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Environmental Transport and Fate Process Descriptors for Propellant Compounds

June E. Mirecki, Beth Porter, and Charles A. Weiss, Jr.

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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-dintrotoluene, 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 resorcylate	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 resorcylate	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 ^{o}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 resorcylate 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 -resorcylate, -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 resorcylate 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 NH_3) 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 ($K_d = [X]_{sorbed}/[X]_{solution}$; 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]	Wentsel 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	Wentsel et al. (1979b) McDougal and Jepson (1998)
Burning-Rate Modifiers							
Lead salicylate							
Lead resorcylate							
Lead stearate							

Compound	K_d	Soil Type	Reference	log K_{oc}[1]	Reference	log K_{ow}	Reference
				Plasticizers			
Dimethyl phthalate	0.189 0.519	Oakville A Oakville B	Altfelder et al. (2001) Altfelder et al. (2001)	2.18 - 2.86 1.3 - 1.8[2] >5.2 1.88, 1.89 4.70-5.20	Banerjee et al. (1985) Ritsema et al. (1989) Ritsema et al. (1989) Zurmühl et al. (1991) SRC (2003)	1.53 1.47 +/- 0.212 1.53 – 2.1[5] 1.56[4] 1.46 – 1.90[5] 1.60 +/- 0.04	Leyder and Boulanger (1983) Howard et al. (1985) Zurmühl et al. (1991) Hansch et al. (1995) Staples et al. (1997) Ellington (1999)
Diethyl phthalate	8.81 83.70 15.86 1.1	Alfisol Podzol Sediment Broome Co. NY soil	Von Oepen et al. (1991) Von Oepen et al. (1991) Von Oepen et al. (1991) Russell & McDuffie (1986)	1.84,2.65[2] 2.0 – 2.2[2] 1.94, 1.99 2.85-3.24	Russell &McDuffie (1986) Ritsema et al. (1989) Zurmühl et al. (1991) Von Oepen et al. (1991)	2.35 2.24 +/- 0.086 2.96 2.47[4] 2.21 – 3.00[5] 2.42 +/- 0.04	Leyder and Boulanger (1983) Howard et al. (1985) Parker et al. (1994) Hansch et al. (1995) Staples et al. (1997) Ellington (1999); Parker et al. (1994)
Di-n-butyl phthalate	22 17.46	Broome Co. NY soil Tsinghua garden	Russell & McDuffie (1986) Wang et al. (1997)	3.14, 3.81 3.5 - 4.02 3.06	Russell &McDuffie (1986) Ritsema et al. (1989) Zurmühl et al. (1991)	4.77 4.57 4.79 +/- 0.234 5.2 4.724 3.74 – 5.155 4.50+/- 0.03	Gledhill et al. (1980) Leyder and Boulenger (1983) Howard et al. (1985) Parker et al. (1994) Hansch et al. (1995) Staples et al. (1997) Ellington (1999)
Butylbenzyl phthalate	270	Broome Co. NY soil	Russell & McDuffie (1986)	4.23 4.02	Russell &McDuffie (1986) Ritsema et al. (1989)	4.91 3.57 +/- 0 4.2 - 5.05 4.78 4.914 3.57 – 4.915	Leyder and Boulanger (1983) Howard et al. (1985) Zurmühl et al. (1991) Parker et al. (1994) Hansch et al. (1995) Staples et al. (1997)
Bis (2-ethylhexyl) phthalate	1,390	Broome Co. NY soil	Russell & McDuffie (1986)	4.94, 4.282 5.7	Russell &McDuffie (1986) Ritsema et al. (1989)	7.94 7.453 +/- 0.061 5.3 – 8.75 5.3 7.454 4.20 – 8.295	Howard et al. (1985) DeBruijn et al. (1989) Zurmühl et al. (1991) Parker et al. (1994) Hansch et al. (1995) Staples et al. (1997)
				Energetic Plasticizers and Binders			
2,4-Dinitrotoluene	12	sediment	Spanggord et al. (1980b)	1.95[2] 2.41 2.56[3]	Spanggord et al. (1980a) Layton et al. (1987) SRC (2003)	1.98	Layton et al. (1987); Burrows et al. (1989); Hansch et al. (1995)

