High Explosives and Propellants Energetics: Their Dissolution and Fate in Soils

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Abstract Live-fire military training scatters energeticcompounds onto range soils. Once deposited on soil the explosives andpropellants ingredients can dissolve in water, experience complexinteractions with soil constituents, and migrate to groundwater.While in contact with soil these chemicals are also subject to biotic and abiotic (hydrolysis, photolysis, and reaction with metals) transformation both in the solid and in the aqueous state. In this chapter we 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. We also describe the key physicochemical properties (aqueous solubility (S_w), pH, octanol-water partitioning coefficient, (K_{ow})) of the energetic compounds in high explosives and propellants and how these parameters influence their biogeochemical interactions with soil. Knowing the reaction routes of these chemicals will help us understand their fate, their ecological impact, and how to enhance in situ remediation.

Keywords High explosives · Dissolution · Soil interactions · Reactive transport

List of Acronyms and Definitions

2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6,-dinitrotoluene
2,4-DANT	2,4-diamino-6-nitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene

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ATSDR	Agency for Toxic Substances and Disease Registry
CEC	Cation exchange capacity
Comp B	Composition B, a high explosive composed of 60-39-1, RDX-TNT-wax
DoD	Department of Defense
DNX	Hexahydro-3,5-dinitroso-1-nitro-1,3,5-triazine
EDAX	Energy dispersive X-ray spectrometer
EOD	Explosives ordnance disposal
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
ER	Environmental restoration
HE	High explosive
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High performance liquid chromatography
K_d	Soil adsorption coefficient
K_{ow}	Octanol-water partition coefficient
K_{OC}	Organic carbon adsorption coefficient
MC	Munitions constituent
MNX	Hexahydro-1-nitroso-3,5-dinitro-triazine
NC	Nitrocellulose
NC or NC + 2,4-DNT	Single-base propellant
NC + NG	Double-base propellant
NC + NG + NQ	Triple-base propellant
NDAB	Nitro-2,4-diazabutanal
NG	Nitroglycerin
NQ	Nitroguanidine
NT	Nitrotoluene
OC	Organic carbon
OM	Organic matter
pK_a	Acid disassociation constant
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
S_w	Aqueous solubility
TAT	2,4,6-triaminotoluene
TNT	2,4,6-trinitrotoluene
TNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine
Tritonal	Explosive made from ~80% TNT and 20% aluminum
UXO	Unexploded ordnance

1 Introduction

Explosives and propellants are highly energetic nitrogen-based chemicals that rapidly release large amounts of energy and gaseous products when detonated or burned. Because of their explosive properties, these chemicals are extensively used by the military and by the construction and mining industries [1, 2]. The US military commonly uses the nitroaromatic 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) in explosives, and DNT (2,4-dinitrotoluene), NG (trinitroglycerine) and NQ (nitroguanidine) in propellants (Fig. 1).

Live-fire military training scatters energetic compounds onto range soils. Once deposited on soil, the explosives and propellants ingredients can dissolve in precipitation and are subject to abiotic (hydrolysis, photolysis, and reaction with metals) and biotic (aerobic and anaerobic biotransformation) reactions both in the solid and in the aqueous state (Fig. 2). If on-site ecological receptors are threatened or contaminated groundwater migrates off a military base, political and regulatory actions can lead to training range closure.

Here we describe the deposition, dissolution and soil adsorption of explosives and energetic compounds and summarize how their key physicochemical properties influence their dissolution and biogeochemical interactions and transport in soil. These data are of interest for two reasons. First, these chemicals are variably toxic

