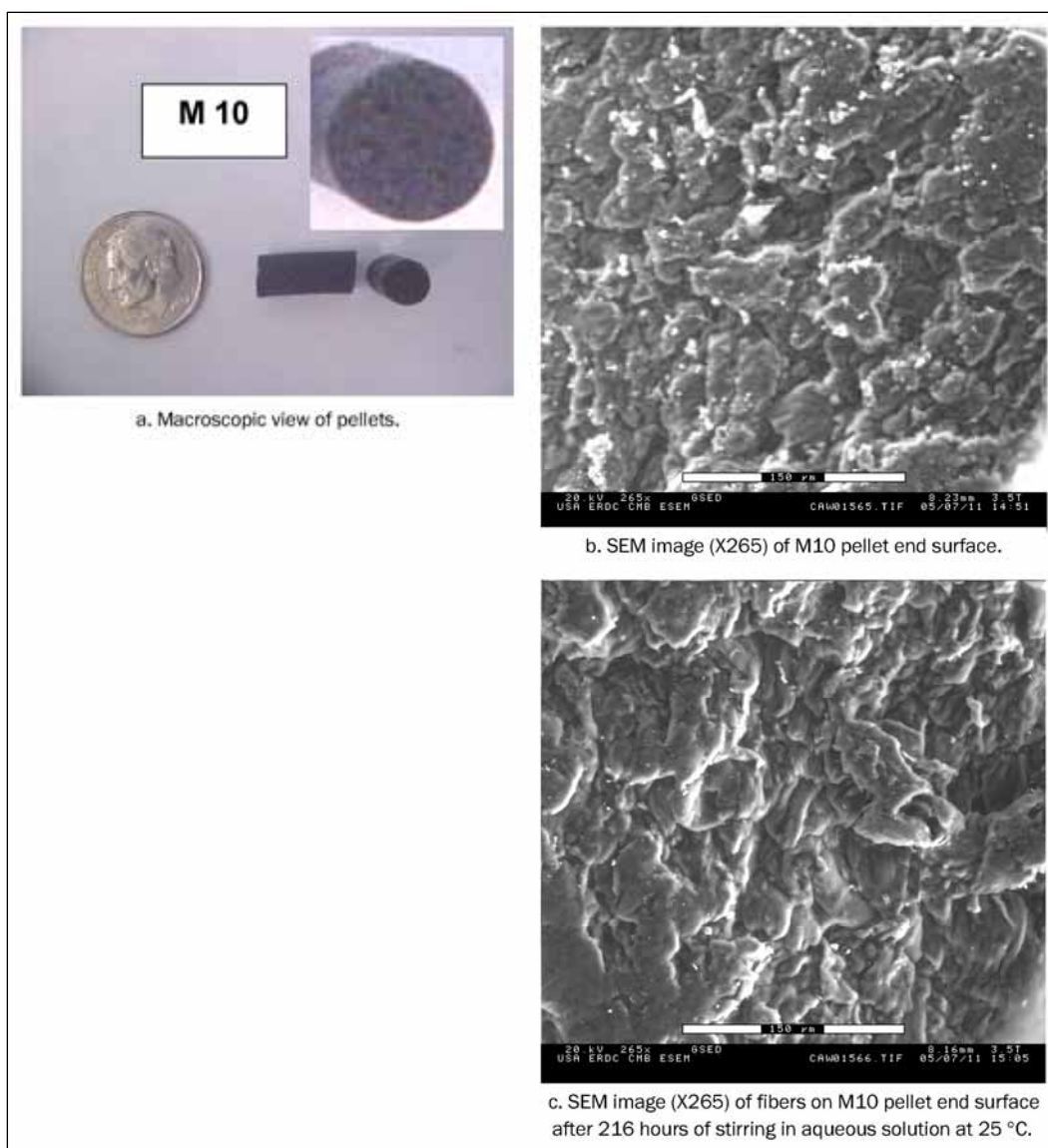


Figure 2. Macroscopic and SEM images of M10 (single-base) propellant.

M9 (double-base) propellant leaching results

M9 propellant consists primarily of nitrocellulose (57.6 to 57.7 weight percent; MIDAS 2005), with nitroglycerin (40 weight percent) and ethyl centralite (0.65 to 0.75 weight percent). The M9 formulation MIL-P-63195 has diphenylamine (0.75 weight percent) instead of EC. This propellant occurs in coarse sand-sized grains rather than pellets. M9 propellant is used in a variety of small (0.50-cal) and large caliber (60-mm, 81-mm, 105-mm, and 4.2-in) ammunition (MIDAS 2005).

Two compounds appeared in aqueous solution from a 1-g sample of M9 propellant grains after 216 hours of stirring: nitroglycerin and ethyl centralite (Figure 3). The maximum mass of energetic compounds available in a 1-g sample (assuming homogeneity) is 400 mg (nitroglycerin) and 7.5 mg (ethyl centralite). The maximum mass of nitroglycerin that leached from the M9 grains was 176 mg, and occurred after 12 hours of stirring. Mean nitroglycerin concentrations reached a plateau after 12 hours, ranging between 135 and 155 mg total mass leached. This plateau suggests that a steady-state condition between solid and solution was reached after 24 hours. Nitroglycerin has high aqueous solubility (Table 2), and presumably can be leached readily from the nitrocellulose matrix. However, concentrations measured throughout this experiment are significantly below saturation. Nitroglycerin is also moderately volatile (Table 4). Some nitroglycerin may have degassed from the solid during storage and sample processing to account for the difference between the leached (176 mg total) and solid (400 mg available) nitroglycerin masses.

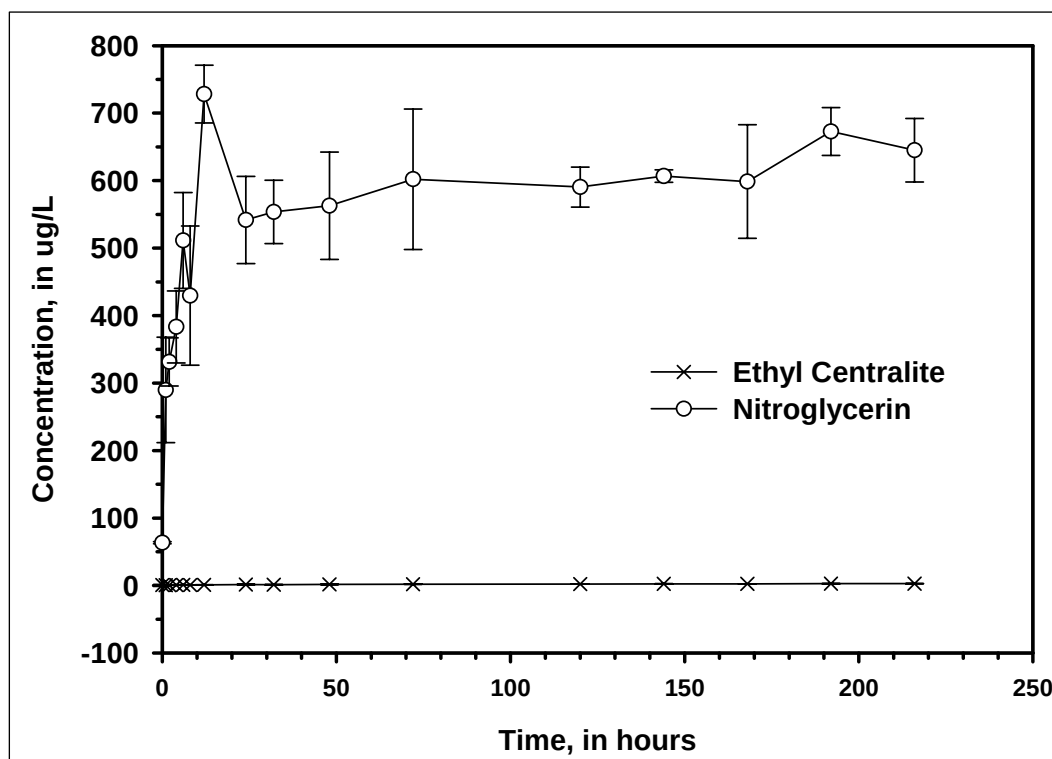


Figure 3. Results of M9 propellant leaching experiment. Concentrations are well below saturation with respect to nitroglycerin (approximately 1,500 mg/L; Table 2) and ethyl centralite (80 mg/L). Circles represent the mean of triplicate analyses +/- standard deviation.

The maximum mass of ethyl centralite that leached from M9 grains was 0.4 mg, (of the ~7.5 mg available). There was no significant change in dissolved ethyl centralite concentration after 24 hours of stirring, suggesting that a steady-state was reached. Ethyl centralite shows low aqueous solubility (Table 2), so it will tend to remain in the solid.

SEM images of M9 grain surfaces before and after the experiment show a rougher, pitted texture after leaching (Figure 4). Pitting suggests preferential dissolution of some component of the propellant solid, most likely the nitroglycerin that serves as a gelatinizer for nitrocellulose.

M30 (triple-base) propellant leaching results

M30 propellant consists primarily of nitrocellulose (27.9 weight percent; MIDAS 2005), with nitroguanidine (47.7 weight percent), nitroglycerin (22.5 weight percent), and ethyl centralite (1.5 weight percent). This propellant occurs as large pellets with longitudinal perforations. M30 propellant is used primarily for large caliber (76-mm, 90-mm, 105-mm, 155-mm, and 8-inch) ammunitions (MIDAS 2005). The pellets consist of compacted white nitrocellulose fibers coated with graphite. The pellets have eight longitudinal perforations to allow more effective conflagration.