Compound	K_d	Soil Type	Reference	log K_{oc}[1]	Reference	log K_{ow}	Reference
Diethylene glycol dinitrate	2.3 +/- 2.8 0.8 +/- 0.9	EPA-5 EPA-18	Haag et al. (1991) Haag et al. (1991)	2.03 2.00, 2.08	Spanggord et al. (1985) Haag et al. (1991)	0.96-0.99 1.13[4] 0.98	Spanggord et al. (1985) 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 resorcylate, 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; Nzengung et al. 1999; Nzengung and Wang 2000). Perchlorate accumulation has been measured in leaves and stems of eucalypts and willows grown in hydroponic bioreactors (Nzengung et al. 1999). French tarragon and spinach showed declining perchlorate concentrations in leaf tissue over time, suggesting enzyme-catalyzed transformation (Nzengung and Wang 2000). During rhizotransformation, perchlorate reduction in solution occurs faster than transpiration. Rhizotransformation of perchlorate has been confirmed in willow roots (Nzengung 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 C^{14}-labelled DPA was transformed under aerobic conditions within 24 hours, with aniline, indole, and 4-hydroxydiphenylamine 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 resorcylate, lead salicylate, and lead stearate. When not complexed to lead, the carboxylic acids resorcylate, 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 Wallnöffer 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 Wallnöffer 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 (Jonnson 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 ^{o}C (Madsen et al. 1999; DiGennaro et al. 2005). Aerobic transformation of DEHP occurs more rapidly at higher temperatures (20 to 63 ^{o}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 CO_2 (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 CO_2; 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 *Penicillum* (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 x 10^{-16} atm-m^3/mol[1]	Burrows et al. (1989)	1.43 x 10^{-11} mm Hg(25 °C) [5]	Burrows et al. (1989)
	<7 x 10^{-6} (dimensionless)[2]	Haag et al. (1990)	<0.04 mm Hg (25 °C)	Dave et al. (2000)
	3.1 x 10^{-14} (dimensionless)[1]	Palmer et al. (1996)	0.03 mm Hg (25 °C)	SRC (2003)
	4.5 x 10^{-12} atm-m^3/mol[3]	SRC (2003)		
Cyanamide	2.6 x 10^{-10} atm-m^3/mol[3]	Swann et al. (1983)	3.75 x 10^{-3} mm Hg (20 °C)	SRC (2003)
Guanidine HCl				
Melamine	1.8 x 10^{-14} atm-m^3/mol[1]	Weber (1970)	3.6 x 10^{-10} mm Hg (20 °C)	SRC (2003)
N-nitrosoguanidine				
Ammonium perchlorate				
Potassium chlorate				
Potassium perchlorate				
Stabilizers and their Transformation Products				
Diphenylamine	2.8 x 10^{-6} atm-m^3/mol[1]	Meylan & Howard (1991)	1 mm Hg (108.3 °C) 6.39 x 10^{-4} mm Hg	Sax (1979) Drzyzga (2003)
N-nitrosodiphenylamine	6.4 x 10^{-4} atm m^3/mol[4] 1.21x 10^{-6} atm-m^3/mol[1]	USEPA (1987b) Meylan & Howard (1991)	0.1 mm Hg (25 °C)	SRC (2003)
2,4-dinitrodiphenylamine				
2-nitrodiphenylamine				
4-nitrodiphenylamine				
Methyl centralite				
Ethyl centralite				
Burning-Rate Modifiers				
Lead resorcylate				
Lead salicylate				

