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Fate and Transport of Munitions Constituents

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List of Acronyms and Definitions

2ADNT	2-amino-4,6-dinitrotoluene
4ADNT	4-amino-2,6,-dinitrotoluene
2,4DANT	2,4-diamino-6-nitrotoluene
2,6DANT	2,6-diamino-4-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
CEC	Cation Exchange Capacity
Comp B	Composition B a high explosive composed of 60-39-1, RDX-TNT-wax
CSIA	Compound Specific Isotope Analysis
DoD	Department of Defense
Double-base propellant = NC+NG	
DNX	Hexahydro-3,5-dinitroso-1-nitro-1,3,5-triazine
EDAX	Energy Dispersive X-ray Spectrometer
ERDC	Engineer Research and Development Center
ER	Environmental Restoration
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High Performance Liquid Chromatography
hydrolysis	
$K_{d,}$	Soil partitioning coefficient
k	Reaction rate constant
k_{ow}	octanol/water partition coefficient
MC	munitions constituents
MNX	Hexahydro-1-nitroso-3,5-dinitro-triazine
NC	Nitrocellulose
NDAB	Nitro-2,4-diazabutanal
NG	Nitroglycerin
NQ	Nitroguanidine
OC	Organic carbon
OM	Organic matter
Photolysis	
Photo-transformation	
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
Single-base propellant = NC+ 2,4-DNT	
SEM	Scanning electron microscope
SIP	Stable Isotope Probing
S_w	Aqueous solubility
TAT	2,4,6-triaminotoluene
TNT	2,4,6-trinitrotoluene
TNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOF MS	Time-of-Flight Mass Spectrometry
Triple-base propellant = NC+NG+NQ	
Tritonal	complete

Acknowledgements

ABSTRACT

Live-fire military training scatters energetic compounds onto range soils. Once deposited on soil the explosives and propellants ingredients can dissolve in water (precipitation, delete), experience complex interactions with soil constituents, and migrate through subsurface soil leading to ground water contamination. While in contact with soil these chemicals are also subject to several abiotic (hydrolysis, photolysis, and reaction with metals) and biotic (biotransformation) reactions both in the solid and in the aqueous state.

In this review we will summarize the current state of knowledge on how energetic residues are deposited on range soils, what the residues look like and how quickly they dissolve in water. We will also describe the key physiochemical properties (S_w, pH, k_{ow}, K_d) of high explosives and propellants and discuss how these parameters influence their geo-biochemical interactions with soil and their chemical and microbial transformation routes in the environment. Knowing the reaction routes, especially the initial steps involved in the decomposition of these chemicals, will help us understand their fate, their ecological impact, and how to enhance *in situ* remediation. This review also identifies knowledge gaps and highlights future research needs.

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1. Introduction

Poly-nitro-organic compounds are highly energetic chemicals that rapidly release large amounts of gaseous products and energy upon detonation. Because of their explosive properties these chemicals are extensively used by the military and in the construction and mining industry (Jenkins et al. 2006). In the US alone close to 313 million kg of N-containing explosives had been released to the environment as of 1992 (Xu et al. 2010). The military in many NATO countries commonly use the aromatic TNT (2,4,6-trinitrotoluene), and the cyclic nitroamines RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) as explosives, and NQ (nitroguanidine), NG (trinitroglycerine) and DNT (2,4-dinitrotoluene) in propellants (Fig. 1).
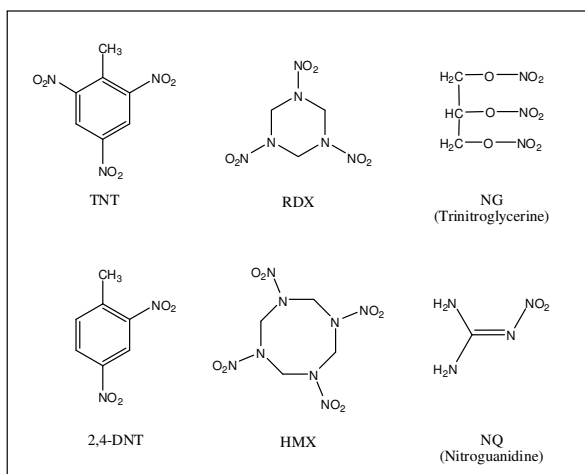
Figure 1. Chemical structure of munitions constituents

Live-fire military training scatters energetic compounds onto range soils. Once deposited on soil the explosives and propellants ingredients can dissolve in water, experience complex interactions with soil constituents, and migrate through subsurface soil leading to ground water contamination (Fig. 2). While in contact with soil these chemicals are also subject to several abiotic (hydrolysis, photolysis, and reaction with

metals) and biotic (biotransformation) reactions both in the solid and in the aqueous state.

Deposition, dissolution and transformation of explosives and energetic compounds are of interest for two reasons. First, these chemicals are toxic and can be deleterious to human, animal and plant health. Second, these labile compounds can migrate through subsurface soil and contaminate groundwater. If contaminated groundwater migrates off a military base, political and regulatory actions can close the base to training.
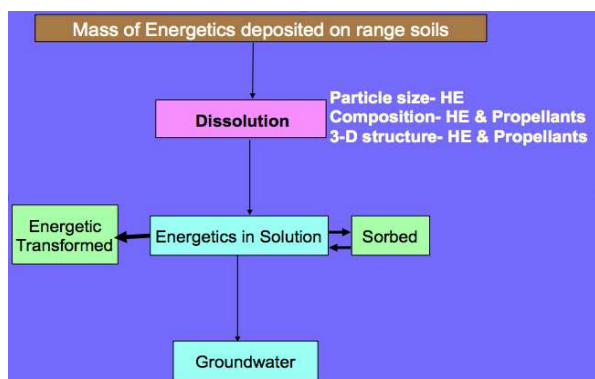
Figure 2. Schematic showing the processes that affect the environmental fate of explosives deposited on training range soils.

This review thus summarizes key physiochemical properties water solubility, S_w, pH, octanol/water partition coefficient, k_{ow}, and soil sorption constants, K_d, of high explosives and propellants and discusses how these parameters influence their geo-biochemical interactions with soil and their chemical and microbial transformation routes in the environment. Understanding the reaction routes of these chemicals will help know their fate, their ecological impact, and help design strategies to enhance *in situ* remediation. In this review we discuss how the highly oxidized explosives react in various redox systems with particular emphasis on the initial steps involved in their decomposition. We will also summarize the current state of knowledge on the environmental fate of these chemicals and identify knowledge gaps to highlight future research needs.

2. Field deposition

Military training scatters explosive and propellant compounds onto the soil surface. The mass of the scattered materials depends on the type of round fired and the manner in which it detonated: high-order, low-order (partial), or blow-in-place detonations. Table 1 lists compounds found in commonly used explosives and propellants.

Table 1. Energetic chemicals found in military propellants and explosives. Note that military grade RDX contains ≈ 10% HMX and military-grade TNT contains ≈ 1% other TNT isomers and DNTs.

Compound	Uses	Chemicals of concern
Propellant formulations		
Single base	Artillery	NC, 2,4-DNT
Double base	Small arms, mortar, artillery	NC, NG
Triple base	155 mm howitzer	NC, NG, NQ
Explosive formulations		
Comp. B	Artillery; mortar	60% RDX, 39% TNT
C4	Demolition explosive	91% Military-grade RDX
Tritonal	Bombs	TNT, aluminum
Comp. A4	40-mm grenades	RDX
TNT	Artillery	TNT
Comp. H-6	Bombs	RDX and TNT, aluminum
Octol	Antitank rockets	HMX and TNT

2.1 Propellants

Propellants are generally composed of nitrocellulose (NC) impregnated with either 2,4-dinitrotoluene (2,4-DNT single-base), nitroglycerin (NG double-base) or nitroglycerin and nitroguanidine (NQ triple-base). Propellant residues are partially burned and unburned particles of the solid propellant deposited on top of the soil surface. The shape of the original propellant grain and the presence or absence of holes (perforations made to increase the burn rate) dictates the appearance of the residue (Taylor et al. 2012). For example, propellants grains with a single perforation

leave rings or crescent shaped residues (Fig. 3a), those with multiple perforations leave slivers (Fig. 3b) and those without perforations leave residues that are smaller versions of the original propellant (Fig. 3c). The size range of propellant residues is limited because most propellant grains are mm in size (some improvement on Fig cap !).
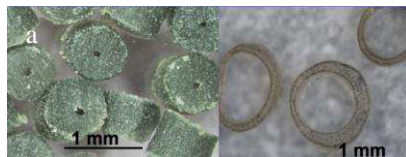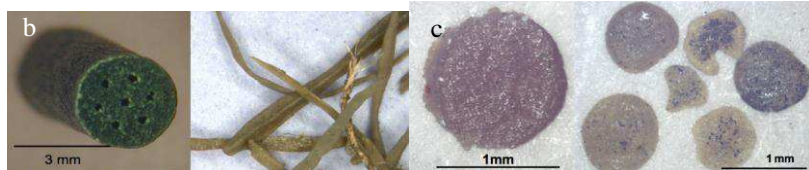

Figure 3. Single-perforated M45 propellant and residue (a), multi-perforated M1 propellant and fiber residues (b), and M9 grain and residues (c)

Tests, where small arms, mortars, artillery, and shoulder-fired antitank rockets were fired and the residues quantified, show that the mass of NG and 2,4-DNT deposited varies substantially for different munitions (Table 2). For example, the mass of NG deposited for a 155-mm howitzer was estimated at 1.2 mg per round fired, while the NG deposition for an 84-mm AT4 shoulder-fired rocket was 20,000 mg per rocket fired. Most of this deposition is as nitrocellulose particles, with NG or 2,4-DNT in the NC matrix (Walsh M.R. et al. 2009; Jenkins et al. 2007). NQ-containing propellants appear to leave little residue (Walsh M.R. et al. 2011).