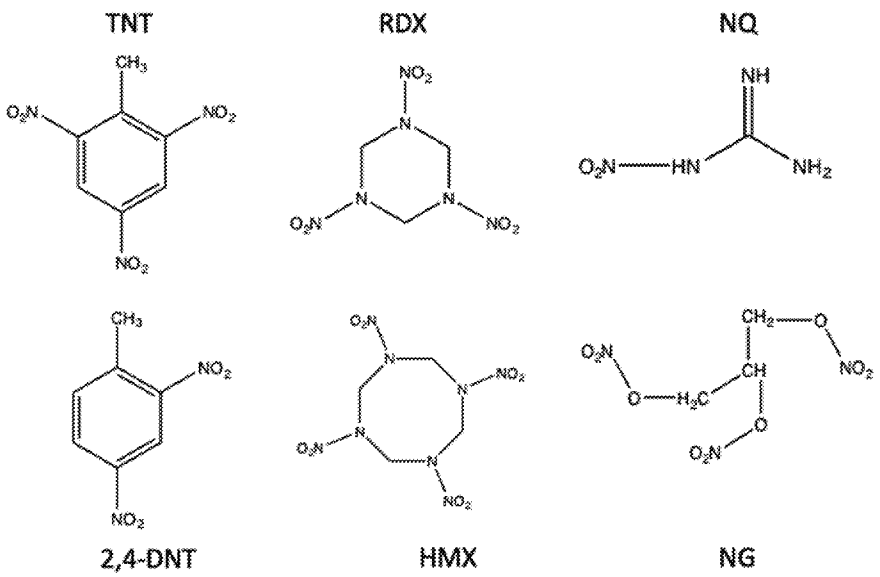

Fig. 1 Chemical structure of common munitions constituents

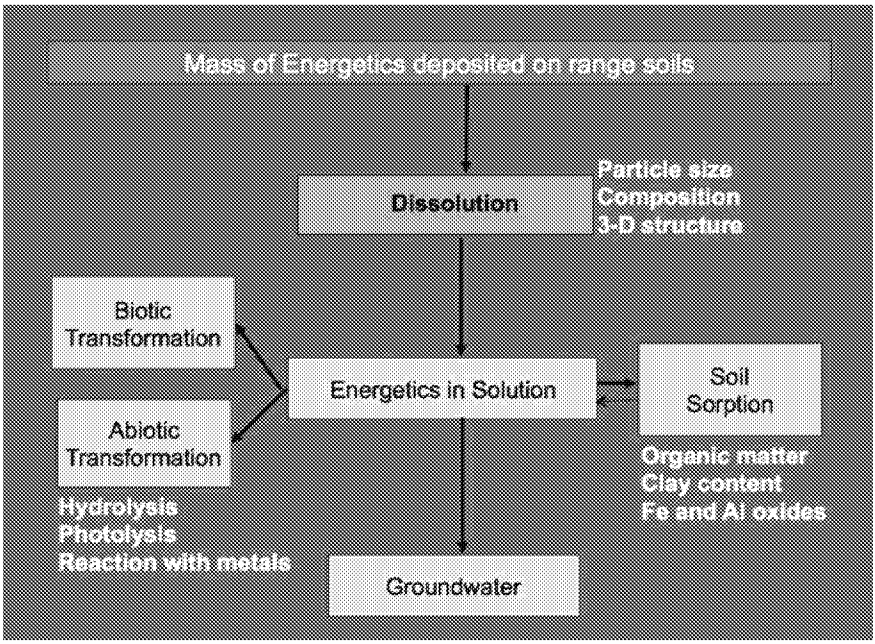

Fig. 2 Schematic showing the processes that affect the environmental fate of explosives deposited on training range soils

and can be deleterious to human, animal and plant health to varying degrees [3]. Second, these compounds can migrate through subsurface soil and contaminate groundwater [4]. Understanding the reaction routes of these chemicals will help us to understand their fate, their ecological impact, and help design remediation strategies.

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), unexploded ordnance (UXO), or blow-in-place detonations of UXO. Table 1 lists compounds found in commonly used explosives and propellants.