Compound	Henry's Law Constant	Reference	Vapor Pressure	Reference
Lead stearate				
Plasticizers				
Dimethyl phthalate	2.0 x 10^{-7} atm-m^3/mol[1]	Banerjee et al. (1985)	1.65 x 10^{-3} mm Hg (25 °C)	Howard et al. (1985)
	2.5 x 10^{-7} atm-m^3/mol[1]	USEPA (1987a)	2.0 x 10^{-3} mm Hg (25 °C)	Staples et al. (1997)
			3.08 x 10^{-3} mm Hg (20 °C)	SRC (2003)
Diethyl phthalate	6.1 x 10^{-7} atm-m^3/mol[1]	Hinckley et al. (1990)	1.65 x 10^{-3} mm Hg (25 °C)	Howard et al. (1985)
	7.8 x 10^{-7} atm-m^3/mol[1]	USEPA (1987a)	1.0 x 10^{-3} mm Hg (25 °C)	Staples et al. (1997)
			2.1 x 10^{-3} mm Hg (25 °C)	SRC (2003)
Di-n-butyl phthalate	4.5 x 10^{-6} atm-m^3/mol	Roy (1995)	7.3 x 10^{-5} mm Hg (25 °C)	Howard et al. (1985)
	2.2 x 10^{-6} atm-m^3/mol[1]	USEPA (1987a)	2.7 x 10^{-5} mm Hg (25 °C)	Staples et al. (1997)
			1 x 10^{-4} mm Hg (25 °C)	CPIA (2000)
			2.01 x 10^{-5} mm Hg (25 °C)	SRC (2003)
Butylbenzyl phthalate	1.2 x 10^{-6} atm-m^3/mol[1]	USEPA (1987a)	5.0 x 10^{-6} mm Hg (25 °C)	Howard et al. (1985)
	4.78 x 10^{-6} atm-m^3/mol[1]	SRC (2003)	6.5 x 10^{-5} mm Hg (25 °C)	Staples et al. (1997)
			8.25 x 10^{-6}mm Hg (25 °C)	SRC (2003)
Bis (2-ethylhexyl) phthalate	1.1 x 10^{-7} atm-m^3/mol[1]	USEPA (1987a)	6.5 x 10^{-5} mm Hg (25 °C)	Howard et al. (1985)
	1.50x 10^{-5} atm-m^3/mol[3]	Meylan & Howard (1991)	7.23 x 10^{-8} mm Hg(25 °C)	SRC (2003)
	1.3x 10^{-7} atm-m^3/mol[1]	SRC (2003)		
Energetic Plasticizers and Binders				
2,4-Dinitrotoluene	3.4 torr /M[1]	Spanggord et al. (1980a)	1.1 x 10^{-4} mm Hg (20 °C)	Pella (1977)
	8.7 x 10^{-2} torr /M[1]	Layton et al. (1987)	0.08 mm Hg	Dave et al. (2000)
	1.86 x 10^{-7} atm-m^3/mole[1]	Burrows et al. (1989)	2.17 x 10^{-4} mm Hg (25 °C) [5]	Burrows et al. (1989)
	1.8 x 10^{-4} (dimensionless)[1]	Palmer et al. (1996)	5.1 x 10^{-3} mm Hg (20 °C)	Spanggord et al. (1980a)
	1.3 x 10^{-7} atm-m^3/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 x 10^{-7} atm-m^3/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 x 10^{-6} (dimensionless)[1]	Palmer et al. (1996)		
Energetic Plasticizers and Binders (continued)				
EGDN	2.8 x 10^{-6} atm-m^3/mol^3	SRC (2003)	0.0490 mm Hg (20 °C)	USA-ARDEC (1983)
	2.52 x 10^{-6} atm-m^3/mol^1	Burrows et al. (1989)	0.0565 mm Hg (22 °C)	
	1.3 x 10^{-4} (dimensionless)	Palmer et al. (1996)	0.07059 mm Hg (25 °C)	
			0.05 mm Hg (20 °C)	Verscheuren (1983)
			0.07043 mm Hg (25 °C)	Holleman et al. (1983)
			0.0706 mm Hg (25 °C)	Burrows et al. (1989)
			0.045 mm Hg	Clayton and Clayton (1993)
Nitrocellulose				
Nitroglycerin	0.06 – 3.3 torr/M	Spanggord et al. (1980a)	2.0 x 10^{-2} mm Hg (20 °C)	Kemp et al. (1957)
	2.71 x 10^{-6} atm-m^3/mol^1	Burrows et al. (1989)	3.8 x 10^{-4} mm Hg (20 °C)	Spanggord et al. (1980a)
	1 x 10^{-6} (dimensionless)[1]	Palmer et al. (1996)	1.8 x 10^{-3} mm Hg (25 °C)	Holleman et al. (1983)
			1.77 x 10^{-3} mm Hg (25 °C)	Pal and Ryon (1986)
			2.5 x 10^{-3} mm Hg	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 x 10^{-6} atmospheres). Significant partitioning to the atmosphere is indicated by larger Henry's law constants (greater than 10^{-6} atm•m^2/mol). Partitioning from water or moist soil surfaces to air is an important transport pathway for diphenylamine, nitroso-diphenylamine, 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 resorcylate, 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 nitratoacetate, 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 (Kemme 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 N_2 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.