At fixed firing positions the propellant residues decrease downrange, except for residues from shoulder-fired rockets, where residues are deposited rearward from the firing positions. For small arms, propellant residues are generally within 5 to 30 m of the firing position and up to 75 m downrange for artillery. For shoulder-fired rocket the residues reside largely in a zone about 30 m behind the firing position. For antitank rockets, propellant residues are also present at impact areas, because all the propellant has not been expended before the rocket hits the target. Often pieces of propellant are visible on the surface.

Over time, the 2,4-DNT, NG, and NQ, initially within the NC matrix, are dissolved by precipitation and travel with the water into the soil. The particles of NC are usually

not transported.

Table 2. Mass of propellant energetic constituent deposited during firing.

Weapon system	Propellant	Constituent	Rounds fired	Residues/ round (mg)	Distance for deposition (m)	Reference
Howitzers						
105-mm	M1-I & II	2,4-DNT	71	34		Walsh M.R. et al. 2009
105-mm	M1	2,4-DNT	22	6.4		Jenkins et al. 2007- Ch 4
155-mm	M1	2,4-DNT	60	1.2		Walsh M.R. et al. 2005a
Mortars						
60-mm	Ignition cartridge	NG	40	0.09	12	Walsh M.R. et al.2006
81-mm	M9 (illuminator)	NG	61	1000	50	Walsh M.R. et al.2006
120-mm	M45	NG	40	350		Walsh M.R. et al. 2005b
Shoulder-fired rocket						
84-mm Carl Gustov	AKB 204/0	NG	39	1055	30*	Jenkins et al. 2008- Ch 4
84-mm AT4	AKB204	NG	5	20,000	50*	Walsh M.R. et al. 2009
Tank (Leopard)						
105-mm	M1	2,4-DNT	90	6.7		Ampleman et al. 2009
Grenade						
40-mmHEDP	M2	NG	144	76	5	Walsh M.R. et al. 2010
40-mm TP	F15080	NG	127	2.2	5	
Small Arms						
5.56-mm Rifle	WC844	NG	100	1.8	10	Walsh M.R. et al. 2007
5.56-mm MG	WC844	NG	200	1.3	30	
7.62-mm MG	WC846	NG	100	1.5	15	
9-mm Pistol	WPR289	NG	100	2.1	10	
12.7-mm MG (.50 cal)	WC860 & WC857	NG	195	11	40	

*Major deposition is behind the firing line for shoulder-fired rockets.

2.2 High explosives

Pieces of high explosives are scattered onto soils when rounds are detonated. For high order detonations these pieces are μm in size. For partial detonations, pieces range from μm to cm in size (Fig. 4). If the round duds, then the entire explosive fill of the round could be available for dissolution, either as a single piece or as many pieces (Fig. 5)
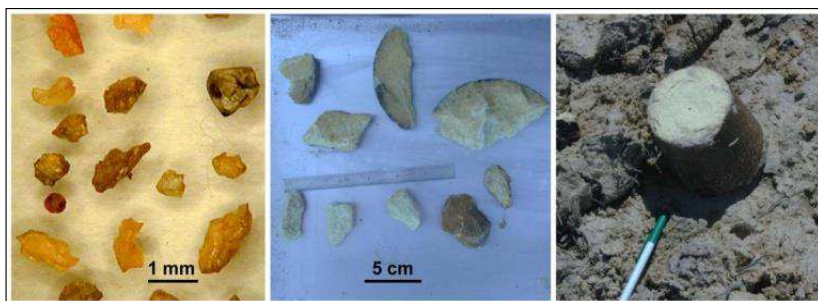
Figure 4. Comp B pieces from a single partial detonation.

Figure 5. Explosive fill exposed by corrosion of UXO casings.

Experiments, conducted to estimate the mass of explosives residues deposited when munitions detonate at impact areas, show that for high-order detonations 99.99% of the mass of Comp B in these rounds was destroyed (Table 3). The small amount of residue deposited is in micrometer-size particles (Taylor et al. 2004, 2006).

Low-order or partial detonations, on the other hand, deposit some fraction of the fill in the rounds (Table 3) as particles and chunks of different size. The percentage of fired rounds that undergo low-order detonations varies from one munition type to another (Dauphin and Doyle 2000). Thus, partial detonations can deposit from 10,000 to 100,000 times more residue per round than high-order detonations. Also, the residues from partial detonations are particles that are much larger than those from high-order detonations, sometimes in the centimeter size range (Taylor et al. 2004, 2006, Taylor et al. Chap. 8,TR-11-13).

When fired, some rounds do not detonate and result in UXO. These UXO are sometimes destroyed using blow-in-place practices by military EOD or contractor UXO technicians. Currently, military EOD personnel use C4 demolition explosive that is 91% RDX. Thus, even if RDX was not present in rounds fired, it is often present in soils when rounds have been destroyed using C4. In general, the masses of residues deposited from high-order, blow-in-place operations are slightly higher than high-order detonations. A blow-in-place detonation, however, can also result in a partial detonation that deposits a significant fraction of its explosive fill (Table 3).

Table 3. Mass of explosives residues deposited from high-order and partial detonations of TNT and Composition B-filled rounds.

	Analyte	# Rounds sampled	% of HE fill deposited	Reference
Mortars-Comp B				
60mm	RDX	11	3×10^{-5}	Hewitt et al. 2005b
	TNT			
81mm	RDX	5	2×10^{-3}	Hewitt et al. 2005b
	TNT	5	3×10^{-4}	
120-mm	RDX	7	2×10^{-4}	Walsh M.R. et al. 2005b
	TNT	7	2×10^{-5}	
Hand grenade-Comp B				
M67	RDX	7	2×10^{-5}	Hewitt et al. 2005b
	TNT			
Howitzer- Comp B				
105-mm	RDX	9	7×10^{-6}	Walsh M.E. et al. 2004
	TNT	9	2×10^{-5}	
155-mm	RDX	7	5×10^{-6}	Walsh M.R.et al. 2005a
	TNT			
PARTIAL-DETONATIONS				
Mortars-Comp B				
60-mm	RDX+TNT		35	Pennington et al. 2006
81-mm	RDX+TNT		42	Pennington et al. 2006
120-mm	RDX+TNT		49	Pennington et al. 2006
Howitzer-Comp B and TNT				
105-mm projectile	RDX+TNT		27	Pennington et al. 2006
155-mm projectile	TNT		29	Pennington et al. 2006

At impact areas, the largest mass of explosives is scattered by partial

detonations (low-order), UXO ruptured from other live-fire detonations, or blow-in-place activities designed to destroy UXO. These residues are not widely distributed and produce a localized zone of high concentrations. The resulting distribution of residues at impact areas is described as one of distributed point sources. Because these concentrations come from individual events, the concentrations across the impact area are not correlated. The short-range heterogeneity of explosives residues is very large, making it difficult to detect any gradient in concentration. Unlike propellants, it is difficult to estimate the mass of HE deposited at an impact area even if the number and type of rounds fired are known. This is because the largest HE mass comes from partial detonations and the number of these occurrences is poorly known. The values provided by Dauphin and Doyle (2000) can be used as a guide, but the mass of residues deposited needs to be determined by sampling.

At antitank ranges, the distance from firing position to target is only a few hundred meters and, hence, most rounds detonate, or rupture, within a small distance of targets. The gradient in residue concentrations is evident with the highest concentrations present next to targets (Thiboutot et al. 1998). For artillery targets, the concentrations of residues are much lower than for antitank rocket targets, and there is no concentration gradient evident as a function of distance away from these targets. The reason is the much greater distance between firing positions and targets, which results in some detonations being far from targets. This same situation is true for mortar targets that often are used for both artillery and mortar practice.

Deposition patterns for energetic residues and how to sample for these on different types of ranges are discussed in Hewitt et al. (2007a,b). However, other types of analytes (e.g., metals) may have different depositional patterns or fate and transport characteristics that would need to be considered for determining their likely spatial distribution.