Three compounds were released to aqueous solution from single M30 pellets after 216 hours of stirring: nitroglycerin, nitroguanidine, and ethyl centralite (Figure 5). The maximum mass of energetic compounds available per pellet is 832 mg (nitroglycerin), 1,740 mg (nitroguanidine), and 55 mg (ethyl centralite). The maximum mass that leached from an M30 pellet after 216 hours was 109 mg (nitroglycerin), 44.6 mg (nitroguanidine), and 4.6 mg (ethyl centralite). Similar to leaching behavior of M10 pellets, significant energetic residues remained in the M30 pellet after 216 hours. Leached concentrations of nitroglycerin, nitroguanidine, and ethyl centralite were below saturation (Table 2). Equilibrium between solid and solution probably was not attained because concentrations of nitroglycerin and nitroguanidine increased toward the end of the experiment. The aqueous solubility of nitroguanidine is approximately two times greater than that for nitroglycerin (Table 2), so it should leach more readily than nitroglycerin. Instead, it appears that nitroglycerin was leached preferentially (Figure 5). Compaction of nitrocellulose fibers into

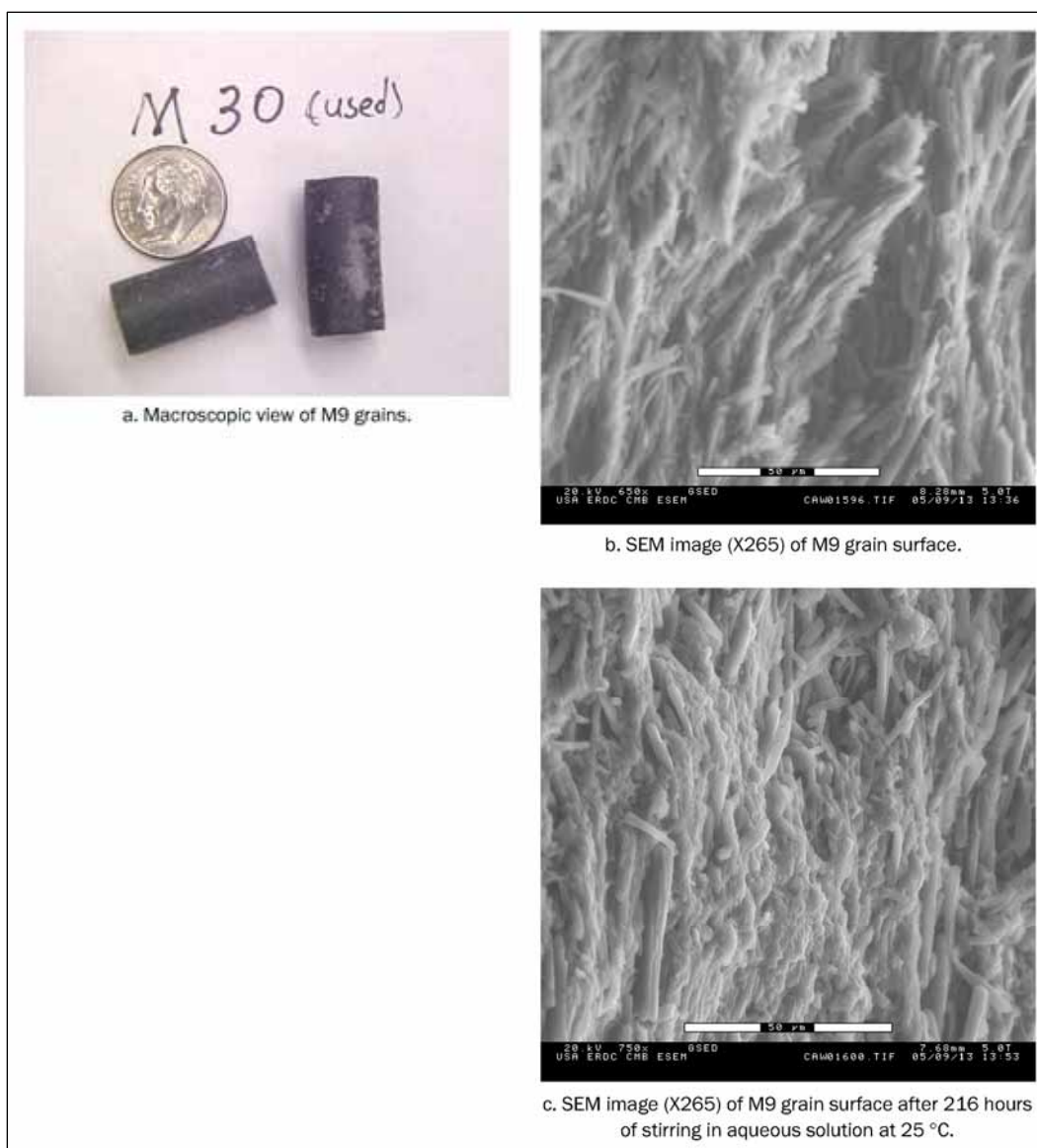


Figure 4. Macroscopic and SEM images of M9 (double-base) propellant.

the pellet morphology will affect the rate and extent of leaching of energetic compounds, even those with high aqueous solubilities. The association of nitroglycerin versus nitroguanidine with the nitrocellulose matrix may be responsible for differential leaching behavior.

M30 pellets were examined by scanning electron microscopy before and after the leaching experiment (Figure 6). Scanning electron microscopy of interior nitrocellulose fibers before and after the leaching experiment show a less fibrous morphology in the latter. This may result from

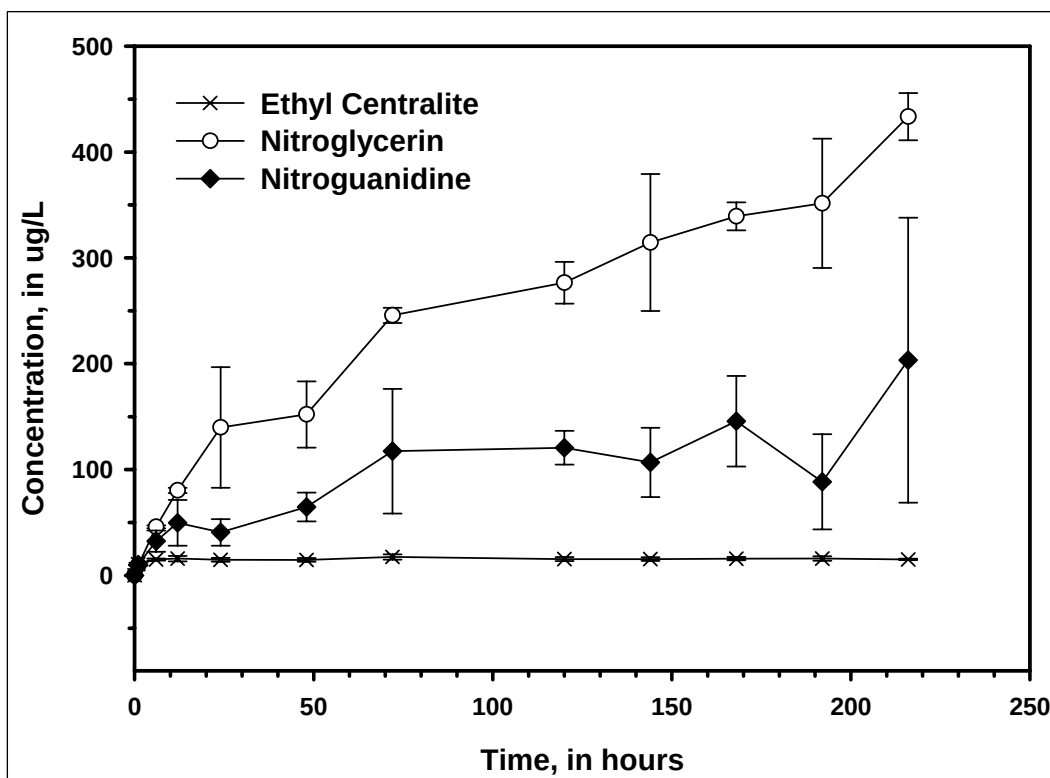


Figure 5. Results of M30 propellant leaching experiment. Concentrations are well below saturation with respect to nitroglycerin (approximately 1,500 mg/L), nitroguanidine (approximately 4 g/L) and ethyl centralite (80 mg/L). Circles represent the mean of triplicate analyses +/- standard deviation.

leaching of energetic compounds from the fibers. Little morphologic change was observed in the graphite coating of pellets before and after the leaching experiment.