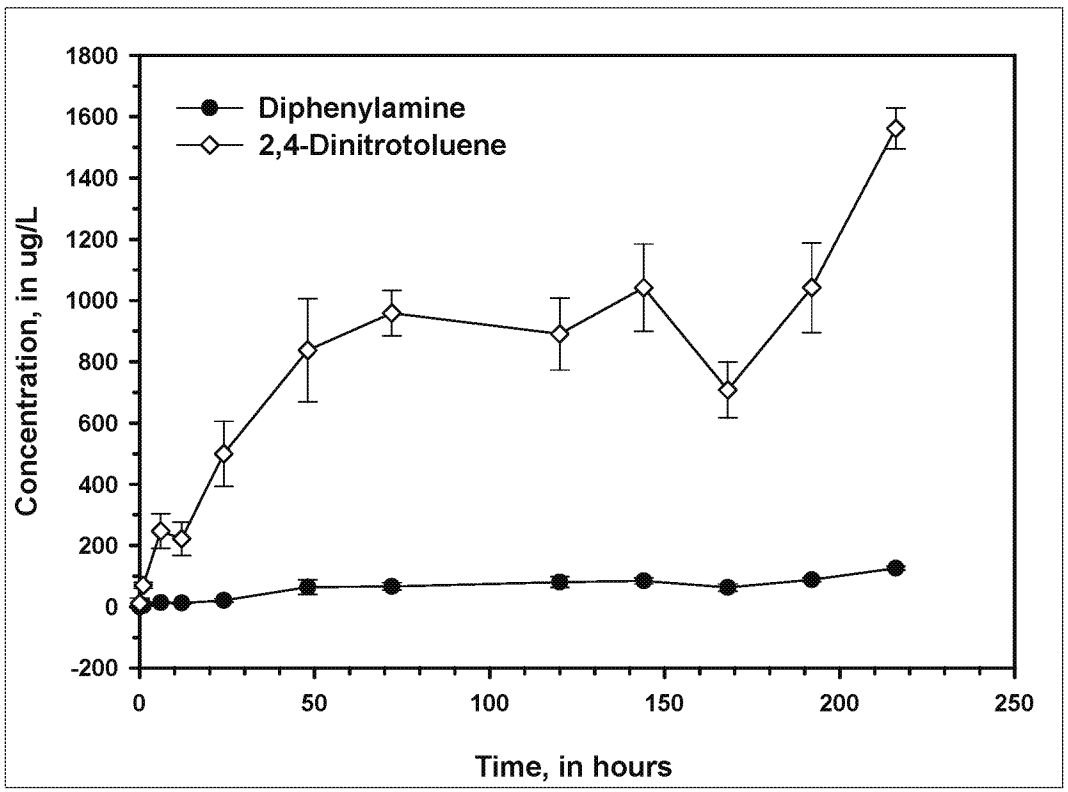