3. Physiochemical Properties of constituents

Different chemicals have different physicochemical properties and thus different environmental interactions, i.e. partitioning and transport between water, soil, and other biological receptors, and different transformation routes, i.e. abiotic and biotic

degradation. The main physicochemical properties molecular weights, MW, S_w, log K_{ow}, and K_d, can provide insight into the fate of chemicals in the environment and the risk associated with their open-field use and applications.

Table 4 summarizes key physicochemical parameters, MW, S_w, and log K_{ow}, of studied explosives. The aqueous solubility is a measure of how much of a compound can dissolve in water given its temperature, pH and ionic strength. The solubility of the compound is related to the size and polarity of the molecule, with smaller more polar molecules having higher solubility.

Energetics in propellants, 2,4-DNT, NG, and NQ, have varying degrees of solubility in water (Table 4). These three chemicals are soluble and have low health screening levels for drinking water. NG, for example, has a solubility limit of around 1500 mg/L at 20°C in water (Yinon 1999) and a screening level of 1.5 µg/L in residential water (U.S. EPA 2012) (Use same units in text and in Table). Nitrocellulose, NC, on the other hand, is not soluble and as it has no known health or environmental risks, the mass of NC deposited for various weapons is usually not estimated (Jenkins et al. 2008).

Energetics in the high explosives, RDX, HMX and TNT have low solubility. HMX is almost insoluble in water (4 mg/L) and does not migrate to the subsurface, while RDX (45 mg/L) and TNT (145 mg/L) (Paquet et la 2010), which are more soluble, can be detected in subsurface environments and in the groundwater of known contaminated sites (Paquet et al. 2010).

Log K_{ow} indicates the potential of an explosive to partition into soil organic matter (OM) (Boddu et al., 2008). The higher the log $K_{ow,}$ the higher the lipophilicity of the chemical, which affects its geobiochemical interactions in the environment, e.g. diffusion through a cellular membrane causes damage to the biological receptor and migration through subsurface (sorption/desorption) causes groundwater contamination. TNT, with its three $-NO_2$ groups, is the most hydrophobic chemical of all (1.8 < log K_{ow} < 2.0) . Therefore transformation of TNT to its amine derivatives, i.e. replacing $-NO_2$ groups by $-NH_2$ groups, reduces its hydrophobicity and increases its water solubility. Reduced TNT amine products, therefore tend to migrate through subsurface soil unless their

migration is slowed down by immobilization mechanisms, e.g. chemisorption by forming –NH-C(O)- bonds with soil humic acids.

Sorption to soil, K_d, is governed by the soil composition, i.e. content of organic matter, clay, iron and aluminum oxides and hydroxides. As K_d increases, the chemical tends to reside mostly on the solid surface and little is transported downward in the moving pore water. As the majority of adsorption of organic contaminants in soils are attributed to soil organic carbon, K_d values are often normalized to soil organic carbon content. The resulting K_{OC} parameter (soil organic carbon partition coefficient) can then be used to calculate adsorption to other soils based on their carbon content. For example, RDX tends to partition to organic carbon (Tucker et al., 2002; Dontsova et al., 2009a), while TNT, which undergoes relatively rapid transformation to its amine derivatives, exhibits very complex sorption behavior. In addition to being adsorbed in clay interlayer surfaces (Haderlein et al., 1996), TNT's amine products can undergo irreversible adsorption to organic matter using –NH-CO linkages (Thorn and Kennedy, 2002). As Table 4 shows solubility changes drastically depending on if whether the chemical is a nitroaromatic (TNT, DNT), a cyclic nitroamine (HMX, RDX), or a nitrate ester (NG).

Table 4. Physicochemical properties of munitions constituents.

Compound	formula	Mol Wt.	Density (gcm^{-3})	S_w (gL^{-1})	Log K_{ow} at 25° C
TNT	$C_7H_5N_3O_6$	227	1.65	0.150[1]	1.86-2.00[1]
2,4-DNT	$C_7H_6N_2O_4$	182	1.52	0.28[1]	1.98[1]
RDX	$C_3H_6N_6O_6$	222	1.82	0.42[2a]	0.87[3]
				0.60	0.81-0.87
HMX	$C_4H_8N_8O_8$	296	1.81	0.0045[4]	0.17[4]
NG	$C_3H_5N_3O_9$	227	1.6	1.8[5]	1.62[5]
				1.5[6]	
NQ	$CH_4N_4O_2$	104	1.71	3.2[7]	-0.68[7]
				2.6[8]	-0.89[5]
				4.4[9]	-0.83[10]

[a] at 20°C; [b] at 18°C
Data from: [1]Rosenblatt et al. 1991; [2]Sikka et al. 1980; [3]Barenjee et al. 1980; [4]Monteil-Rivera et al., 2004; [5]HSDB Hazardous Substances Data Bank; [6]Yinon 1999; [7]DRDC Technical Reports; [8]Haag et al. 1990; [9]Van der Schalie 1985; [10] Dave et al. 2000.

4. Dissolution of energetic compounds

Dissolution is thought to be the rate-limiting step for aqueous transport to groundwater. Fig. 6 shows experimental techniques that measure the dissolution of individual highly energetic particles (Taylor et al. 2009a). Each technique isolates dissolution from the confounding effects of soil interaction and scales dissolution directly with dripping (rainfall) rate. These tests mimic field conditions on training ranges, where residues are scattered on the soil surface and whose constituents are dissolved by precipitation and were similar to those successfully used to measure dissolution of explosives (Lever et al. 2005).
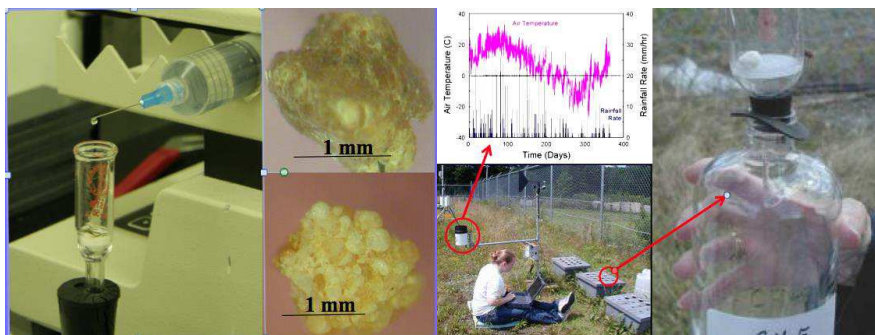

Fig. 6. Laboratory drip tests (left) and outdoor dissolution tests (right) Taylor et al. 2010.

4.1. Propellants

Single-base propellants containing 2,4-DNT are used to fire artillery, mainly 105- and 155-mm rounds from Howitzers. **Figure 7a** shows the % of DNTs dissolved during drip tests on a variety of M1 propellants (Taylor et al. 2012). Note that for the unfired grains the dissolution rate was quite linear and that even after 500 days the maximum DNT loss is only 10%. The larger propellant grains lost more DNT than the smaller grains but a smaller percentage of what they contained. The residues from M1 seven-perforation propellant (12 fibers) lost the highest percentage of their 2,4-DNT owing the their large surface to volume ratios, although the total mass was small. The mass loss curve for the residues was not linear. It rose rapidly initially but after day 20 it becomes more linear but still had a positive slope (**Figure 7a**).

Double-base propellants are the most common and are used to fire small arms, mortars, and rockets. In the drip tests unfired double-base propellants show initial rapid dissolution of NG followed by much slower dissolution. Most double base propellants lost NG in proportion to how much NG they contained. For example, the M9 propellant with 40% NG lost a greater percentage of its NG than a propellant that contained less. Taylor et al. 2012 found that the mass of NG dissolved was a function of the NG/NC ratio in the propellant and the data are plotted this way (**Figure 7b**). Clustering of the data using this normalization suggests that NC binds 10 to 20% of the NG and that any extra NG is not well retained.

Exceptions from this trend are the ball propellants, used to fire small arms, and the M45 propellant, used to fire mortars from the Stryker. The ball propellants all contain ~10 NG, yet variable amounts of NG are dissolved independent of their NC content. The M45 propellant also contains 10% NG yet it looses <1% during the drip tests (**Figure 7b**). The M45 is a squat grain with a central perforation. The central perforation should increase its surface area and, therefore, increase its NG loss. This result was observed suggesting that the nitrocellulose in M45 was not fully nitrated when it was manufactured so that the NG was effectively bound to the NC.