Table 1 Energetic chemicals found in military propellants and explosives

Compound	Uses	Chemicals of concern
Propellant formulations		
Single base	Howitzers (M1)	2,4-DNT
Double base	Small arms, mortars, howitzers	NG
Triple base	Howitzers (M31)	NG and NQ
Explosive formulations		
Comp B	Howitzers; mortars	RDX, TNT
C4	Demolition explosive	Military-grade RDX
Tritonal	Aerial bombs	TNT, Al
Comp A4	40-mm grenades	RDX
TNT	Howitzers	TNT
Comp H-6	Aerial bombs	RDX and TNT, Al
Octol	Antitank rockets	HMX and TNT

Note that military grade RDX contains ≈ 10% HMX and military-grade TNT contains ≈ 1% other TNT isomers and technical grade DNT contains ≈ 90% 2,4-DNT and 10% 2,6-DNT

2.1 Propellants

Propellants are generally composed of nitrocellulose (NC) impregnated with either 2,4-dinitrotoluene (called single-base), nitroglycerin (called double-base) or nitroglycerin and nitroguanidine (called triple-base). Propellant residues are partially burned and unburned particles of the solid propellant deposited on the soil surface. The shape of the original propellant grain and the presence or absence of perforations (made to increase the burn rate) dictates the appearance of the residue [5]. For example, propellant 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 constrained by the size of the original propellant grains, many of which are millimeters in size.

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 occurs as NC particles, with NG or 2,4-DNT located in the NC matrix [6]. NQ-containing propellants appear to leave little residue when used to fire 155-mm howitzer rounds [7].

The patterns of distribution for the residues vary depending on how the propellants are used. 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 5–30 m of the firing position (Table 2). For artillery, propellants are found

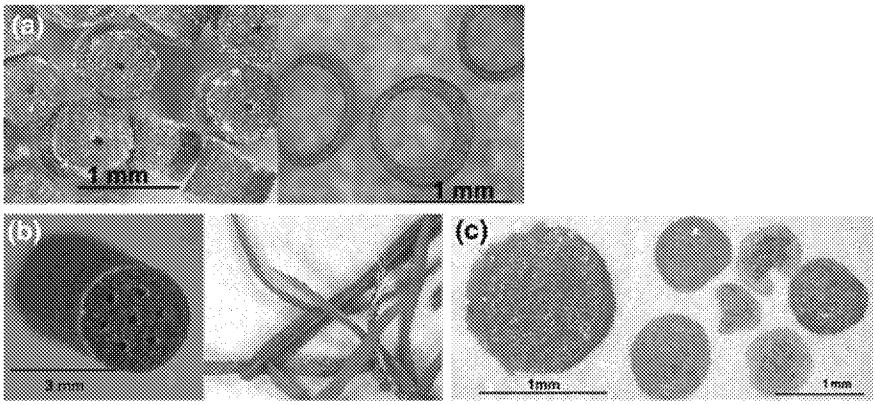

Fig. 3 Single perforated M45 propellant grains and residues (**a**), a multi-perforated M1 propellant and residues (**b**), and an M9 grain and residues (**c**) from Taylor et al. [5]

up to 75 m downrange. 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 the impact area, as all the propellant has generally not been expended before the rocket hits the target.

Pieces of propellant are often visible on training range soils and although the propellant particles are usually not transported, the 2,4-DNT, NG, and NQ, initially within the NC propellant matrix, can dissolve in precipitation and travel with the water into the soil. Taylor et al. [8] found that for unfired grains any NG near the surface of the propellant is readily dissolved. However, energetics in the center of the grain take time to diffuse through the insoluble NC matrix. Disposal of unused propellants by burning bags on the soil can scatter partially burned grains and contaminate the soil. A burn pan designed for this purpose is a much cleaner option [9].

2.2 *High Explosives*

Pieces of high explosives are scattered onto soils when rounds are detonated. For high order detonations 99.99% of the mass in these rounds is consumed in the detonation (Table 3) and the small amounts of residue deposited are μm-size particles [10, 11]. Low-order or partial detonations, on the other hand, deposit some fraction of the fill (Table 3) as particles and chunks (Fig. 4). These large pieces can deposit from 10,000 to 100,000 times more residue per round than high-order detonations [7]. The percentage of fired rounds that undergo low-order detonations varies from one munition type to another and was studied by Dauphin and Doyle [12].