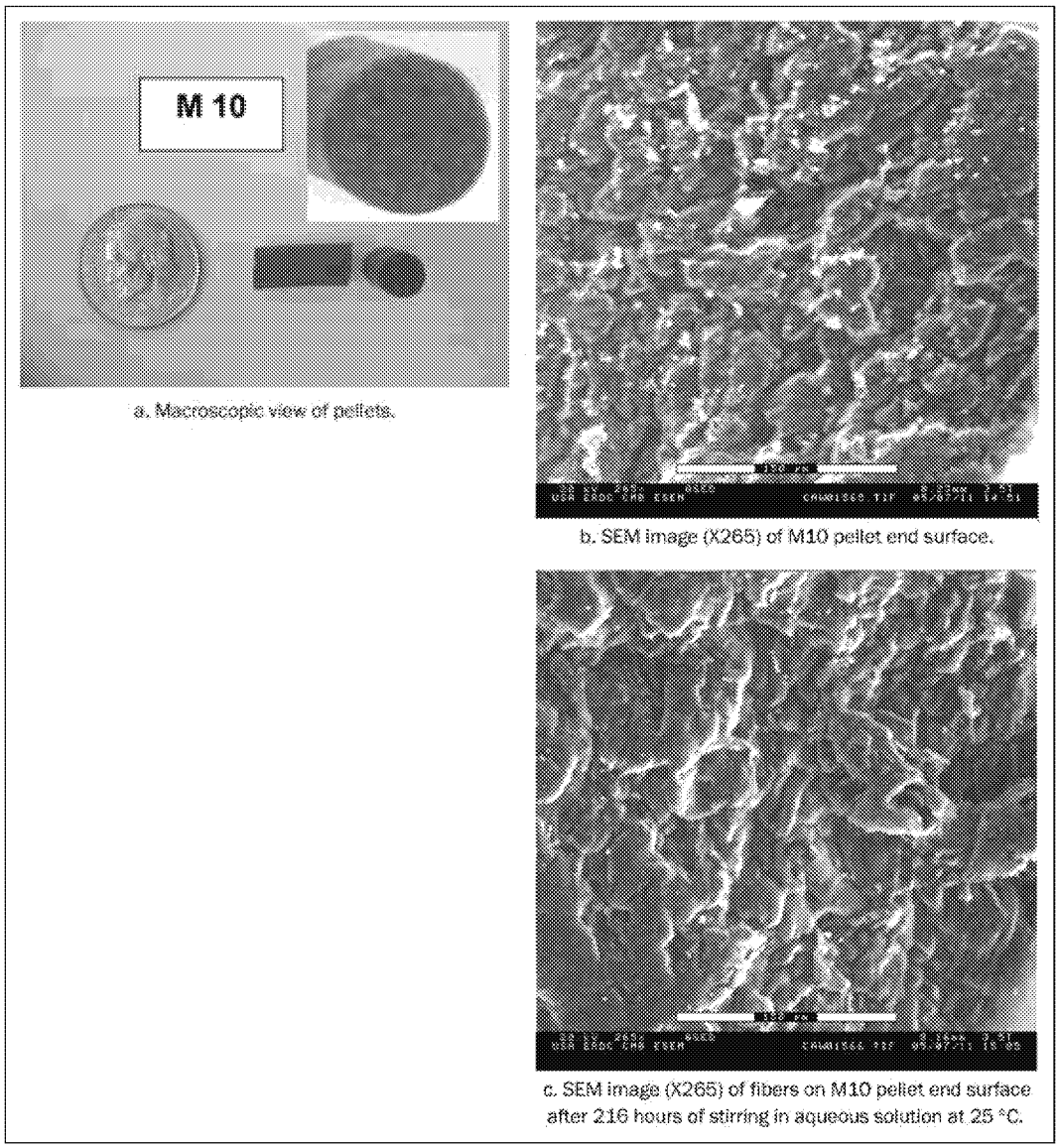