Both fired residue and unfired grains were collected from double-base ball propellants used to fire small arms. Concentration of NG in the unfired grains were within the variability given in the technical manual whereas the fired residues contained about 80% of the NG on a mass basis. **Figure 8a** shows that more NG was dissolved from the unfired propellants (15-20%) than from their residues (3 to 7%). For the unfired propellants the shape of the cumulative mass loss versus time curves were consistent with rapid loss of the NG from the surface of the grain followed by slower diffusion of the NG from the interior of the grain. The high aqueous solubility of NG suggests that NG could be rapidly dissolved by contact with water. If NG existed as fine liquid droplets within an NC
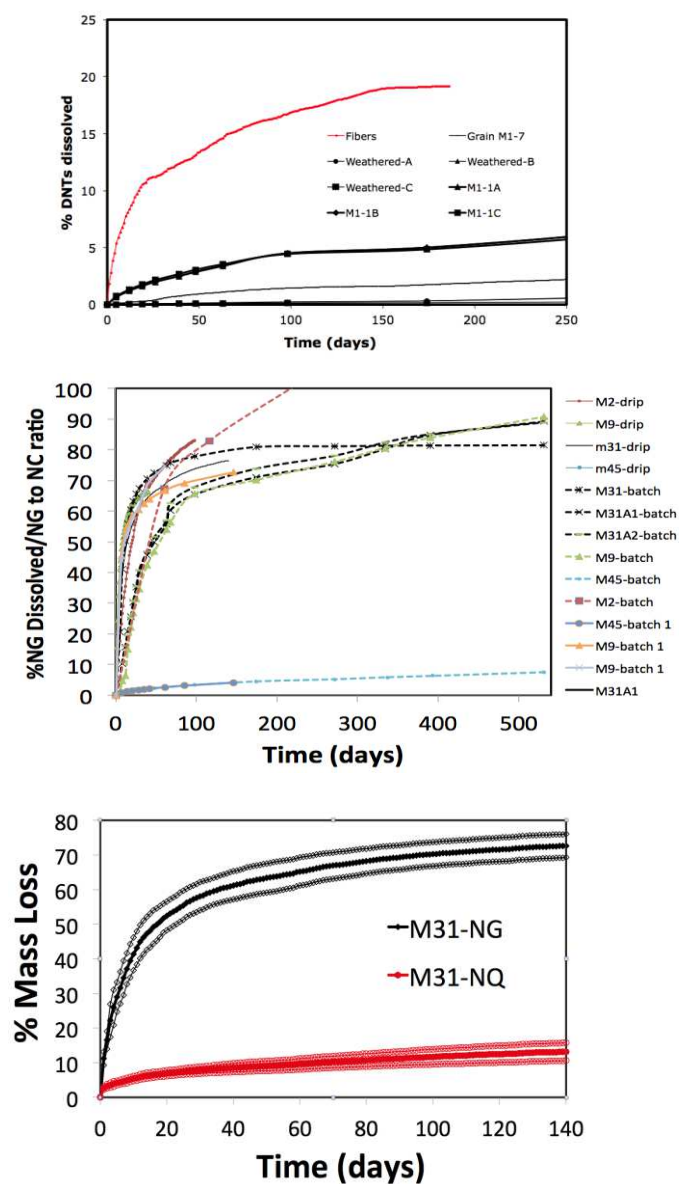
Figure 7. (a) Percent of 2,4-DNT and 2,6-DNT dissolved into water from unfired seven perforation M1 propellant grains (black) and from fired residues (red). (b) Plot showing the % NG dissolved normalized by the NG/NC ratio versus time. All of the data from NG containing propellants, except for the small arms, are plotted on this figure. **(c)** Percent NG and NQ dissolved (Ave. ± 1 sigma, n=8) versus time for unfired M31 single-perforation propellants (from Taylor et al. 2012).

matrix rather than as dispersed molecules, droplets at the grain surface would be in

direct contact with water whenever the grain was wet. Once this outer layer of liquid NG was depleted, NG would need to diffuse through the NC matrix to reach the water, with considerably lower diffusivity ($\sim 10^{-14}$ $cm^2 s^{-1}$) (Taylor et al. 2011). Late time dissolution would thus be limited by molecular diffusion.

Scanning electron microscopy images of the small arm propellants show pits that are about 5μm in diameter and similarly deep (**Figure 8b**), consistent with the depth needed to produce the decrease in concentration. All dissolution of NG from fired grains would thus be limited by molecular diffusion. The linear shape of the cumulative mass loss curves, the slower dissolution rate of NG from the fired residues and their 20% lower NG concentration compared to unfired grains are explained if NG near the surface is burned during firing.

Triple base propellants are also used to fire artillery and contain NQ. Although there is more NQ than NG in the M31 propellant (55% vs. 20%), and NQ is more soluble than NG (Table 4), both by mass and by percentage more NG was dissolved than NQ (**Fig. 7c**, Taylor et al. 2011). This results because during manufacture of the propellant, NG is added as a liquid, whereas NQ is mixed in as a solid.

Tests to measure how well the components in triple-based propellants were mixed (Yazici and Kalyen, 1998) showed that NG is not as well mixed as NC and NQ and that there is more NG near the surface and less in the interior of the grain. These authors suggest that after a certain threshold (27%NG for a 12.2% nitrated NC) the NG does not effectively bond to the NC and it migrates to the propellant surface as a low viscosity fluid. This migration would make liquid NG available near the surface of the propellant where it would be removed when in contact with water. The NQ on the other hand would have to dissolve to leave the propellant.
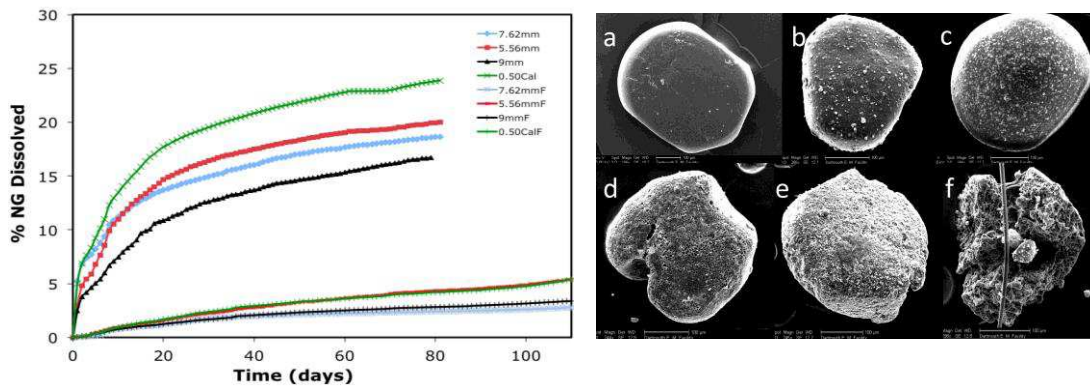
Figure 8. (A) Percent NG dissolved versus time for unfired (top) and fired (bottom) small arms propellants. **(B)** Images of 9-mm propellant grains showing progressive heating; a) an unfired grain; b) pits visible on surface; c) bubbly surface; d) gas bubbles open holes on surface; e) metals and other elements within the propellant become concentrated on the surface; f) breakdown of nitrocellulose structure.

4.2. High explosives

The dissolution of pieces and particles of TNT, Comp B, and Tritonal were measured both in the laboratory (Taylor et al. 2009) and in the field (Taylor et al. 2009, 2010). The TNT particles became smoother and smaller but retained their original shapes as they dissolved. The Comp B particles became noticeably bumpier and "sugary-looking" as dissolution of the surface TNT revealed the larger (~ 0.1 mm), slower-dissolving RDX crystals. The Tritonal particles became smaller and slightly bumpier as TNT dissolved exposing the aluminum grains. (**Fig. 9a & b**).
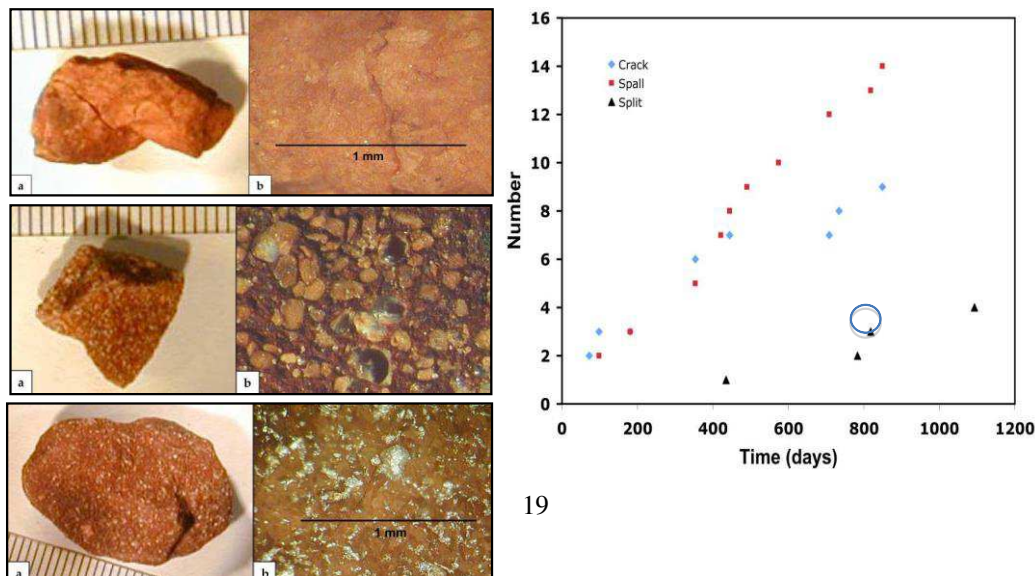

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Figure 9. (a) Photograph of particle and (b) close-up of its surface for TNT, Comp B and tritonal (c) Number of HE chunks that cracked, spalled off a 1 mm piece, or split into multiple millimeter-size pieces over the three-year test. For example, the circled triangle indicates that 3 of the 34 chunks had split by day 810 of the test.