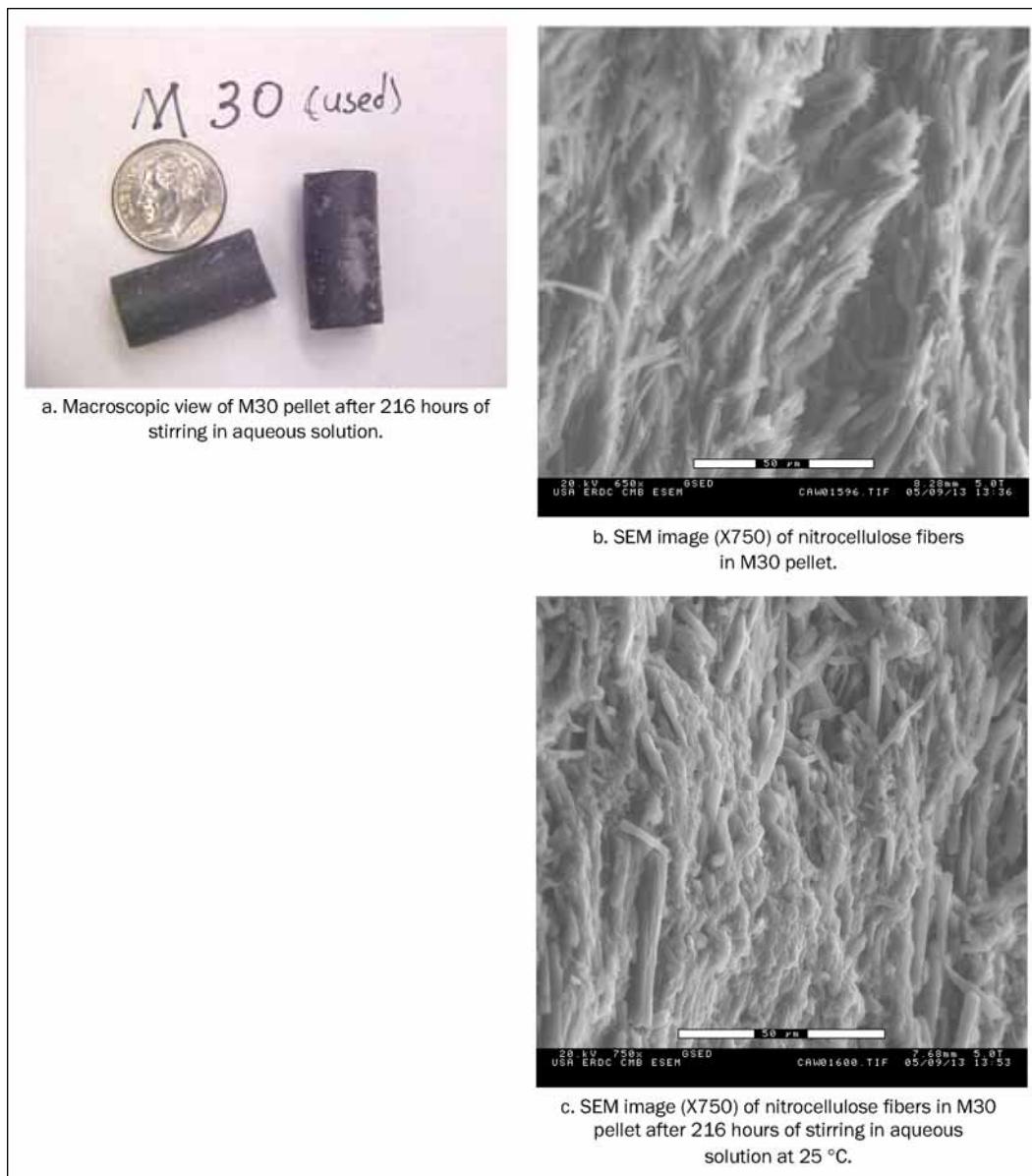


Figure 6. Macroscopic and SEM images of M30 (triple-base) propellant.

4 Conclusions and Recommendations

Conclusions

This report reviews the predominant reaction processes that control the transport and fate of propellant compounds in soils, surface water, and ground water. Processes described include dissolution, hydrolysis, sorption, biotransformation, volatilization, and phototransformation. Most descriptors reviewed here characterize the extent or equilibrium condition of a process, rather than the rate. Extent of a process is indicated by equilibrium solute concentration as a reflection of solubility, or partition coefficients such as K_d , K_{ow} , K_{oc} , and Henry's law constants. There are few works that quantify the rates of propellant compound transformations. The most common examples of rate determinations are for biotransformation reactions, in which compound disappearance is expressed as a half-life measured under controlled conditions. For some transformation processes, notably phototransformation, reaction mechanisms and products are not yet clearly defined.

There is significant variation in some process descriptors for certain propellant compounds. Considering aqueous solubilities, the values reported for highly soluble compounds (such as nitroguanidine and perchlorate) are in close agreement. In contrast, aqueous solubilities for sparingly soluble compounds (such as diphenylamine and transformation products, and ethyl and methyl centralite) are more problematic and poorly quantified. A similar condition exists for vapor pressure, and Henry's law constants. An important, fairly volatile compound such as nitroglycerin shows vapor pressure values and Henry's law constants that vary over two orders of magnitude. Less volatile, but also important is 2,4-dinitrotoluene, for which reported vapor pressures vary over two orders of magnitude. Vapor pressures and Henry's law constants for diphenylamine and transformation products are not well quantified.

Conventional propellants used in artillery ammunition are composite materials that consist primarily of energetic compounds and stabilizers within a nitrocellulose matrix. The process parameters tabulated here only describe transport and fate processes after the compounds are released

from the nitrocellulose matrix. Simple leaching experiments conducted here indicate that aqueous solubility alone does not control the release of propellant compounds from the nitrocellulose matrix for the following reasons: 1) prolonged exposure to saturated conditions releases only a small fraction of energetic compound mass; and 2) textural changes after prolonged saturation are subtle, suggesting that the nitrocellulose matrix is chemically and structurally stable. Therefore, leaching of soluble components becomes increasingly diffusion-limited as leaching progresses toward completion. Release of energetic compounds from nitrocellulose may be accelerated under conditions that favor nitrocellulose breakdown, probably by biodegradation and phototransformation processes that work in concert to reduce the barrier to propellant leaching and reactive transport in soil and ground water environments.

Recommendations

Transport and fate processes of propellant-associated compounds in the environment require further definition and refinement. A conceptual model that describes the release of propellant material in the context of training activities is needed to support the development of risk assessments at Army training ranges. The association of high explosives concentrations near low-order detonations has been well-quantified; however, the extent to which propellant compounds (nitrocellulose and other energetic compounds) are distributed near low-order detonations or other potential point sources is not well known. On-going efforts are beginning to quantify propellant residues and fluxes at potential source areas (e.g., Hewitt and Bigl 2005).

A major issue that constrains our ability to define the transport and fate of propellant compounds is the lack of a suitable method to quantify nitrocellulose fiber residues in soils. Anecdotal evidence indicates that nitrocellulose fibers are imbued with explosives and propellant compound residues, so that the distribution of these residues in soil environments is in part controlled by the distribution of nitrocellulose. An analytical method to quantify nitrocellulose fiber mass and concentration is in development (Macmillan in review), and this will lead to better quantification of propellant residues in soils.

More thorough experiments should be conducted to quantify the environmental biogeochemical variables that control the leaching of soluble propellant compounds from nitrocellulose matrices.

References

- Ainsworth, C. C., S. D. Harvey, J. E. Szecsody, M. A. Simmons, V. I. Cullinan, T. C. Resch, and G. M. Mong. 1993. *Relationship between the leachability characteristics of unique energetic compounds and soil properties*. ADA 267580. Richland, WA: Batelle Memorial Institute, Pacific Northwest Laboratory.
- Accashian, J. V., R. T. Vinopal, B-J. Kim, and B. F. Smets. 1998. Aerobic growth on nitroglycerin as the sole carbon, nitrogen, and energy source by a mixed bacterial culture. *Applied and Environmental Microbiology* 64(9): 3300-3304.
- Accashian, J. V., B. F. Smets, and B-J. Kim. 2000. Aerobic biodegradation of nitroglycerin in a sequencing batch reactor. *Water Environment Research* 72(4): 499-506.
- Adrian, N. R. 1996. *The biodegradation of propellants M31A1E1 and NOSIH-AA2 in compost, soil slurries, and liquid cultures*. Technical Report 96/83. Champaign, IL: U.S. Army Construction Engineering Research Laboratories.
- Altfelder, S., T. Streck, M. A. Maraqa, and T. C. Voice. 2001. Nonequilibrium sorption of dimethylphthalate – compatibility of batch and column techniques. *Soil Science Society of America Journal* 65:102-111.
- Angelidaki, I., A. S. Mogensen, and B. K. Ahring. 2000. Degradation of organic contaminants found in organic waste. *Biodegradation* 11: 377-383.
- Ase, P., W. Eisenberg, S. Gordon, K. Taylor, and A. Snelson. 1985. Propellant combustion product analyses on an M16 rifle and a 105-mm caliber gun. *Journal of Environmental Science and Health A20*(3): 337-368.
- Ashford, R. D. 1994. *Ashford's dictionary of industrial chemicals*. 82 and 758. London, England: Wavelength.
- Attaway, H. J. 1994. *Biodegradation of nitroglycerin and perchlorate in propellant wastewater*. AFRL-ML-TY-TR-1998-4547 (ADA361298). Tyndall Air Force Base, FL: Air Force Research Laboratory.
- Banat, F. A., S. Prechtel, and F. Bischof. 1999. Experimental assessment of bio-reduction of di-2-ethylhexyl phthalate (DEHP) under aerobic thermophilic conditions. *Chemosphere* 39(12): 2097-2106.
- Banerjee, P., M. D. Piwoni, and K. Ebeid. 1985. Sorption of organic contaminants to a low carbon subsurface core. *Chemosphere* 14(8): 1057-1067.
- Baughman, G. L., and T. A. Perenich. 1988. Fate of dyes in aquatic ecosystems: I. Solubility and partitioning of some hydrophobic dyes and related compounds. *Environmental Toxicology and Chemistry* 7: 183-199.