Figure 1. Results of M10 propellant leaching experiment. Concentrations are well below saturation with respect to 2,4-DNT (approximately 200 mg/L; Table 2) and DPA (approximately 40 mg/L). Circles represent the mean of triplicate analyses +/- standard deviation.

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.



a. Macroscopic view of pellets.

b. SEM image (X265) of M10 pellet end surface.

c. SEM image (X265) of fibers on M10 pellet end surface after 216 hours of stirring in aqueous solution at 25 °C.

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.

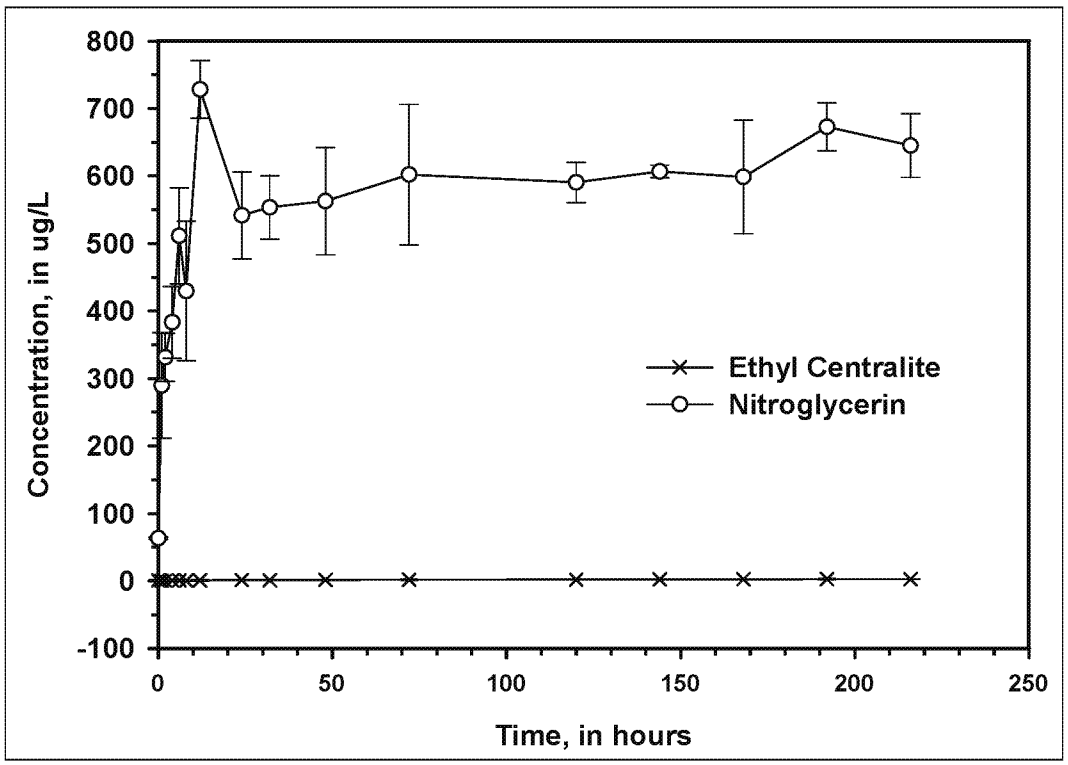


Figure 3. Results of M9 propellant leaching experiment. Concentrations are well below saturation with respect to nitroglycerin (approximately 1,500 mg/L; Table 2) and ethyl centralite (80 mg/L). Circles represent the mean of triplicate analyses +/- standard deviation.

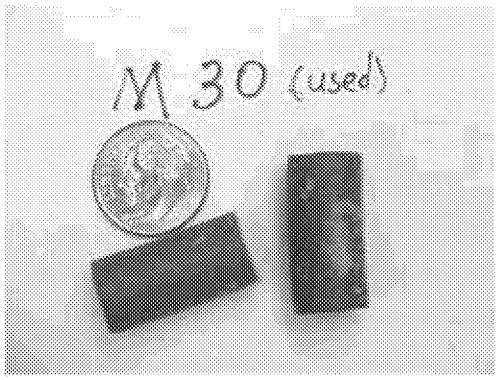
The maximum mass of ethyl centralite that leached from M9 grains was 0.4 mg, (of the ~7.5 mg available). There was no significant change in dissolved ethyl centralite concentration after 24 hours of stirring, suggesting that a steady-state was reached. Ethyl centralite shows low aqueous solubility (Table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

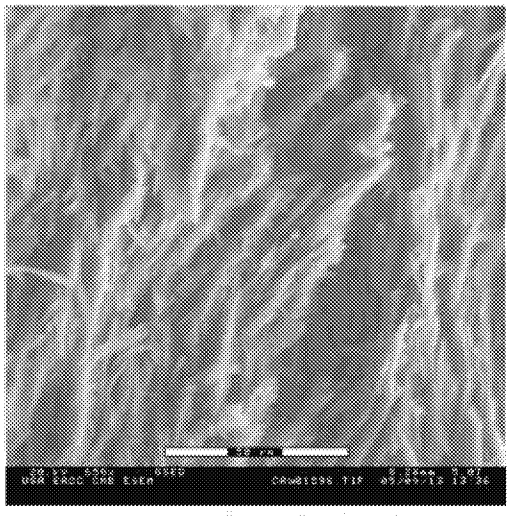
M30 (triple-base) propellant leaching results

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.