The outdoor dissolution tests showed that Comp B, Tritonal, and TNT particles all turned rust red with occasional shiny, almost iridescent, black patches. Following heavy rains, the reddish product washed off some surface areas, exposing the lighter-colored explosive beneath. Four of the 34 HE chunks split naturally during the tests and others spalled small flakes or cracked (**Fig. 9c, 10b**).

The cumulative mass losses for TNT pieces are shown in **Fig. 10a**. Data for Comp B, Tritonal and C4 are in Taylor et al. 2010. A dissolution model for explosives and validation studies are presented in Lever et al. 2005; Taylor et al. 2009, 2010. Except for the chunks that split (TNT 3 and 5) the shapes of the cumulative mass loss curves are similar among all the chunks. Although the largest chunks lost the most mass, the small HE chunks lost a larger percentage of their initial mass due to a larger ratio of surface area to mass.
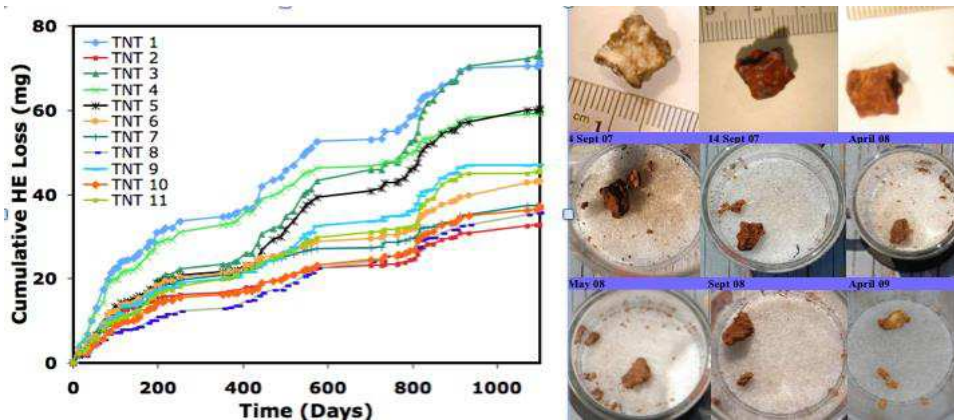

Figure 10. (a)Cumulative mass loss of TNT (mg) versus time as measured by HPLC; (b) Images of TNT 3 over the course of the experiment.

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Figure 11 summarizes the mass loss for each HE chunk after three years. Note that two types of measurements are plotted against each other: mass loss measured by electronic balance, and cumulative dissolved mass obtained via HPLC analysis. Mass losses measured with the electronic balance were larger than dissolved masses, and the losses grew with time. These results were unexpected because the two measurement methods had low uncertainties, and there was very good mass balances for TNT, Tritonal, and Comp B in the laboratory tests (Lever et al. 2005, Taylor et al. 2009).
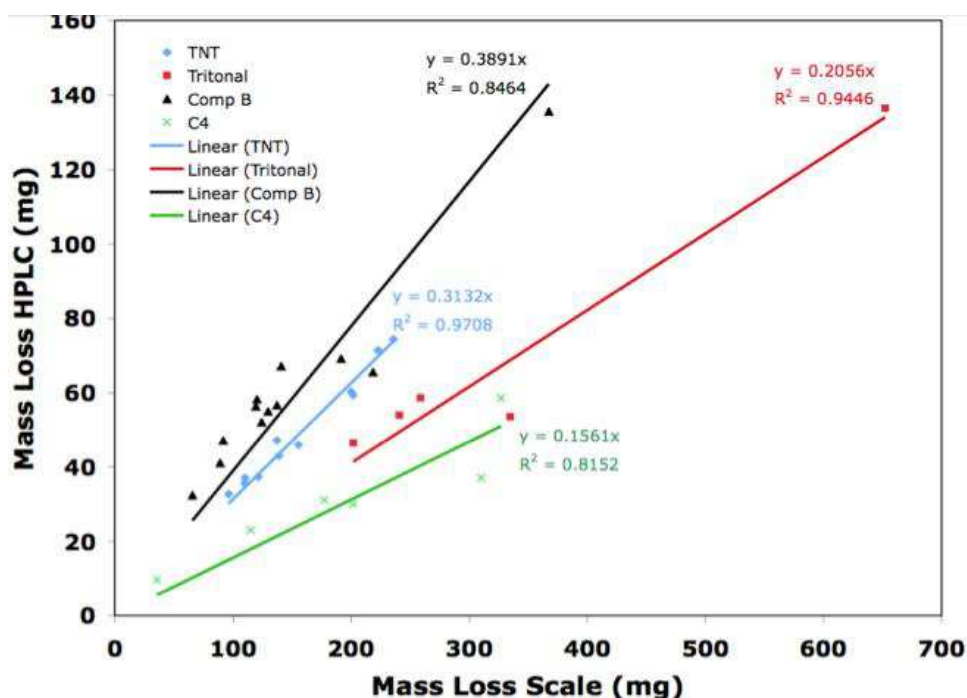
Fig. 11. Over 60% of the mass lost from the HE pieces, as measured by electronic balance, were not measured as dissolved explosives by the HPLC. The unaccounted for masses were larger than dissolved explosive masses, they scaled closely with surface area of each particle and they grew with time.

Mass balance discrepancies could be attributed to several factors including abiotic degradation caused by photolysis of the particle's surface or by hydrolysis on the wetted surface of the particle. Photo-transformation of TNT in solution has been well documented, but the transformation measured occurred on solid pieces of all the explosives, including C4 that contains only RDX. Solid RDX does photo-transform to

other compounds (Bedford et al. 1996). However, anecdotal accounts suggest that RDX is much more stable in sunlight than TNT, so that the rate may not be high enough to account for missing mass.

Photo-transformation is inherent to outdoor weathering of explosives and the lack of mass closure for these tests indicates that photoproducts ==produced== could not quantified by Method 8330B (you may delete this sentence too!). Taylor et al 2010 noted that TNT, Tritonal and Comp B pieces, all containing TNT, ==changed color to red upon exposure to light, indicating the potential formation of Meisenheimer complexes.== Also found was 2-amino-4,6-dinitrobenzoic acid in quantities similar to those measured for TNT.   The poor mass balance of RDX was attributed to photo-destruction of the high explosive when formaldehyde and nitrate were detected in photo-degradation studies (Taylor et al. 2010). Interestingly, photo-degradation of solid HEs differs from photo-degradation of these chemicals in aqueous solutions both in the kinetics and in the products formed. On training ranges, these transformation products likely constitute additional HE-based contaminant influx into range soils.

5. Soil interactions

Explosives are N-based organics that are rich in functional groups, a property that makes them susceptible to various mechanisms of biogeochemical interactions in the environment. Interactions of explosive constituents with soil, i. e. sorption/desorption, provide insights into their environmental fate and the risk associated with their use in the field. Soil constituents, including organic matter, phyllosilicate clays, iron and aluminum oxides and hydroxides, can all adsorb energetic compounds due to their high surface areas (e.g. Dontsova et al. 2009). The soil type, can therefore, drastically influence the extent of soil/contaminant interactions (**Table 5**).

The -NO_2 functional group(s) in explosives can transform to the corresponding – NH_2 (amino-) group(s) under various environmental redox conditions (Pennington and Patrick, 1990, Spain et al. 2000). Different products have different physicochemical properties (Sw, pKa, Kow) and thus partition differently between water and soil (Haderlein and Schwarzenbach, 1995; Rieger and Knackmuss, 1995; Elovitz and Weber, 1999; Thorn and Kennedy, 2002).   For example, Haderlein et al., (1996)

reported that reversible sorption to montmorillonite decreased with the number of nitro groups and followed the order TNT> DNT> NT. Clearly sorption depends on the explosive compound and the type and the extent of substitution it has and on the type and composition of the soil (Table 5).

Table 5. Soil-water partition coefficients, K_d, for energetic compounds in natural and model systems.