When fired, some rounds do not detonate and result in UXO that will eventually release all of their explosives into the environment if they are not removed or

Table 2 Mass of propellant energetic constituent deposited during firing

Weapon system	Propellant	Constituent	Rounds fired	Residues/round (mg)	Deposition distance (m)	References
Howitzers						
105-mm	M1-I and II	2,4-DNT	71	34		[66]
105-mm	M1	2,4-DNT	22	6.4		[6, Ch. 4]
155-mm	M1	2,4-DNT	60	1.2		[67]
Mortars						
60-mm	Ignition cartridge	NG	40	0.09	12	[68]
81-mm	M9 (illuminator)	NG	61	1000	50	[68]
120-mm	M45	NG	40	350		[69]
Shoulder-fired rocket						
84-mm Carl Gustov	AKB 204/0	NG	39	1055	30[a]	[28, Ch. 4]
84-mm AT4	AKB 204	NG	5	20,000	50[a]	[66]
Tank (Leopard)						
105-mm	M1	2,4-DNT	90	6.7		[70]
Grenade						
40-mm HEDP	M2	NG	144	76	5	[71]
40-mm TP	F15080	NG	127	2.2	5	–
Small arms						
5.56-mm rifle	WC844	NG	100	1.8	10	[72]
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 (0.50 cal)	WC860 & 857	NG	195	11	40	–

[a]Major deposition is behind the firing line for shoulder-fired rocket

destroyed (Fig. 5). UXO are sometimes destroyed using blow-in-place practices by military Explosive Ordnance Disposal (EOD) technicians or contractor UXO technicians. Currently, military EOD personnel use C4, a demolition explosive that is 91% RDX, for blow-in-place operations. Thus, even if RDX was not present in the UXO, it is often present in soils when rounds have been blown in place. Blow-in-place operations that detonate UXO high order are almost as clean as high-order detonations of fired rounds. 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 Comp B-filled rounds

High-order detonations	Analyte	# Rounds sampled	Ave. HE fill deposited (%)	References
Mortars—Comp B				
60-mm	RDX	11	3×10^{-5}	[73]
	TNT	11	1×10^{-5}	
81-mm	RDX	5	2×10^{-3}	[73]
	TNT	5	3×10^{-4}	
120-mm	RDX	7	2×10^{-4}	[69]
	TNT	7	2×10^{-5}	
Hand grenades—Comp B				
M67	RDX	7	2×10^{-5}	[73]
	TNT	7	Not detected	
Howitzers—Comp B				
105-mm	RDX	9	7×10^{-6}	[74]
	TNT	9	2×10^{-5}	
155-mm	RDX	7	5×10^{-6}	[67]
	TNT	7		
Partial-detonations				
Mortars—Comp B				
60-mm	RDX + TNT	6	35	[51]
81-mm	RDX + TNT	4	42	[51]
120-mm	RDX + TNT	4	49	[51]
Howitzers—Comp B and TNT				
105-mm	RDX + TNT	15	27	[51]
155-mm	TNT	12	29	[51]

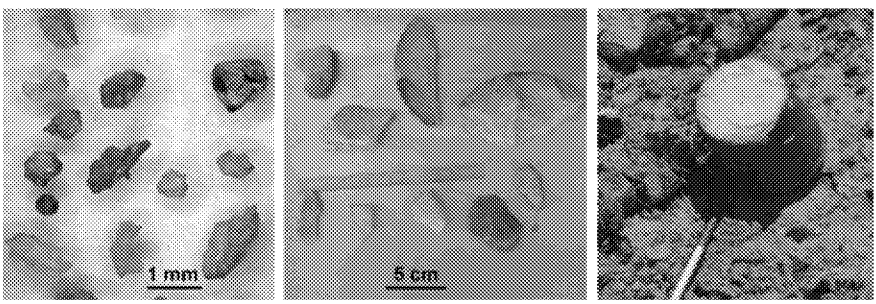

Fig. 4 Comp B pieces from a single partial detonation [11]