- Beeder, J., T. Torsvick, and T. Lien. 1995. *Thermodesulforhabdus norvegicus* gen. nov., sp. nov., a novel thermophilic sulfate-reducing bacterium from oil field water. *Archives of Microbiology* 164(5): 331-336.
- Benckiser, G., and J. C. G. Ottow. 1982. Metabolism of the plasticizer di-normal-butylphthalate by *Pseudomonas pseudoalcaligenes* under anaerobic conditions, with nitrate as the only electron-acceptor. *Applied and Environmental Microbiology* 44(3): 576-578.
- Bergens, A., K. Lundström, and J. Asplund. 1985. Voltammetric determination of the stabilizing additives acardite II, centralite I, and diphenylamine in propellants. *Talanta* 32(9): 893-899.
- Bhaumik, S., C. Christodoulatos, G. P. Korfiatis, and B. W. Brodman. 1997. Aerobic and anaerobic biodegradation of nitroglycerin in batch and packed bed bioreactors. *Water Science and Technology* 36(2-3): 139-146.
- Bissett, F. H., and L. A. Levasseur. 1976. *Analytical methods for nitroguanidine and characterization of its degradation products*. Technical Report-76/47 (ADA-034-455). Natick, MA: U.S. Army Natick Research and Development Command.
- Bleher, D. S., K. L. Knoke, B. G. Fox, and G. H. Chambliss. 1997. Regioselectivity of nitroglycerin dinitration by flavoprotein nitroester reductases purified from two *Pseudomonas* species. *Journal of Bacteriology* 179(22): 6912-6920.
- Boudeau, D. T. 1993. Military energetic materials: explosives and propellants. In *Occupational health-the soldier and the industrial base*, ed. D. P. Deeter and J. C. Gaydos, 205-357. Washington, DC: Office of the Surgeon General, Walter Reed Medical Center.
- Bradley, P. M., F. H. Chapelle, J. E. Landmeyer, and J. G. Schumacher. 1994. Microbial transformation of nitroaromatics in surface soils and aquifer material. *Applied and Environmental Microbiology* 60(6): 2170-2175.
- Bradley, P. M., F. H. Chapelle, J. E. Landmeyer, and J. G. Schumacher. 1997. Potential for intrinsic bioremediation of a DNT-contaminated aquifer. *Ground Water* 35(1): 12-17.
- Budavari, S., et al., ed. 1996. *The Merck Index – An encyclopedia of chemicals, drugs, and biologicals*. 12th ed., 420 and 924. Whitehouse Station, NJ: Merck & Co.
- Burrows, W. D., M. O. Schmidt, R. H. Chyrek, and C. I. Noss. 1988. *Photochemistry of aqueous nitroguanidine*. Technical Report 8808 (ADA-203200). Fort Detrick, MD: U.S. Army Biomedical Research and Development Laboratory.
- Burrows, E. P., D. H. Rosenblatt, W. R. Mitchell, and D. L. Parmer. 1989. *Organic explosives and related compounds. Environmental and health considerations*. ADA210554, USABRDL-TR-8901. Fort Detrick, MD: U.S. Army Biomedical Research and Development Laboratory.

- Cannizzo, L. F., G. L. Mower, L. R. Huntsman, W. R. Achatz, and W. W. Edwards. 1995. Hydrolysis of the energetic materials present in a composite modified double base solid rocket propellant. *Journal of Energetic Materials* 13: 331-356.
- Capellos, C., W. J. Fisco, C. Ribaudo, V. D. Hogan, J. Campisi, F. X. Murphy, T. C. Castorina, and D. H. Rosenblatt. 1984. Basic hydrolysis of glyceryl nitrate esters, III. Trinitroglycerine. *International Journal of Chemical Kinetics* 16: 1027-1051.
- Chang, B. V., C. M. Yang, C. H. Cheng, and S. Y. Yuan. 2004. Biodegradation of phthalate esters by two bacteria strains. *Chemosphere* 55(4): 533-538.
- Chaudhuri, S. K., S. M. O'Connor, R. L. Gustavson, L. A. Achenbach, and J. D. Coates. 2002. Environmental factors that control microbial perchlorate reduction. *Applied and Environmental Microbiology* 68(9): 4425-4430.
- Cheng, J., M. T. Suidan, and A. D. Venosa. 1998. Anaerobic biotransformation of 2,4-dinitrotoluene with ethanol, methanol, acetic acid and hydrogen as primary substrates. *Water Research* 32(10): 2921-2930.
- Christodoulatos, C., A. D. Koutsospyros, B. W. Brodman, and G. P. Korfiatis. 1997a. Biodegradation of diphenylamine by selected microbial cultures. *Journal of Environmental Sciences and Health A32*(1): 15-30.
- Christodoulatos, C., H. Syamalendu, and B. W. Brodman. 1997b. Anaerobic biodegradation of nitroglycerin. *Water Research* 32(6): 1462-1470.
- Christodoulatos, C., T. L. Su, and A. Koutsospyros. 2001. Kinetics of the alkaline hydrolysis of nitrocellulose. *Water Environment Research* 73(2): 185-191.
- Christopher, H. J., G. D. Boardman, and D. L. Freedman. 2000. Aerobic biological treatment of 2,4-dinitrotoluene in munitions plant wastewater. *Water Research* 34(5): 1595-1603.
- Clark, D. T., and P. J. Stephenson. 1982. An ESCA study of the surface chemistry of cellulose nitrates and double based propellants, with particular reference to their degradation in ultra-violet light. *Polymer Degradation and Stability* 4(3): 185-193.
- Clayton, G. D., and F. E. Clayton, ed. 1993. Patty's industrial hygiene and toxicology. In *Toxicology*. 4th ed., 2(A,B,C), 629, 638. New York, NY: John Wiley.
- Coates, J. D., U. Michaelidou, S. M. O'Connor, R. A. Bruce, and L. A. Achenbach. 2000. The diverse microbiology of (per)chlorate reduction. In *Perchlorate in the environment*, ed. E. T. Urbansky, 257-270. New York, NY: Kluwer Academic/Plenum.
- Cornell, J. H., T. M. Wendt, N. G. McCormick, D. L. Kaplan, and A. M. Kaplan. 1981. *Biodegradation of nitrate esters used as military propellants*. ADA-149665, NATICK/TR-81/029. Natick, MA: U.S. Army Natick Research and Development Center.

- CPIA (Chemical Propulsion Information Agency). 2000. *CPIA/M3, Solid propellant ingredients manual*. ed. E. J. Mulder. Columbia, MD: Johns Hopkins University.
- Curtis, N. J. 1987. *Syntheses and characterizations of derivatives of ethyl centralite*. Technical Report WSRL-0563-TR (ADA198333). Adelaide, Australia: Weapon Systems Research Lab.
- Dave, G., E. Nillson, and A-S. Wernersson. 2000. Sediment and water phase toxicity and UV-activation of six chemicals used in military explosives. *Aquatic Ecosystem Health and Management* 3: 291-299.
- DeBruijn, J., F. Busser, W. Seinen, and J. Hermens. 1989. Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the 'slow-stirring' method. *Environmental Toxicology and Chemistry* 8: 499-512.
- Diehl, C. A., C. T. Jafvert, K. A. Marley, and R. A. Larson. 2002. Surfactant-assisted UV-photolysis of nitroarenes. *Chemosphere* 46: 553-560.
- DiGennaro, P., E. Collina, A. Franzetti, M. Lasagni, A. Luridiana, D. Pitea, and G. Bestetti. 2005. Bioremediation of diethylhexyl phthalate contaminated soil: a feasibility study in slurry- and solid-phase reactors. *Environmental Science & Technology* 39(1): 325-330.
- Drzyzga, O. 2003. Diphenylamine and derivatives in the environment: a review. *Chemosphere* 53: 809-818.
- Drzyzga, O., and K-H. Blotevogel. 1997. Microbial degradation of diphenylamine under anoxic conditions. *Current Microbiology* 35: 343-347.
- Drzyzga, O., A. Schmidt, and K-H. Blotevogel. 1995. Reduction of nitrated diphenylamine derivatives under anaerobic conditions. *Applied and Environmental Microbiology* 61(9): 3282-3287.
- Drzyzga, O., A. Schmidt, and K-H. Blotevogel. 1996. Cometabolic transformation and cleavage of nitrodiphenylamines by three newly isolated sulfate-reducing bacterial strains. *Applied and Environmental Microbiology* 62(5): 1710-1716.
- DuBois, F. W., and J. F. Baytos. 1991. *Weathering of explosives for twenty years*. Los Alamos Scientific Laboratory Report LA-11931. Los Alamos, NM: Los Alamos National Laboratory.
- Ducrocq, C., C. Servy, and M. Lenfant. 1989. Bioconversion of glyceryl trinitrate into mononitrates by *Geotrichum candidum*. *FEMS Microbiology Letters* 65(1-2): 219-222.
- Dutta, S. K., G. P. Hollowell, F. M. Hashem, and L. D. Kuykendall. 2003. Enhanced bioremediation of soil containing 2,4-dinitrotoluene by a genetically modified *Sinorhizobium melilotic*. *Soil Biology and Biochemistry* 35: 667-675.
- Ejlertsson, J., U. Meyerson, and B. H. Svensson. 1996. Anaerobic degradation of phthalic acid esters during digestion of municipal solid waste under landfilling conditions. *Biodegradation* 7(4): 345-352.