Soils	Clay (%)	TOC (%)	K_d (L kg^{-1})					
			TNT	2,4DNT	RDX	HMX	NG	NQ
Newport	5.6	3.5	2.3[5]	-	-	-		
Lonestar	10.0	0.06	2.5[5]	-	-	-		
Cornhuskers	20.0	0.83	4.1[5]	-	-	-		
Crane	20.6	2.8	3.7[5]	-	-	-		
Joliet	23.8	3.6	6.8[5]	-	-	-		
Holston B	43.8	1.2	3.0[5]	-	-	-		
Sharkey Clay	54.4	2.4	11[5]	-	-	-		
K^+- LAAP D[a]	32	0.20	167[6]	12.5	0.66[6]	1.73[6]		
Aqua-gel	> 87	ND	130[7]	130[7]	6.6[7]	8.9[7]		
Sassafras loam	11[1] 16.4[9]	0.33[1] 1.30[9]	-	2.34[9]		0.7[1]	0.26[9]	0.60[9]
Catlin silt loam	15.7[9]	3.75[9] 4.23[11]	17.9[11]	15.30[9]	2.03[11]		1.27[9]	0.24[9]
Kenner muck		35.4	285.2[11]		36.19[11]			
Benndale fine sandy loam		0.89	1.77[11]		0.78[11]			
Adler silt loam	4.2 4.5[10]	0.29	2.4[10]		0.48[10]	0.48[10]	0.08[13]	
Plymouth sandy loam	14.4[9] 5.0[10]	1.72[9]	1.6[10]	5.06[9] 0.28-2.01[12]	0.65[10]	0.43[10]	1.41[9]	0.44[9]
Yokena/Shar key Clay	48.7	2.4	10[14]	12.5[16] 9.43[18]	3.5[BP]	12.1[17]		0.43[15]
Picatinny	5	0.63		2.06[18]		4.25[17]	3.8[19]	
Grange Hill	10	0.29		0.43[18]		0.12[17]		0.15[15]
Varennes	4	8.4	4.2[4]		1.9[4]	2.5[1]		
LAAP Ab	6	0.31	26[6]			1[6]		
LAAP Cb	12	0.08	64[6]		0.3[6]			
LAAP Db	32	0.2	167[6]	1.67[16]	0.7[6]	2[6]		
Minerals								
K^+-mont.	NA	ND	21500[8]	7400[8]	1.2[8]			

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K$^+$-illite	NA	ND		12500[8]	3650[8]			
K$^+$-kaolinite	NA	ND		1800[8]	690[8]			
Ca^{2+}- mont.	NA	ND		1.7[8]				
Ca^{2+}-illite	NA	ND		1.2[8]				
Ca^{2+}-kaol.	NA	ND		0.3[8]				
K$^+$-mont.	NA[b]	ND[c]		414[6]		3.17[6]	22.1[6]	

[a] LAAP, Louisiana Army Ammunition Plant; [b] NA: Non applicable; [c] ND: Not determined. Data from: (1) Monteil-Rivera et al., 2003; (2) (3) Sheremata et al., 1999; (4) Sheremata et al., 2001; (5) Pennington and Patrick, 1990; (6) Brannon et al., 2002; (7) Leggett, 1985; (8) Haderlein et al., 1996; (9) Taylor et al., 2012; (10) Dontsova et al. 2006; (11) Dontsova et al. 2009a; (12) Dontsova et al., 2009b; (13) Dontsova et al., 2007: (14) Townsend et al. 1995: (15) Pennington et al., 2004; (16) Pennington et al., 2001; (17) Brannon et al. 1999; (18) Pennington et al., 2003; (19) Pennington et al., 2002.
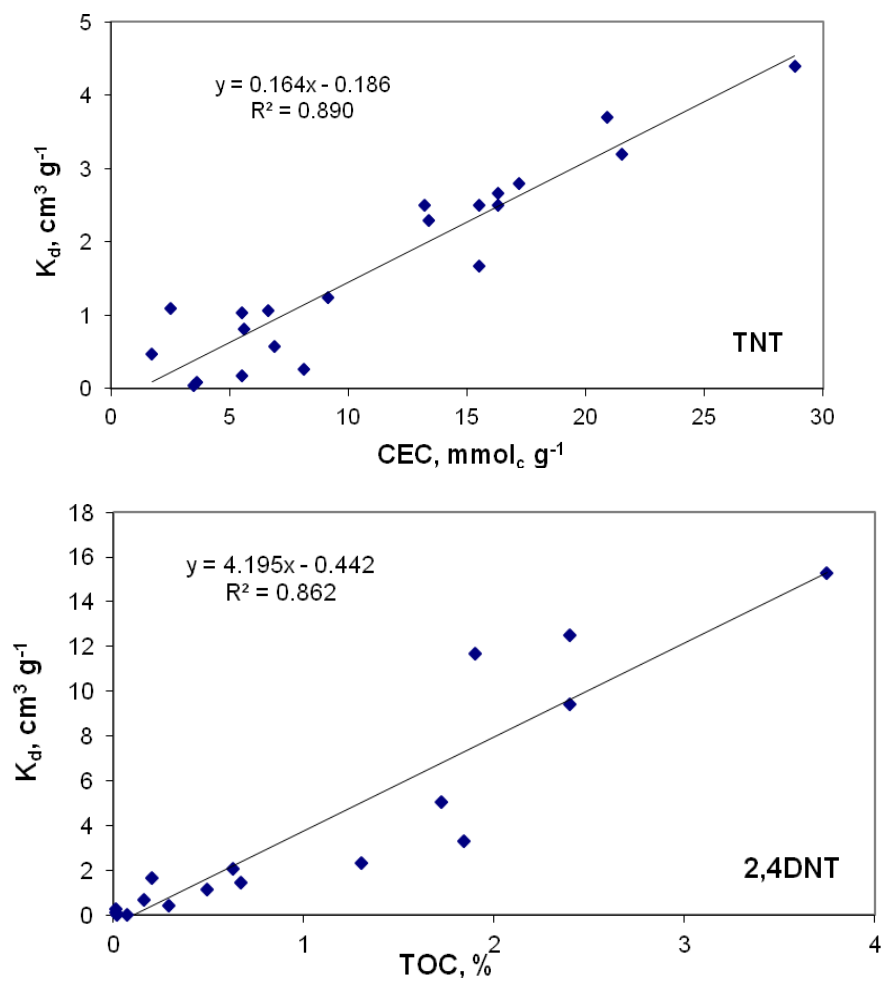
Figure 12. Linear correlation between a) measured TNT absorption coefficients (K_d) and cation exchange capacity (CEC) ($P = 1.5 * 10^{-10}$) for the soils as representation of both clay and OM in the soil; b) measured 2,4DNT K_ds and percent organic carbon (TOC) in the soil ($P = 7.61 * 10^{-8}$).

5.1. Nitroaromatic compounds and their transformation products

Nitroaromatic compounds (NACs) such as TNT and DNT, interact both with organic matter in the soils and with phyllosilicate clays. Haderlein et al. (1996) showed that K-saturated clays have very high affinities for both TNT and DNT. Same clays that are saturated with other cations have affinities for nitroaromatics that are several orders

of magnitude lower (Haderlein et al., 1996). In the environment, clays usually have a variety of cations present with K^+ being responsible for a small fraction of total cation exchange capacity. In addition, soil clays are coated with organic matter and oxides resulting in lower measured adoption in the soils compared to pure clays (Dontsova et al., 2009a). Still, high adsorption coefficients were measured for fine-textured soils (e.g. Sharkey clay/Yokena) (Brannon & Pennington, 2002).

High affinity of nitroaromatics for K^+-exchanged clays has been explained by electron donor-acceptor (EDA) complex formation with oxygen present at the external siloxane surface(s) of clay minerals, π-bond (Haderlein et al., 1996 ; Weissmahr et al., 1998 ; Weissmahr et al., 1999); or by interaction between multiple $-NO_2$ groups with exchangeable K^+ (Boyd et al., 2001). Independent of the mechanism, while K^+ saturation is not common in soils, experiments with soils indicate that clays play role in soil adsorption of nitroaromatics (Dontsova et al., 2009a ; Weissmahr et al., 1999).

Organic matter (OM) has also been shown to affect adsorption of TNT in soils (Dontsova et al., 2009a). Log k_{ow} for nitroaromatic compounds (Table 4) indicate potential for nonspecific hydrophobic partitioning to OM (Li et al., 1997). This mechanism was thought to be important for particulate organic matter (Eriksson and Skyllberg 2001); while more polar soluble organic carbon interacts with TNT and its transformation products through more ionic bonds with functional groups present in humic substances (Li et al., 1997 ; Eriksson & Skyllberg, 2001).

Pure iron oxides (magnetite, hematite, lepidocrocite, and goethite) do not show significant sorption of TNT and other nitroaromatics (Weissmahr et al., 1998). In soils, Ainsworth et al. (1993) showed a negative relationship between dithionite-citrate extractable iron (Fe_d) content and TNT adsorption. Removal of poorly-crystalline iron oxides (oxalate extractable) increased adsorption of TNT by soil clays (Dontsova et al., 2009a). Likely reason for negative effect of iron oxides on TNT adsorption is that they can cover clay surfaces and interfere with adsorption of nitroaromatics by the clay minerals.