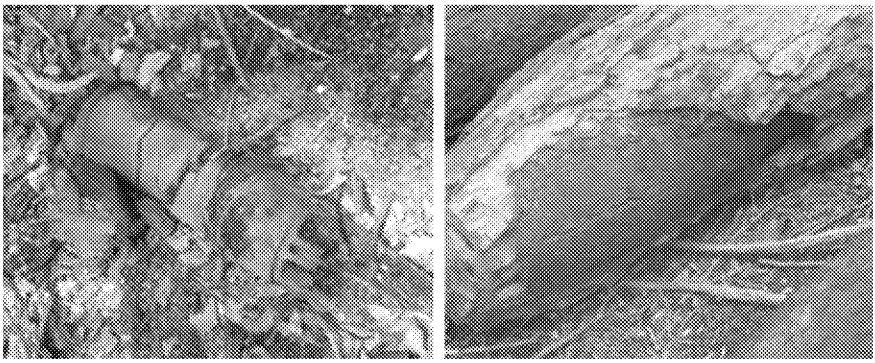

Fig. 5 Explosive fill exposed by corrosion of unexploded ordnance (UXO) casings [65]

At antitank rocket ranges, the distance from the firing position to the target is only a few hundred meters and, so, most rounds detonate, or rupture, near the targets. The highest concentrations are next to targets and decrease with distance from the target [13]. Unlike antitank ranges, soils near artillery targets have much lower concentrations of residues and there is no concentration gradient with distance from the targets. The much larger distances between artillery firing positions and their targets results in a much larger impact area around the targets. This situation also exists for mortar targets that often are used for both artillery and mortar testing and training.

Unlike propellants, there is generally no well-defined depositional pattern for high explosive residues. The largest sources of scattered explosives at impact areas derive from partial detonations (low-order), UXO ruptured by shrapnel from nearby live-fire detonations, or blow-in-place activities that produce low order detonations. Residues from these sources produce a localized zone of high concentration, 'point sources', that are not correlated across the range. Because the number of UXO and partial detonations is poorly known, it is difficult to estimate the mass of HE present at an impact area even if the number and type of rounds fired are known. The values provided by Dauphin and Doyle [12] can be used as a guide, but the mass of residues deposited needs to be determined by sampling.

Deposition patterns for energetic residues and how to sample for these on different types of ranges are discussed in [14, 15]. For other types of contaminants resulting from firing (e.g., metals) one would need to consider how these are deposited and any patterns in their spatial distributions [8, 16].

3 Dissolution of Energetic Compounds

Dissolution is thought to be the rate-limiting step for aqueous transport of energetic compounds to groundwater. Figure 6 shows experimental techniques that measure the dissolution of individual post-detonation HE particles, both in the laboratory and in an outdoor setting [17]. Each technique isolated dissolution from the confounding effects of soil interaction and scaled dissolution directly with drip rate (lab tests) or with the precipitation rate (outdoor tests). These tests mimic field conditions on training ranges, where residues are scattered on the soil surface and whose constituents are dissolved by precipitation. Such tests were successfully used to measure and model dissolution of high explosives [18].

3.1 Propellants

Single-base propellants containing 2,4-DNT are used to fire artillery, mainly 105- and 155-mm rounds from Howitzers. From drip tests Taylor et al. [5] showed that 2,4-DNT dissolved from unfired grains slowly but at a constant rate: after 500 days the maximum DNT loss was 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. The mass loss curves were not linear. They initially rose rapidly and then became more linear but still had a positive slope.

Double-base propellants are the most common type of propellant 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. [5] found that the mass of NG

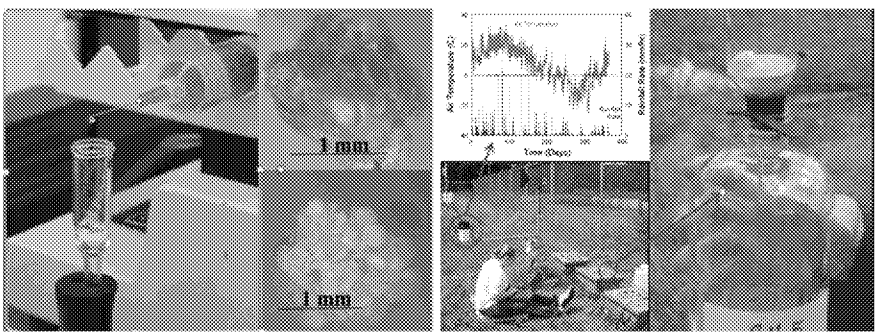

Fig. 6 Laboratory drip tests (*left*) and outdoor dissolution tests (*right*) [24]