- Ejlertsson, J., M. Alnervik, S. Jonsson, and B. H. Svensson. 1997. Influence of water solubility, side-chain degradability, and side-chain structure on the degradation of phthalic acid esters under methanogenic conditions. *Environmental Science and Technology* 31(10): 2761-2764.
- Ellington, J. J. 1999. Octanol/water partition coefficients and water solubilities of phthalate esters. *Journal of Chemical Engineering Data* 44(6): 1414-1418.
- Englehardt, G., and P. R. Wallnöfer. 1978. Metabolism of di- and mono-butyl phthalate by soil bacteria. *Applied and Environmental Microbiology* 35(2): 243-246.
- Fetter, C. W. 1999. *Contaminant hydrogeology*. 2nd ed., 121-144. Upper Saddle River, NJ: Prentice Hall.
- Fortner, J. D., C. Ahang, J. C. Spain, and J. B. Hughes. 2003. Soil column evaluation of factors controlling biodegradation of DNT in the vadose zone. *Environmental Science & Technology* 37(15): 3382-3391.
- Freedman, D. L., B. M. Caenepeel, and B. J. Kim. 1996. Biotransformation of nitro-cellulose under methanogenic conditions. *Water Science and Technology* 34(5-6): 327-334.
- Freedman, D. L., J. M. Cashwell, and B. J. Kim. 2002. Biotransformation of explosive-grade nitrocellulose under denitrifying and sulfidogenic conditions. *Waste Management* 22: 283-292.
- Gallus, C., and B. Schink. 1998. Anaerobic degradation of α -resorcyate by *Ithauera aromatica* strain AR-1 proceeds via oxidation and decarboxylation to hydroxyhydroquinone. *Archives of Microbiology* 169(4): 333-338.
- Gardner, A. M., G. H. Alvarez, and Y. Ku. 1982. Microbial degradation of ¹⁴C-diphenylamine in a laboratory model sewage sludge system. *Bulletin of Environmental Toxicology and Chemistry* 28: 91-96.
- Gavala, H. N., F. Alatrliste-Mondragon, R. Iranpour, and B. K. Ahring. 2003. Biodegradation of phthalate esters during mesophilic anaerobic digestion of sludge. *Chemosphere* 52: 673-682.
- Gibbs, T. R., and A. Popolato. 1980. *LASL explosive property data*. 61-68. Berkeley, CA: University of California.
- Giblin, T., D. Herman, M. A. Deshusses, and W. T. Frankenberger, Jr. 2000. Removal of perchlorate in ground water with a flow-through reactor. *Journal of Environmental Quality* 29: 578-583.
- Gledhill, W. E., R. G. Kaley, W. J. Adams, O. Haley, P. R. Michael, V. W. Saenger, and G. A. LeBlanc. 1980. An environmental safety assessment of butyl benzyl phthalate. *Environmental Science & Technology* 14: 301-305.
- Grayson, M., ed. 1985. *Kirk-Othmer concise encyclopedia of chemical technology*. 3rd ed., 1318. New York, NY: John Wiley.

- Gupta, G., H. Bhaskaran, G. Kananen, and J. Okoh. 2004. Biodegradation of 2,4-dinitrotoluene using poultry litter leachate. *Journal of Hazardous Materials* B113: 135-140.
- Gurol, M. D., and K. Kim. 2000. Investigation of perchlorate removal in drinking water sources by chemical methods. In *Perchlorate in the environment*, ed. E. T. Urbansky, 271-283. New York, NY: Kluwer Academic/Plenum.
- Haag, W. R., R. Spanggord, T. Mill, R. T. Podoll, T-W. Chou, D. S. Tse, and J. C. Harper. 1990. Aquatic environmental fate of nitroguanidine. *Environmental Toxicology and Chemistry* 9: 1369-1367.
- Haag, W. R., R. Spanggord, T. Mill, R. T. Podoll, T-W. Chou, D. S. Tse, and J. C. Harper. 1991. Fate of diethylene glycol dinitrate in surface waters. *Chemosphere* 23(2): 215-230.
- Haberman, J. 1986. *High performance liquid chromatography of propellants, part I: Analysis of M1, M6, and M10 propellants*. Technical Report ARAED-TR-86017 (ADA168206). Dover, NJ: U.S. Army Armament Research and Development Center.
- Hansch, C., A. Leo, and D. Hoekman. 1995. Exploring QSAR. In *Hydrophobic, electronic and stearic constants*, 2:368. Washington, DC: American Chemical Society.
- Hashimoto, Y., K. Tokura, K. Ozaki, and W. M. J. Strachen. 1982. A comparison of water solubilities by the flask and micro-column methods. *Chemosphere* 11(10): 991-1001.
- Hashizume, K., J. Nanya, C. Toda, T. Yasui, H. Nagano, and N. Kojima. 2002. Phthalate esters detected in various water samples and biodegradation of the phthalates by microbes isolated from river water. *Biological Pharmacology Bulletin* 25(2): 209-214.
- Herman, D. C., and W. T. Frankenberger, Jr. 1999. Bacterial reduction of perchlorate and nitrate in water. *Journal of Environmental Quality* 28: 1018-1024.
- Hewitt, A.D., and S. R. Bigl. 2005. *Elution of energetic compounds from propellant and composition B residues*. ERDC/CRREL TR-05-13. Hanover, NH: U.S. Army Engineer Research and Development Center. Available for download at http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR05-13.pdf.
- Hinckley, D. A., T. R. Bidleman, W. T. Foreman, and J. R. Tuschall. 1990. Determination of vapor pressures for non-polar and semipolar organic compounds from gas chromatographic retention data. *Journal of Chemical Engineering Data* 35: 232-237.
- Holleman, J. W., R. H. Ross, and J. W. Carroll. 1983. *Problem definition study on the health effects of diethyleneglycol dinitrate, triethyleneglycol dinitrate, and trimethylo-ethane trinitrate and their respective combustion products*. ADA127846, ORNL/EIS-202. Oak Ridge, TN: Oak Ridge National Laboratory.

- Howard, P. H., S. Banerjee, and K. H. Robillard. 1985. Measurement of water solubilities, octanol/water partition coefficients and vapor pressures of commercial phthalate esters. *Environmental Toxicology and Chemistry* 4: 653-661.
- Hughes, J. B., C. Y. Want, and C. Zhang. 1999. Anaerobic biotransformation of 2,4-dinitrotoluene and 2,6-dinitrotoluene by *Clostridium acetobutylicum*: a pathway through dihydroxlamino intermediates. *Environmental Science & Technology* 33(7): 1065-1070.
- IPI (Island Pyrochemical Industries Inc.). 2003. Propellant stabilizers, <http://www.islandgroup.com/PropellantStabilizers.html> (5 Jun 2003).
- Jenkins, T. F. 1989. Development of an analytical method for the determination of extractable nitroaromatics and nitramines in soils. PhD. diss., Univ. of New Hampshire.
- Jobling, S., T. Reynolds, R. White, M. G. Parker, and J. P. Sumpter. 1995. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103: 582-587.
- Johnson, B. T., M. A. Heitkamp, and J. R. Jones. 1984. Environmental and chemical factors influencing the biodegradation of phthalic acid esters in freshwater sediments. *Environmental Pollution B*(8): 101-118.
- Jonsson, S., J. Ejlertsson, and B. H. Svensson. 2003. Behavior of mono- and diesters of *o*-phthalic acid in leachates released during digestion of municipal solid waste under landfill conditions. *Advances in Environmental Research* 7(2): 429-440.
- Kaplan, D. L., J. T. Walsh, and A. M. Kaplan. 1981. *Decomposition of glycols from nitrate ester propellants*. Natick/TR-81/017. Natick, MA: U.S. Army Natick Research and Development Center.
- Kaplan, D. L., J. H. Cornell, and A. M. Kaplan. 1982. Decomposition of nitroguanidine. *Environmental Science & Technology* 16: 488-492.
- Kaplan, D. L., and A. M. Kaplan. 1985. *Degradation of nitroguanidine in soils*. Natick/TR-85/047, (ADA157859). Natick, MA: U.S. Army Natick Research and Development Center.
- Karegoudar, T. B., and B. G. Pujar. 1984. Metabolism of diethylphthalate by a soil bacterium. *Current Microbiology* 11(6): 321-324.
- Kemme, M. R., and M. Lateulere. 1999. *Reducing air pollutant emissions from solvent multi-base propellant production*. CERL TR 99/71. Champaign, IL: U.S. Army Engineer Research and Development Center.
- Kemp, M. D., S. Goldhagen, and F. A. Zihlman. 1957. Vapor pressures and cryoscopic data for some aliphatic dinitroxy and trinitroxy compounds. *Journal of Physical Chemistry* 61(2): 240-242.

- Kenyon, K. F. 1982. *A data base assessment of environmental fate aspects of nitro-guanidine*. Technical Report 8412. Fort Detrick, MD: U.S. Army Bioengineering Research and Development Laboratory.
- Kim, K., and B. E. Logan. 2001. Microbial reduction of perchlorate in pure and mixed culture packed-bed bioreactors. *Water Research* 35(13):3071-3076.
- Kim, Y-H., J. Lee, J-Y. Ahn, M. B. Gu, and S-H. Moon. 2002. Enhanced degradation of an endocrine-disrupting chemical, butyl benzyl phthalate, by *Fusarium oxysporum* f. sp. *pisi* Cutinase. *Applied and Environmental Microbiology* 68(9): 4684-4688.
- Kirchner, D. B., J. C. Gaydos, and M. C. Battigelli. 1993. Combustion products of propellants and ammunition. In *Occupational health – the soldier and the industrial base*. ed. D. P. Deeter and J. C. Gaydos, 359-396. Washington, DC: Walter Reed Medical Center, Office of the Surgeon General.
- Kitchens, J. F., W. E. Harward III, D. M. Lauter, R. S. Wentsel, and R. S. Valentine. 1978. Preliminary problem definition study of 48 munitions-related chemicals, vol. II. *Propellant-related chemicals*, ADA066308. Alexandria, VA: Atlantic Research Corp.
- Kleerebezem, R., L. W. Hulshoff Pol, and L. Lettinga. 1999a. Anaerobic biodegradability of phthalic acid isomers and related compounds. *Biodegradation* 10:63-73.
- Kleerebezem, R., L. W. Hulshoff Pol, and G. Lettinga. 1999b. Anaerobic degradation of phthalate isomers by methanogenic consortia. *Applied and Environmental Microbiology* 65(3): 1152-1160.
- Lau, T. K., W. Chu, and N. Graham. 2005. The degradation of endocrine disruptor di-n-butyl phthalate by UV irradiation: A photolysis and product study. *Chemosphere* 60(8): 1045-1053.
- Layton, D., B. Mallon, W. Mitchell, L. Hall, R. Fish, L. Perry, G. Snyder, K. Bogen, W. Malloch, C. Ham, and P. Dowd. 1987. *Conventional weapons demilitarization: A health and environmental effects database assessment*. UCRL-21109, 427. Livermore, CA: Environmental Sciences Division, Lawrence Livermore Laboratory.
- Letinski, D. J., M. J. Connelly, Jr., D. R. Peterson, and T. F. Parkerton. 2002. Slow-stir water solubility measurements of selected alcohols and diesters. *Chemosphere* 48: 257-265.
- Leyder, F., and P. Boulanger. 1983. Ultraviolet adsorption, aqueous solubility, and octanol-water partition coefficients for several phthalates. *Bulletin of Environmental Contamination and Toxicology* 30:152-157.
- Lieb, R. J., and J. M. Heimerl. 1994. *Characteristics of JAX gun propellants*. ARL-TR-465, AMSRL-WT-PA. Aberdeen Proving Ground, MD: U.S. Army Research Laboratory.
- Logan, B. E. 1998. A review of chlorate- and perchlorate-respiring microorganisms. *Bioremediation Journal* 2(2): 69-79.