Once the NACs TNT and DNT transform to their corresponding amine derivatives, these chemicals can irreversibly bind to soil OM through amide linkages with soil humic acids (Thorn & Kennedy, 2002 ; Thorn et al., 2008) or undergo

, undergo reversible adsorption in soils (Brannon & Pennington, 2002 ; Dontsova
et al., 2006).

Brannon and Pennington (2002) reviewed batch-determined fate and transport
parameters for explosives and propellants used by the military, including TNT, 2,4 and
2,6DNTs. A plot of K_d values assembled in this study and also reported in Taylor et al.
(2012) for DNT to determine the best bulk predictors of TNT and DNAN adsorption to
soils and sediments. Since both OM and clay are reacting with TNT, the strongest
indicator of adsorption is cation exchange capacity (CEC) that reflects both OM and clay
content in the soil (Figure 12). For 2,-DNT, adsorption to the clays is lower (Table 5) and
OC in the soil serves as a better predictor of adsorption to soils (Figure 12)

5.2. Cyclic nitroamines

RDX and HMX are heterocyclic compounds. They are more polar compared to nitro-
aromatic TNT and DNT, with smaller K_{ow} values (Table 4). This affects their interactions
in soils. They have not been shown to adsorb specifically to clay minerals (Haderlein et
al., 1996), and have lower affinity for soils that is influenced primarily by OM only
(Figure 12).

Measured soil adsorption coefficients (K_d) were reviewed by Brannon and
Pennington (2002) and Tucker et al. (2002). Significant linear regression between RDX
K_d values and soil OC content was observed by Tucker et al. (2002) indicating that
adsorption to organic matter is the main mechanism of RDX interaction with the soils.
Adsorption isotherms for RDX are generally linear and reversible (Tucker et al., 2002)
confirming partitioning as the principal sorption mechanism. Haderlein et al. (1996)
showed that RDX does not exhibit specific adsorption to clay surfaces as shown for
nitroaromatic compounds; however, it can participate in hydrogen bonding with clays
(Ainsworth et al., 1993). HMX has similar behavior to RDX but higher measured K_d
values (Table 5).

While presence of iron oxides that coat clay particles was hypothesized to affect sorption and Ainsworth et al. (1993) used amount of dithionite-extractable iron as one of several predictors of RDX adsorption, it has not been confirmed in other studies. Szecsody et al. (2004) observed no dependence of RDX adsorption on iron oxide content in studied sediments. When soil clays were treated to remove iron oxides (both amorphous and crystalline), it also did not affect adsorption of RDX (Dontsova et al., 2009a). Therefore it can be concluded that similarly to nitroaromatics, RDX does not adsorb to iron oxides.

5.3. Nitroglycerine

Reported nitroglycerin soil adsorption coefficients range from 0.08 to 3.8 cm^3 g^{-1} (Table 5) (references). These are lower than the ones determined for 2,4-DNT but similar to TNT that have similar K_{ow} values (Table 4) indicting that K_{ow} may not be a strong predictor of soil behavior for energetics. Reported K_{ow} values for NG (Table 4) can vary depending on the method used to estimate them (Mirecki et al., 2006), but generally indicate a preference for non-polar interactions. However, NG adsorption coefficients do not exhibit a strong relationship with organic matter content (P=0.4945, explain P), suggesting that other mechanisms are responsible for adsorption. NG is a polar molecule (Winkler, 1985) and may form dipole-dipole and hydrogen bonds with polar moieties in the soils.

5.4. Nitroguanidine

NQ is a highly polar compound and is very soluble in water with a negative log k_{ow}, i.e. sorption becomes questionable. However, reported pKa values (12.8) indicate that it is not protonated in environmental pH range (Spanggord et al., 1987). It has low sorption and degradation in soils and is very mobile. Batch studies report K_d values between 0.15 and 0.60 cm^3 g^{-1} (Taylor et al., 2012 ; Pennington et al., 2006). Column transport studies also showed limited potential for NQ adsorption, with K_d values ranging from 0 to 0.14 cm^3 g^{-1} (Dontsova et al., 2007). Log of NQ adsorption coefficient values normalized for soil organic carbon content (K_{oc}) were similar between the previously mentioned studies: 1.25–2.12 for Pennington et al. (2004), 0.82-1.66 for Taylor et al.

(2012) and 1.83–2.22 for Dontsova et al. (2007). However, NQ adsorption coefficients do not correlate with OC content in the soil (P=0.1585, Is P here k_{oc}?) indicating lack of partitioning behavior. This is likely related to the polar nature of the NQ molecule with negative log K_{ow} values (Table 4), which results in low affinity for non-polar organic matter in the soils.

6. Transformation pathways of munitions constituents

N-based organic explosives are rich in functional groups, most notably $-NO_2$, and thus are prone to abiotic and biotic degradation in the environment. Nitroaromatic explosives such TNT and DNT as well as cyclic and acyclic nitro-organic explosives such as RDX, HMX, NG and NQ can degrade abiotically by photolysis, hydrolysis, and reaction with zero valent iron (ZVI) an important element that is abundant in the environment (Halasz and Hawari, 2011) and be degraded by soil microorganisms under both aerobic and anaerobic conditions (Hawari and Halasz, 2002).

6.1 Propellants constituents

Nitroguanidine decomposes by photolysis to guanidine, hydroxyguanidine, urea, cyanoguanidine, ammonia and nitrosoguanidine (Haag et al. 1990; Spanggord et al. 1987; Burrows et al. 1988). When in contact with ZVI nano particles, NQ reduces to produce mainly aminoguanidine (unpublished data). Others reported that NQ can be reduced by catalytic hydrogenation to nitrosoguanidine and aminoguanidine (Lieber and Smith, 1936).

Biotically, soil microbes degraded NQ aerobically in the presence of a supplementary carbon but no degradation occurred under anaerobic conditions (Perreault et al 2012). An aerobic NQ-degrading bacterium, *Variovorax* strain VC1, was then isolated from the soil and degraded NQ when NQ was the sole nitrogen source. The products produced were NH_3, nitrous oxide (N_2O) and CO_2. A key intermediate was also detected that was identified as nitrourea by comparing it with a reference material (Perreault et al 2012). Nitrourea is unstable in water and decomposes to NH_3, N_2O and CO_2 (Fig. 13).
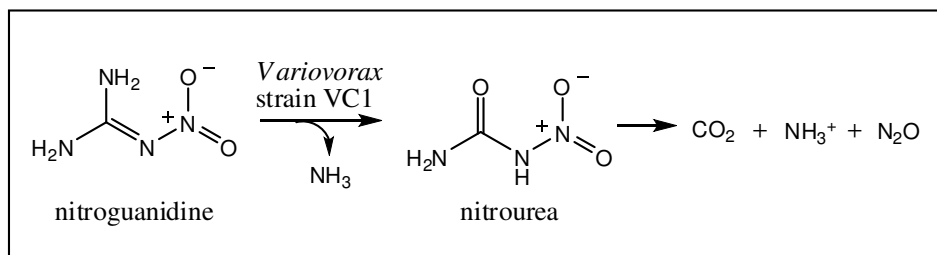
Figure 13. Degradation pathway of nitroguanidine (NQ) with *Variovorax paradoxus*

NG was degraded to glycerol and ammonium using ZVI nano particles (Saad et al. 2010). The disappearance of TNG was accompanied by the transition formation of the denitrated compounds 1,3-DNT, 1,2-DNT and MNGs and NO_2^-. Also Oh et al. (2004) reported the reduction of NG with cast iron (200 mg mL^{-1}) to produce glycerol and nitrite which was further reduced to ammonium ions.

The hydrolysis of nitroglycerine (NG) has been studied (Tsaplev 2004; Smith et al. 1983; Capellos et al. 1984), but little information is available on the eventual fate of the nitrate ester. Under mild alkaline conditions (pH 9) using microwave heating at 50 ^{0}C the trinitrate ester, NG, was easily denitrated (Halasz et al. 2010). The environmental significance of the reaction lies in the transformation of the xenobiotic and hazardous chemical to simple more ubiquitous ones such as nitrite, nitrate, HCOOH, glycolic acid and compound I, O=CHCH(OH)HC=O (Fig. 14).