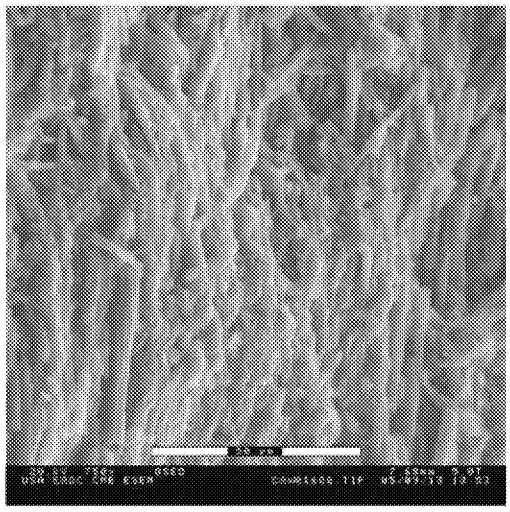
Three compounds were released to aqueous solution from single M30 pellets after 216 hours of stirring: nitroglycerin, nitroguanidine, and ethyl centralite (Figure 5). The maximum mass of energetic compounds available per pellet is 832 mg (nitroglycerin), 1,740 mg (nitroguanidine), and 55 mg (ethyl centralite). 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



a. Macroscopic view of M9 grains.



b. SEM image (X265) of M9 grain surface.



c. SEM image (X265) of M9 grain surface after 216 hours of stirring in aqueous solution at 25 °C.

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

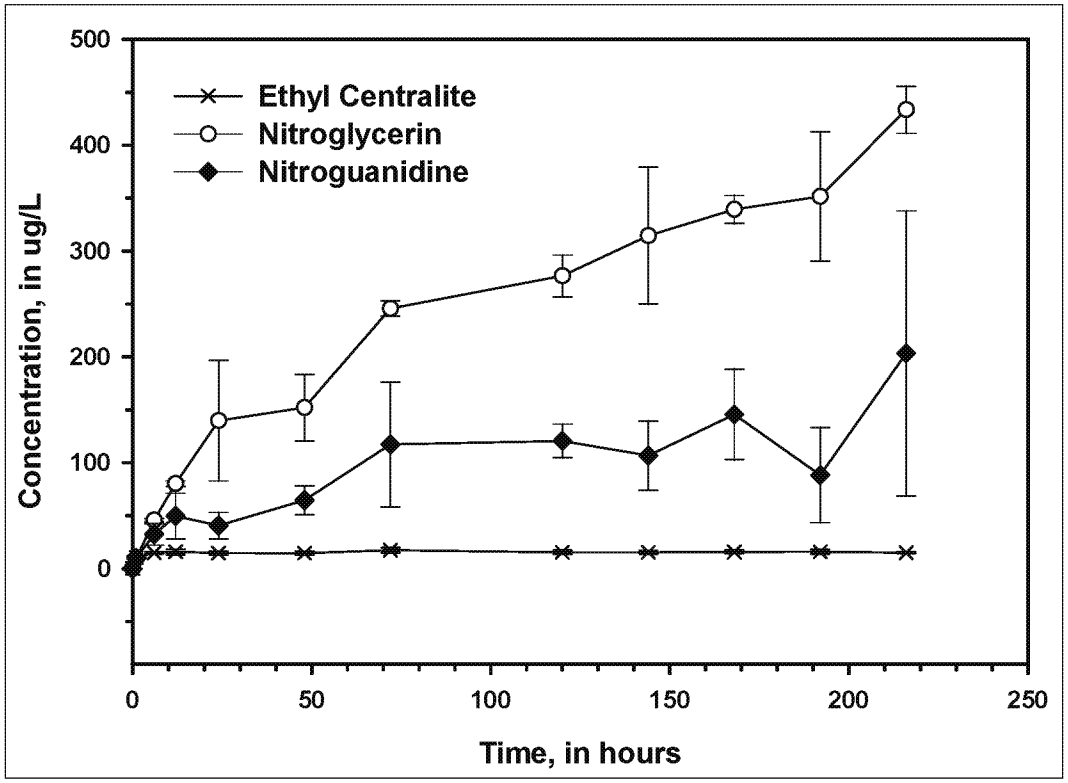
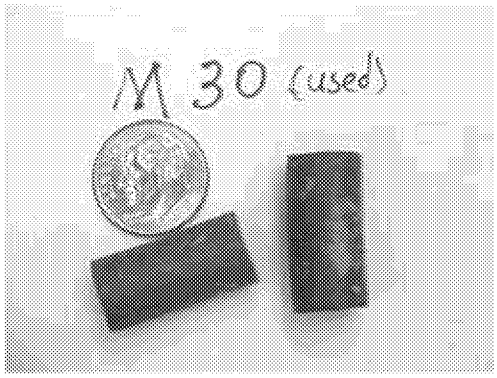
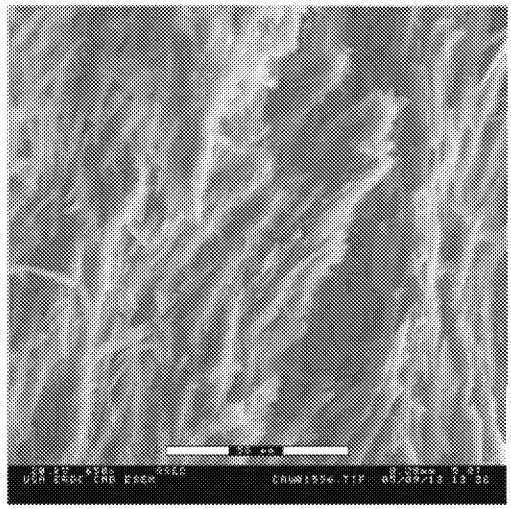