- Logan, B. E., J. Wu, and R. F. Unz. 2001. Biological perchlorate reduction in high salinity solutions. *Water Research* 35(12): 3034-3038.
- Lyman, W. J., D. H. Rosenblatt, and W. F. Reehl. 1990. *Handbook of chemical property estimation methods: Environmental behavior of organic compounds*. 960. London: Oxford University.
- Mackay, D., W. Y. Shiu, and R. P. Sutherland. 1979. Determination of Henry's law constants for hydrophobic pollutants. *Environmental Science and Technology* 12: 333-337.
- Macmillan, D. K. (in review). A reproducible method for determination of nitrocellulose in soil. Submitted to *Journal of Environmental Monitoring*, January 2006.
- Madsen, P. L., J. B. Thyme, K. Henriksen, P. Moldrup, and P. Roslev. 1999. Kinetics of di-(2-ethylhexyl)phthalate mineralization in sludge-amended soil. *Environmental Science & Technology* 33(15): 2601-2606.
- Mallick, M. A. B., and K. Tesfai. 1981. Transformation of nitrosamines in soil and *in vitro* by soil microorganisms. *Bulletin of Environmental Contamination and Toxicology* 27: 115-121.
- Marshall, S. J., and G. F. White. 2001. Complete denitration of nitroglycerin by bacteria isolated from a washwater soakway. *Applied and Environmental Microbiology* 67(6): 2622-2626.
- McCormick, N. G., J. H. Cornell, and A. M. Kaplan. 1978. Identification of biotransformation products from 2,4-dinitrotoluene. *Applied and Environmental Microbiology* 35(5): 945-948.
- McCormick, N. G., T. D. Peltonen, and A. M. Kaplan. 1985. *Biotransformation of waste water constituents from ball powder production*. Natick/TR-85/050, (ADA164148). Natick, MA: U.S. Army Natick Research and Development Center.
- McDougal, J. N., and G. W. Jepson. 1998. *Assessment of the dermal absorption potential of modified M1 propellants, WC732 and PAP7993*. AFRL-HE-WP-TR-1999-0161. Dayton, OH: U.S. Air Force Research Laboratory, Wright-Patterson Air Force Base.
- McGrath, C. J. 1995. *Review of formulations for processes affecting the subsurface transport of explosives*. Technical Report IRRP-95-2. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- McKay, A. F. 1952. Nitroguanidines. *Chemical Reviews* 51: 301-346.
- Meng, M., W-Q. Sun, L. A. Geelhaar, G. Kuman, A. R. Patel, G. F. Payne, M. K. Speedie, and J. R. Stacy. 1995. Denitration of glycerol trinitrate by resting cells and cell extracts of *Bacillus/thuringiensis/cereus* and *Enterobacter agglomerans*. *Applied and Environmental Microbiology* 61(7): 2458-2553.
- Meylan, W. M., and P. H. Howard. 1991. Bond contribution method for estimating Henry's law constants. *Environmental Toxicology and Chemistry* 10: 1283-1293.

- Meylan, W. M., and P. H. Howard. 1993. Computer estimation of the atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. *Chemosphere* 25(12): 2293-2299.
- Meylan, W., P. H. Howard, and R. S. Boethling. 1992. Molecular topology/fragment contribution method for predicting soil sorption coefficients. *Environmental Science and Technology* 26: 1560-1567.
- Michaelidou, U., L. A. Achenbach, and J. D. Coates. 2000. Isolation and characterization of two novel (per)chlorate-reducing bacteria from swine waste lagoons. In *Perchlorate in the environment*, ed. E. T. Urbansky, 271-283. New York, NY: Kluwer Academic/Plenum.
- MIDAS (Munitions Items Disposal Action System). 2003, 2005. McAlester, OK: Defense Ammunition Center. <https://206.37.241.30/midashomesecure.asp> (5 Jun 2005).
- Miller, M. S. 1997. *Thermochemical properties of six solid gun propellants*. ARL-TR-1322. Aberdeen Proving Ground, MD: Army Research Laboratory.
- Montgomery, J. H., and L. M. Welkom. 1989. *Groundwater chemicals desk reference*. 1 and 640. Chelsea, MI: Lewis Publishing.
- Moore, A. M., C. H. DeLeon, and T. M. Young. 2003. Rate and extent of perchlorate removal by iron surfaces. *Environmental Science & Technology* 37: 3189-3198.
- Morris, J. B. 2002. *Extraction of nitroguanidine (NQ) from triple-base gun propellant*. ARL-TR-2669. Aberdeen Proving Ground, MD: Army Research Laboratory.
- Motzer, W. E. 2001. Perchlorate: problems, detection, and solutions. *Environmental Forensics* 2: 301-311.
- Mulherin, N. D., T. J. Jenkins, and M. E. Walsh. 2005. *Stability of nitroguanidine in moist, unsaturated soils*. ERDC/CRREL TR-05-2. Hanover, NH: U.S. Army Engineer Research and Development Center. Available for download at http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR05-2.pdf.
- National Academy of Sciences. 1999. *Hormonally active agents in the environment*. Washington, DC: National Academy.
- Niazi, J. H., D. T. Prasad, and T. B. Karegoudar. 2001. Initial degradation of dimethyl-phthalate by esterases from *Bacillus* species. *FEMS Microbiology Letters* 196(2): 201-205.
- Nishino, S. F., J. C. Spain, H. Lenke, and H-J. Knackmuss. 1999. Mineralization of 2,4 and 2,6-dinitrotoluene in soil slurries. *Environmental Science & Technology* 33(7): 1060-1064.
- Nishino, S. F., G. C. Paoli, and J. C. Spain. 2000. Aerobic degradation of dinitrotoluenes and pathway for bacterial degradation of 2,6-dinitrotoluene. *Applied and Environmental Microbiology* 66(5): 2139-2147.

- NTPCR (National Toxicology Program Chemical Repository). 2002. *Database of the National Institutes of Environmental Health*. http://ntp-db.niehs.nih.gov/htdocs/Chem_Hs_Index.html (5 Jun 2005).
- Nzengung, V., C. Wang, and G. Harvey. 1999. Plant-mediated transformation of perchlorate into chloride. *Environmental Science & Technology* 33(9): 1470-1478.
- Nzengung, V., and C. Wang. 2000. Influences on phytoremediation of perchlorate-contaminated water. In *Perchlorate in the environment*, ed. E. T. Urbansky, 219-229. New York, NY: Kluwer Academic/Plenum.
- Okeke, B. C., T. Giblin, and W. T. Frankenberger, Jr. 2002. Reduction of perchlorate and nitrate by salt-tolerant bacteria. *Environmental Pollution* 118: 357-363.
- Pal, B. C., and M. G. Ryon. 1986. *Database assessment of pollution control in the military explosives and propellants production industry*. ORNL-6202. Oak Ridge, TN: Oak Ridge National Laboratory.
- Palmer, W. C., M. J. Small, J. C. Dacre, and J. C. Eaton. 1996. Toxicology and environmental hazards. In *Organic energetic compounds*, ed. P. L. Marinkas, 289-382. Hauppauge, NY: Nova Science.
- Parker, W. J., H. D. Monteith, and H. Melcer. 1994. Estimation of anaerobic biodegradation rates for toxic organic compounds in municipal sludge digestion. *Water Research* 28(8):1779-1789.
- Pella, P. A. 1977. Vapor pressures of TNT, 2,4-DNT, 2,6-DNT, and EGDN. *Journal of Chemical Thermodynamics* 9:301.
- Pennington, J. C., and J. M. Brannon. 2002. Environmental fate of explosives. *Thermo-chimica Acta* 384:163-172.
- Pesce-Rodriguez, R., R. Leffers, and P. Sagar. 1997. *Effect of a warm, moist environment on JA2 gun propellant*. ARL-TR-1529, (ADA331765). Aberdeen Proving Ground, MD: Army Research Laboratory.
- Petrova, O. E., N. B. Tarasova, and M. N. Davydova. 2002. Biotechnological potential of sulfate-reducing bacteria for the transformation of nitrocellulose. *Anaerobe* 8:315-317.
- Phelan, J. M., and J. L. Barnett. 2000. *Solubility of 2,4-dinitrotoluene and 2,4,6-trinitrotoluene in water*. SAND2000-2986. Sandia, NM: Sandia National Laboratory.
- Powell, S., P. D. Franzmann, R. Cord-Ruwisch, and S. Toze. 1998. Degradation of 2-nitrodiphenylamine, a component of Otto fuel II, by *Clostridium* spp. *Anaerobe* 4:95-102.
- Ramos, J. L., A. Haiedour, E. Duque, G. Pinar, V. Calvo, and J-M. Oliva. 1996. Metabolism of nitrate esters by a consortium of two bacteria. *Nature Biotechnology* 14(3):320-322.