Photo-degradation of 2,4-DNT in aqueous solution was reported under photo-oxidative conditions (Mary Celin et al. 2003; Ho 1986) and in the presence of cationic surfactant (Diehl et al. 2002), humic acids, or sodium salt (Mihas et al. 2007). Zero valent iron reduced 2,4-DNT's -NO_2 group to -NH_2 at the *para* position, while graphite-mediated reduction favored reduction of the *ortho* nitro group (Oh et al. 2002). 2,4-DNT was found to resists hydrolysis under alkaline conditions in soil (Davis et al. 2006). As for biodegradation, 2,4-DNT was found to undergo biotransformation under both aerobic and anaerobic conditions as summarized in Table 6.
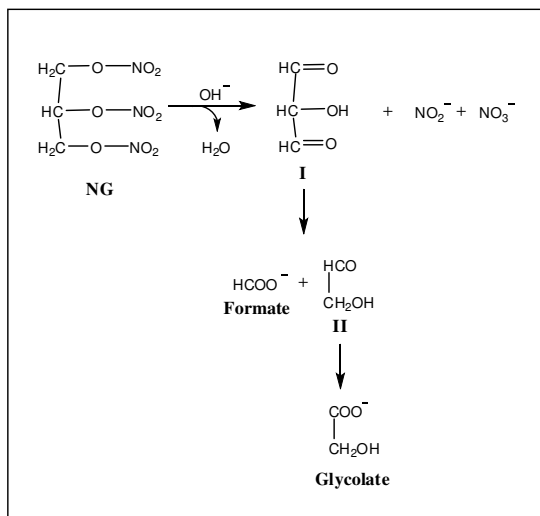
$H_2C-O-NO_2$
$HC-O-NO_2$ $\xrightarrow[H_2O]{OH^-}$ $HC=O$
$H_2C-O-NO_2$ $HC-OH$ $+$ NO_2^- $+$ NO_3^-
$HC=O$

NG **I**

$HCOO^-$ $+$ $\begin{array}{c} HCO \\ | \\ CH_2OH \end{array}$

Formate **II**

$\begin{array}{c} COO^- \\ | \\ CH_2OH \end{array}$

Glycolate

Figure 14. Proposed degradation pathways for NG alkaline hydrolysis

Table 6 Biodegradation of the propellant constituents

Substrate	Microorganisms	[ref]		
	Aerobic		Anaerobic	
2,4-DNT	*Burkholderia* sp.	[1]	Consortium	[2]
	Pseudomonas sp.	[3,4]	*Pseudomonas aeruginosa*	[5]
	Pseudomonas aeruginosa	[5]	*Clostridium acetobutylicum*	[6]
	Consortia	[7]	Indigenous microflora	[8]
NG	Consortium	[9]	Consortia	[10]
	Pseudomonas sp.	[11]		
	Arthrobacter sp.	[12]		
	Agrobacterium radiobacter	[13]		
	Pseudomonas putida	[14]		
	Rhodococcus sp.	[14]		
NQ	*Variovorax* strain VC1	[15]	Consortium	[16]

References: [1] Nishino et al. 2000; [2] Liu et al. 1984; [3] Spanggord et al. 1991; [4] Haidur and Ramos, 1996; [5] Noguera and Freedman,1996; [6] Hughes et al. 1999; [7] Snellinx et al. 2003; [8] Yang et al. 2008; [9] Accashian et al. 2000; [10] Christodoulatos et al.1997; [11] Blehert et al.1997; [12] Husserl et al. 2010; [13] White et al. 1996; [14] Marshall and White, 2001; [15] Perrault et al. 2012; [16] Kaplan et al. 1982.

6.2 High explosives compounds

Transformation pathways for the two cyclic nitroamines, RDX and HMX, and for the nitroaromatic TNT have been published (Spain, 1995; Spain et al. 2000, Hawari and Halasz, 2002, Halasz and Hawari 2011). RDX and HMX degrade abiotically (with ZVI, hydrolysis, photolysis) and biotically under laboratory and field conditions (Hawari et al. 2000; Hawari et al. 2002; Balakrishnan et al. 2003; Monteil-Rivera et al. 2005; Naja et al.2008). Degradation rates are higher for RDX and occur *via* 1) initial denitration followed by ring cleavage and 2) stepwise reduction of RDX N-NO$_2$ functional groups leading to the formation of the corresponding nitroso derivatives MNX, DNX, and TNX (Halasz et al. 2012 and 2010). During RDX transformation in soils several key intermediate ring cleavage products were detected which helped construct the degradation pathways of the cyclic nitroamine explosive. One of these key products, 4-nitro-2,4-diazabutanal (NDAB), has been detected in the field at known RDX contaminated sites thus providing vivid experimental evidence that *in situ* natural attenuation of RDX occurs (Paquet et al. 2011).

Explosives are labile molecules that are subject to abiotic and biotic transformation in the environment. In the case of RDX and HMX, the degradation pathways that we described earlier clearly show that degradation is initiated by the cleavage of the chemical bonds N–N, N–C, or N–O during chemical or microbial attack. Nitroaromatic compounds such as TNT undergo sequential reduction to their corresponding amino derivatives that depend on redox conditions used and on the position of the –NO$_2$ group on the aromatic ring (Spain, 1995; Spain et al. 2000 Hawari and Halasz, 2002). In the majority of cases TNT undergoes reductive reactions that form mono- and di-amino derivatives. This process can occur abiotically and biotically under both aerobic and anaerobic conditions. Only under strictly anaerobic conditions can the third –NO$_2$ groups reduces further giving the triamine derivative 2,4,6-triaminotoluene (TAT) (Crawford 1995; Rieger and Knackmuss1995; Hawari et al. 1998). TNT can also degrade *via* the formation of an unstable Meisenheimer complex, whose denitration leads to the decomposition of the aromatic ring (Pak et al. 2000; Vorbeck et al. 1998).

7. FUTURE WORK

Despite progress made in our understanding of the degradation pathways of explosives in controlled laboratory experiments, researchers need more sensitive and specific analytical tools suitable for detection of propellants and explosives constituents together with their transformation products, which are normally formed in trace amounts in the environment. For example, using the sensitive and specific technique TOF MS, we were able to detect two key products for RDX and HMX, namely, methylenedinitramine (MEDINA) and 4-nitro-2,4-diazabutanal (NDAB), that are currently used as markers to monitor the fate of RDX and HMX in contaminated terrestrial and aquatic environments (Halasz and Hawari, 2011; Fournier et al 2004).

Generally speaking, explosives are labile molecules that are subject to both abiotic and biotic transformation in the open in environment. For example, in the case of RDX and HMX, the degradation pathways we described earlier clearly show that chemical bonds, i.e., N–N, N–C, N–O can break during chemical or microbial attack. Information on the type and order of bond cleavage would thus be useful in identifying and isolating bacteria capable of degrading the explosive. Two techniques provide this type of information: compound specific isotope analysis (CSIA) (Sagi-Ben Moshe 2010) and stable isotope probing (SIP) (Schmidt et al. 2004). In the case of CSIA, the method relies on the fact that bacteria break the chemical bond with the lighter isotope faster than the bond with heavier isotope (e.g., cleavage of $^{14}N - ^{14}N$ rather than $^{15}N- ^{14}N$) leading to enrichment in the heavier isotopes within the residual parent molecules as biodegradation proceeds. By comparing measured stable isotope ratios of a contaminant in a field sample and in the original chemical we should be able to get useful information on the source of contamination, the occurrence of natural attenuation, and the mechanisms of degradation. In this respect, CSIA analysis has been used to quantify RDX biodegradation in groundwater (Bernstein et al 2008) and to quantify aerobic biodegradation of 2,4-DNT and TNT (Amaral et al. 2009). The second technique, SIP, uses microorganisms that can utilize the energetic chemical, e,g, RDX, TNT, or DNT, enriched with either $^{13}C-$ or $^{15}N-$atoms. The $^{13}C-DNA$ or $^{15}N-DNA$ produced during the growth of the microorganism on a spin-labeled $^{13}C-$ or $^{15}N-$ is then resolved from $^{12}C-DNA$ and $^{14}N-DNA$, respectively, by density-gradient centrifugation

(Radajewski et al 2010). The isolated spin-labeled DNA can be used as a biomarker to identify and isolate microorganisms responsible for *in situ* degradation of the explosive. Recently Roh et al. (2009) identified microorganisms responsible for RDX biodegradation and TNT-utilizing anaerobic bacteria in sediment (Gallagher et al 2010) using the SIP technique. As SIP and CSIA are showing promise for identifying and isolating RDX degraders more research and optimization is needed. Also other molecular tools suitable for on site monitoring of explosive transformation are worth pursuing.

CONCLUSIONS

We have summarized how explosives used by NATO countries are deposited in the field, the characteristics of these explosive and propellant particles and how they migrate and transform in the environment. We discussed key environmental physicochemical parameters (dissolution, S_w, pH, log K_{ow}, k_d) that give insight into the migration potential of these chemicals through subsurface soil. We also presented the primary routes involved in the degradation of these chemicals. The take home message here is once the chemicals described above are released to the environment they will be subjected to various mechanisms of transport and transformation routes. The resulting transformation products and the extent of their interactions with soil and sediment will have detrimental role on the bioavailability, ecological impact, and health risks associated with these HEs and their products. We hope the data presented in this report will help site managers support sustainable training at ranges.

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