Figure 5. Results of M30 propellant leaching experiment. Concentrations are well below saturation with respect to nitroglycerin (approximately 1,500 mg/L), nitroguanidine (approximately 4 g/L) and ethyl centralite (80 mg/L). Circles represent the mean of triplicate analyses +/- standard deviation.

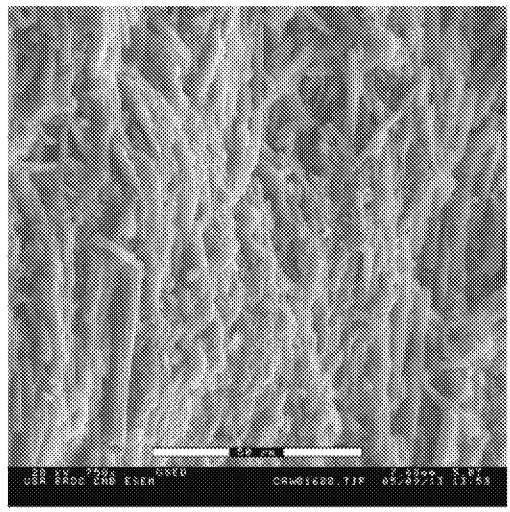
leaching of energetic compounds from the fibers. Little morphologic change was observed in the graphite coating of pellets before and after the leaching experiment.



a. Macroscopic view of M30 pellet after 216 hours of stirring in aqueous solution.



b. SEM image (X750) of nitrocellulose fibers in M30 pellet.



c. SEM image (X750) of nitrocellulose fibers in M30 pellet after 216 hours of stirring in aqueous solution at 25 °C.

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.

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Appendix A: Propellant Leaching Experiment Data

Table A1. Propellant compound concentrations (µg/L) in M10 (single-base) leaching experiment.

Time, in Hours	Mean Diphenylamine, in µg/L	Std. Deviation, Diphenylamine (n=3)	Mean 2,4-DNT, in µg/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 (µg/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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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.

15. SUBJECT TERMS
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Diphenylamine
Double-base
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Propellants
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Triple-base
2-4-dinitrotoluene

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