- Ribbons, D. W., P. Keyser, D. A. Kunz, and B. F. Taylor. 1984. Microbial degradation of phthalates. In *Microbial degradation of organic compounds*, ed. D. T. Gibson, 371-398. New York, NY: Marcel Dekker.
- Ritsema, R., W. P. Cofino, P. C. M. Frintrop, and U. A. T. Brinkman. 1989. Trace-level analysis of phthalate esters in surface water and suspended particulate matter by means of capillary gas chromatography with electron capture and mass-selective detection. *Chemosphere* 18 (11/12):2161-2175.
- Rosenblatt, D. H. 1986. *Contaminated soil cleanup objectives for Cornhusker Army Ammunition Plant*. USAMBRDL-TR-8603, (ADA169179). Fort Detrick, MD: Army Medical Bioengineering Research and Development Laboratory.
- Roslev, P., P. L. Madsen, J. B. Thyme, and K. Henriksen. 1998. Degradation of phthalate and di-(2-ethylhexyl)phthalate by indigenous and inoculated microorganisms in sludge-amended soil. *Applied and Environmental Microbiology* 64(12):4711-4719.
- Ross, R. H., B. C. Pal, R. S. Ramsey, R. A. Jenkins, S. Lock, W. H. Griest, and M. R. Guerin, 1988. *Problem definition study on techniques and methodologies for evaluating the chemical and toxicological properties of combustion products of gun systems*. 1, AD-ORNL-6334/V1, (ADA091290). Oak Ridge, TN: Oak Ridge National Laboratory.
- Roy, W. R. 1995. Groundwater contamination from municipal landfills in the USA. In *Contamination of Groundwaters*, ed. D. C. Adriano, A. K. Iskandar, and A. P. Murarka, 538. St. Lucie CRC, FL.
- Russell, D. J., and B. McDuffie. 1986. Chemodynamic properties of phthalate esters: Partitioning and soil migration. *Chemosphere* 15(8):1003-1022.
- Sax, N. I. 1979. *Dangerous properties of industrial materials*. 5th ed., 522. New York, NY: Van Nostrand Reinhold.
- Scholz, N., R. Diefenbach, I. Rademacher, and D. Linnemann. 1997. Biodegradation of DEHP, DBP, and DINP: Poorly water-soluble and widely used phthalate plasticizers. *Bull. of Environmental Contamination and Toxicology* 58:527-534.
- Seidell, A. 1941. *Solubilities of organic compounds*. New York, NY: Von Nostrand.
- Selwitz, C. 1988. Cellulose nitrate in conservation. In *Research in conservation*. 2. John Paul Getty Trust, CA: The Getty Conservation Institute. Available for download at http://www.getty.edu/conservation/publications/pdf_publications/nitrate.pdf (5 Jun 2005).
- Simmons, M. S., and R. G. Zepp. 1986. Influence of humic substances on photolysis of nitroaromatic compounds in aqueous systems. *Water Research* 20(7):899-904.
- Shiu, W. Y., K. C. Ma, D. Mackay, J. N. Seiber, and R. D. Wauchope. 1990. Solubilities of pesticide chemicals in water part II: data compilation. *Reviews of Environmental Contamination and Toxicology* 116:15-201.

- Shizuka, H., Y. Takayama, I. Tanaka, and T. Morita. 1970. Kinetics and mechanisms of the photocyclization of diphenylamines. I. The photochemical primary processes of diphenylamines. *Journal of the American Chemical Society* 92(25):7270-7277.
- Smets, B. J., and R. J. Mueller. 2001. Metabolism of 2,4-dinitrotoluene (2,4-DNT) by *Alcaligenes* sp. JS867 under oxygen-limited conditions. *Biodegradation* 12(4):209-217.
- Smith, L. L., J. Carrazza, and K. Wong. 1983. Treatment of wastewaters containing propellants and explosives. *Journal of Hazardous Materials* 7:303-316.
- Snellinx, Z., S. Taghavi, J. Vangronsveld, and D. van der Lelie. 2003. Microbial consortia that degrade 2,4-DNT by interspecies metabolism: Isolation and characterization. *Biodegradation* 14:19-29.
- Spain, J. C., ed. 1995. Bacterial degradation of nitroaromatic compounds under aerobic conditions. In *Biodegradation of nitroaromatic compounds*. 19-35. New York, NY: Plenum.
- Spanggord, R. J., T. Mill, T-W. Chou, J. H. Smith, and S. Lee. 1980a. *Environmental fate studies on certain munitions wastewater constituents; final report, phase I – Literature review*. SRI Project number LSU-7934. Menlo Park, CA: SRI International.
- Spanggord, R. J., T. Mill, T-W. Chou, J. H. Smith, and S. Lee. 1980b. *Environmental fate studies on certain munitions wastewater constituents; final report, phase II – Laboratory studies*. SRI Project number LSU-7934, (ADA099256). Menlo Park, CA: SRI International.
- Spanggord, R. J., T-W. Chou, T. Mill, R. T. Podoll, J. C. Harper, and D. S. Tse. 1985. *Environmental fate of nitroguanidine, diethyleneglycol dinitrate, and hexachloroethane smoke*. SRI project number LSU-7706, (ADA185050). Menlo Park, CA: SRI International.
- Spanggord, R. J., J. C. Spain, S. F. Nishino, and K. E. Mortelmans. 1991. Biodegradation of 2,4-dinitrotoluene by a *Pseudomonas* sp. *Applied and Environmental Microbiology* 57(11):3200-3205.
- SRC (Syracuse Research Corporation). 2003. Hazardous substance database, <http://toxnet.nlm.nih.gov> (5 Jun 2005).
- Staples, C. A., D. R. Peterson, T. F. Parkerton, and W. J. Adams. 1997. The environmental fate of phthalate esters: A literature review. *Chemosphere* 35(4):667-749.
- Sundaram, S. T., A. Sharma, Y. Z. Zhang, and B. W. Brodman. 1995. Biodegradation of nitrocellulose. *Journal of Energetic Materials* 13:283-298.
- Sur, D., P. Purkayastha, and P. Chattopadhyay. 2000. Kinetics of the photoconversion of diphenylamine in β -cyclodextrin environments. *Journal of Photochemistry and Photobiology A: Chemistry* 134(1-2):17-21.

- Sursala, S., S. T. Bacchus, N. O. Wolfe, and S. C. McCutcheon. 1999. Phytotransformation of perchlorate and identification of metabolic products in *Myriophyllum aquaticum*. *International Journal of Phytoremediation* 1:97-107.
- Swann, R. L., D. A. Laskowski, P. J. McCall, K. Vander Kuy, and H. J. Disburger. 1983. A rapid method for estimation of the environmental parameters octanol/water partition coefficient, soil sorption constant, water-to-air ratio, and water solubility. *Residue Reviews* 85:17-28.
- Tabak, H. H., S. A. Quave, C. I. Mashni, and E. F. Barth. 1981. Biodegradability studies with organic priority pollutant compounds. *Journal of the Water Pollution Control Federation* 53(10): 1503-1518.
- Tew, R. W., and L. S. Jaffe. 1973. *Mammalian toxicology and toxicity to aquatic organisms of nitrocellulose, a waterborne munition waste pollutant – a literature evaluation*. AD777807. Fort Frederick, MD: U.S. Army Medical Research and Development Command.
- Tipton, D. K., D. E. Rolston, and K. M. Scow. 2003. Transport and biodegradation of perchlorate in soils. *Journal of Environmental Quality* 32:40-46.
- U.S. Army Armament Research and Development Command (USA-ARDEC). 1983. *Encyclopedia of explosives and related items*, ed. B. T. Fedoroff, C. G. Dunkel, H. Walter, and D. C. McLean. Dover, NJ: Picatinny Arsenal.
- U.S. Environmental Protection Agency (USEPA). 1987a. *Health and environmental effects profile for phthalic acid esters*. EPA/600/X-87/384. Cincinnati, OH: Environmental Criteria and Assessment Office.
- U.S. Environmental Protection Agency (USEPA). 1987b. *Health effects assessment for N-nitrosodiphenylamine*. EPA/600/8-88/051. Cincinnati OH: Environmental Criteria and Assessment Office.
- U.S. Environmental Protection Agency (USEPA). 1992. *Drinking water toxicity profiles (nitrosodiphenylamine)*. PB93-122406. Washington, DC: Human Risk Assessment Branch.
- U.S. Environmental Protection Agency (USEPA). 2005a. Melamine, cyanamide, guanidine, and nitrosoguanidine as a contaminant of concern at National Priority List (Superfund) sites. <http://cfpub1.epa.gov/supercpad/cursites/srchsites.cfm> (2 Jun 2005).
- U.S. Environmental Protection Agency (USEPA). 2005b. Method 8270C, semivolatile organic compounds by gas chromatography/ mass spectroscopy (GC/MS). <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf> (6 Aug 2005).
- Valli, K., B. J. Brock, D. K. Joshi, and M. H. Gold. 1992. Degradation of 2,4-dinitrotoluene by the lignin-degrading fungus *Phanerochaete chrysosporium*. *Applied and Environmental Microbiology* 58(1):221-228.

- Vanderloop, S. L., M. T. Suidan, M. A. Moteleb, and S. W. Maloney. 1999. Biotransformation of 2,4-dinitrotoluene under different electron acceptor conditions. *Water Research* 33(5):1287-1295.
- Van der Schalie, W. H. 1985. *The toxicity of nitroguanidine and photolyzed nitroguanidine to freshwater aquatic organisms*. Technical Report 8404 (ADA153-045). Fort Detrick, MD: U.S. Army Medical Bioengineering Research and Development Laboratory.
- Vega, D., and J. Bastide. 2003. Dimethylphthalate hydrolysis by specific microbial esterase. *Chemosphere* 51:663-668.
- Verscheuren, K. 1983. *Handbook of environmental data on organic chemicals*. 2nd ed., 1310. New York, NY: Van Nostrand Reinhold.
- Von Oepen, B., W. Kordel, and W. Klein. 1991. Sorption of nonpolar and polar compounds to soils: processes, measurements, and experience with their applicability of the Modified OECD-Guideline '06. *Chemosphere* 22(3-4):285-304.
- Wang, J., L. Ping, S. Hanchang, and Q. Yi. 1997. Biodegradation of phthalic acid esters in soil by indigenous and introduced microorganisms. *Chemosphere* 325(8):1747-1754.
- Wang, J., L. Ping, and Y. Qian. 1999. Microbial metabolism of di-butyl phthalate (DBP) by a denitrifying bacterium. *Process Biochemistry* 34:745-749.
- Wang, J., L. Chen, H. Shi, and Y. Qian. 2000. Microbial degradation of phthalic acid esters under anaerobic digestion of sludge. *Chemosphere* 41:1245-1248.
- Weast, R. C., ed. 1979. *Handbook of chemistry and physics*. 60th ed., C-108. Boca Raton, FL: CRC.
- Weber, J. B. 1970. Adsorption of s-triazines as a function of pH and molecular structure. *Soil Science Society of America Proceedings* 34:401-404.
- Wendt, T. M., J. H. Cornell, and A. M. Kaplan. 1978. Microbial degradation of glycerol nitrates. *Applied and Environmental Microbiology* 36:693-699.
- Wentsel, R. S., W. E. Jones III, W. H. Fitzpatrick, and J. F. Kitchens. 1979a. *Problem definition study on TAX (1-acetylhexahydro-3,5-dinitro-1,3,5-triazine), SEX (1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazine), lead salicylate and lead beta-resorcyate, 2-nitrodiphenylamine and ethyl centralite*. Final Report (ADA099749). Alexandria, VA: Atlantic Research Corporation.
- Wentsel, R. S., W. E. Jones III, W. H. Fitzpatrick, and J. F. Kitchens. 1979b. *Problem definition study: ethyl centralite*. Final Report (ADA955469). Alexandria, VA: Atlantic Research Corporation.
- White, G. F., J. R. Snape, and S. Nicklin. 1996. Biodegradation of glycerol trinitrate and pentaerythritol tetranitrate by *Agrobacterium radiobacte*. *Applied and Environmental Microbiology* 62(2):637-642.

- Williams, R. T., W. E. Sisk, and A. R. MacGillivray. 1989. Degradation of nitroguanidine wastewater components in soil. *Environmental Toxicology and Chemistry* 8:469-475.
- Wolfe, N. L., L. A. Burns, and W. C. Steen. 1980. Use of linear free energy relationships as an evaluative model to assess the fate and transport of phthalate esters in the aquatic environment. *Chemosphere* 9(7-8):393-402.
- Yalkowsky, S. H., and Y. He. 2002. *The AQUASOL database of aqueous solubility*. 6th ed. Tucson, AZ: University of Arizona, College of Pharmacy. <http://www.pharmacy.arizona.edu/outreach/aquasol/> (5 Jun 2005).
- Yazici, R., D. M. Kalyon, and D. Fair. 1998. *Microstructure and mixing distribution analysis in M30 triple base propellants*. Picatinny Arsenal, PA: U.S. Army Armament Research, Development and Engineering Center.
- Yinon, J. 1999. *Forensic and environmental detection of explosives*. 285. Chichester, UK: John Wiley.
- Yuan, S. Y., C. Liu, C. S. Liao, and B. V. Chang. 2002. Occurrence and microbial degradation of phthalate esters in Taiwan River sediments. *Chemosphere* 49(10):1295-1299.
- Zeng, F., K. Cui, X. Li, J. Fu, and G. Sheng. 2004. Biodegradation kinetics of phthalate esters by *Pseudomonas fluorescences* FS1. *Process Biochemistry* 39(9):1125-1129.
- Zhang, C., J. B. Hughes, S. F. Nishino, and J. C. Spain. 2000. Slurry-phase biological treatment of 2,4-dinitrotoluene and 2,6-dinitrotoluene: Role of bioaugmentation and effects of high dinitrotoluene concentrations. *Environmental Science & Technology* 34: 2810-2816.
- Zhang, Y. Z., S. T. Sundaram, A. Sharma, and B. W. Brodman. 1997. Biodegradation of glyceryl trinitrate by *Penicillium corylophilum* Dierckx. *Applied and Environmental Microbiology* 63(5):1712-1714.
- Zhao, X-K., G-P. Yang, Y-J. Wang, and X-C. Gao. 2004. Photochemical degradation of dimethyl phthalate by Fenton reagent. *Journal of Photochemistry and Photobiology A: Chemistry* 161(2-3):215-220.
- Zheng, H., M. A. Bruns, and B. E. Logan. 2002. Perchlorate reduction by a novel chemolithoautotrophic hydrogen-oxidizing bacterium. *Environmental Microbiology* 4(10):570-576.
- Zurmühl, T., W. Durner, and R. Herrmann. 1991. Transport of phthalate-esters in undisturbed and unsaturated soil columns. *Journal of Contaminant Hydrology* 8:111-13.

Appendix A: Propellant Leaching Experiment Data

Table A1. Propellant compound concentrations ($\mu\text{g/L}$) in M10 (single-base) leaching experiment.

Time, in Hours	Mean Diphenylamine, in $\mu\text{g/L}$	Std. Deviation, Diphenylamine (n=3)	Mean 2,4-DNT, in $\mu\text{g/L}$	Std. Deviation 2,4-DNT (n=3)	Percent Recovery (3,4-DNT)
0	0.0	0.0	12	17	45
1	4.0	0.8	70	10	58
6	13.5	2.8	247	56	85
12	12.1	3.4	222	54	73
24	21.1	5.3	500	106	92
48	64.2	24.0	837	169	107
72	66.8	12.2	959	74	112
120	80.3	17.6	890	118	130
144	85.0	10.3	1042	142	126
168	63.1	11.7	708	91	123
192	88.2	5.8	1042	146	132
216	126.1	5.6	1561	67	131

Table A2. Propellant compound concentrations ($\mu\text{g/L}$) in M9 (double-base) leaching experiment.

Time, in Hours	Mean Ethyl Centralite, in mg/L	Std Deviation, Ethyl Centralite (n = 3)	Mean Nitroglycerin, in mg/L	Std. Deviation, Nitroglycerin (n = 3)	Percent Recovery (3,4-DNT)
0	0.7	0.7	63	1	154 (59)
1	0.5	0.1	290	78	(61)
2	0.5	0.0	331	36	(66)
4	0.8	0.1	383	53	(67)
6	1.0	0.1	511	71	112
8	0.7	0.1	430	103	(66)
12	0.9	0.2	728	43	(51)
24	1.5	0.1	542	65	120 (74)
32	1.3	0.1	554	47	(64)
48	1.6	0.1	563	80	104 (66)
72	1.9	0.3	602	104	92
120	2.3	0.2	590	30	96
144	2.4	0.2	607	9	119
168	2.5	0.1	599	84	128
192	2.8	0.2	673	35	116
216	2.7	0.1	645	47	117

¹ Experiment conducted in two batches, 1 (0-216 hr) and 2 (0-48 hr). Percent recoveries from batch 2 in parentheses.

Table A3. Propellant compound concentrations (mg/L) in M30 (triple-base) leaching experiment.

Time, in Hours	Mean Ethyl Centralite, in mg/L	Std. Deviation, Ethyl Centralite (n=3)	Mean Nitroglycerin, in mg/L	Std. Deviation, Nitroglycerin (n=3)	Mean Nitro-guanidine, in mg/L	Standard Deviation, Nitro-guanidine (n=3)	Percent Recovery, 3,4-DNT
0	0.1	0.0	0.3	0.0	0.0	0.0	65
1	10.7	1.3	9.6	0.3	10.1	0.3	96
6	15.0	1.0	45.9	1.3	32.4	10.0	85
12	15.9	2.5	80.3	2.5	49.6	21.6	85
24	14.8	1.8	139.9	56.9	40.7	12.5	96
48	14.7	1.7	152.1	31.3	64.7	13.6	111
72	17.4	2.6	245.6	7.2	117.4	58.9	116
120	15.4	1.9	276.6	19.7	120.7	15.9	113
144	15.4	1.7	314.4	64.7	106.8	32.7	119
168	15.8	1.6	339.2	13.3	145.7	42.7	136
192	16.0	2.1	351.6	61.0	88.4	45.0	129
216	15.1	0.6	433.5	22.3	203.3	134.6	115

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14. ABSTRACT Sustainable management of Army training ranges requires quantification of the distribution, transport, and fate of munitions constituents (propellants and explosives) in soil, surface and groundwater. Propellant formulations are mixtures consisting of energetic compounds, binders, stabilizers, and burning-rate modifiers. Factors that affect the transport and fate of these diverse compounds include dissolution, sorption, biotransformation, volatilization, and photochemical transformation. This report summarizes the current understanding of these processes, and provides process descriptors for propellant compounds. Results of leaching experiments on representative single-base, double-base, and triple-base propellant mixtures also are presented.					
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