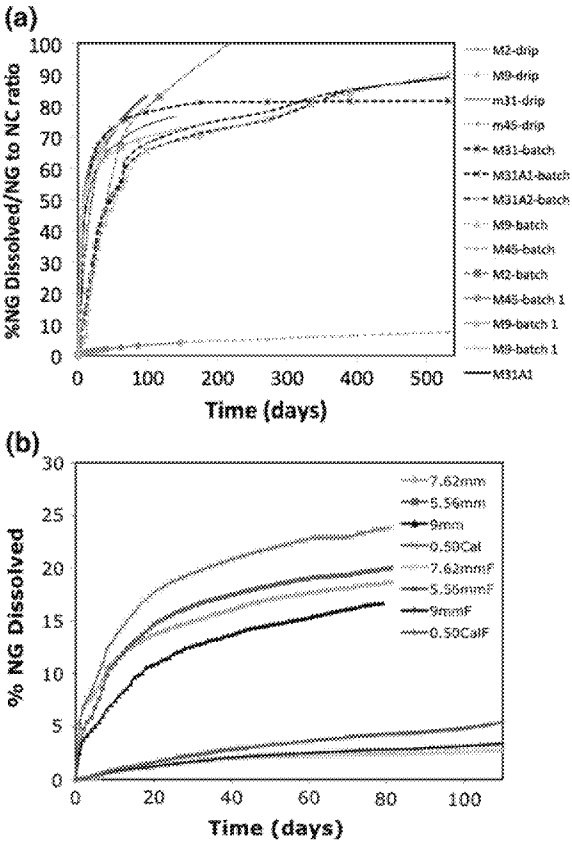

Fig. 7 **a** Plot showing the % NG dissolved normalized by the NG/NC ratio versus time. All of the data from NG containing propellants, except for the small arms, are plotted on this figure. **b** Plot of the percent NG dissolved versus time for unfired (*top*) and fired (*bottom*) of the same four small arms propellants

dissolved was a function of the NG/NC ratio in the propellant (Fig. 7a). Clustering of the data using this normalization technique suggests that NC binds 10–20% of the NG and that any extra NG is easily dissolved.

Exceptions from this trend were the ball propellants, used to fire small arms, and the M45 propellant used to fire mortars. The ball propellants all contained ~10% NG, yet variable amounts of NG were dissolved independent of their NC content. The M45 propellant also contained 10% NG yet it lost less than 1% during the drip tests (Fig. 7a). The M45 is a squat grain with a central perforation, which should increase its NG loss. The low NG loss suggests that the nitrocellulose in M45 was not fully nitrated when it was manufactured so that the NG was effectively bound to the NC.

Dissolution data were collected from both fired residue and unfired grains from double-base ball propellants used to fire small arms. The concentrations of NG in the unfired grains were within the variability given in the technical manuals whereas the fired residues contained about 80% of the original NG on a mass basis. Figure 7b shows that more NG was dissolved from the unfired propellants

(15–20%) than from their residues (3–7%). For the unfired propellants 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 (S_w) of NG suggests it could be rapidly dissolved by contact with water if it existed as fine liquid droplets within an NC matrix. Droplets at the grain surface would quickly be dissolved by precipitation leaving the NG within the grain that would need to diffuse ($\sim 10^{-14}$ cm^2 s^{-1}) through the NC matrix to reach the water [19]. Late time dissolution would thus be limited by molecular diffusion.

Diffusion-limited dissolution also qualitatively accounts for the much lower dissolution rates observed for fired grains. Firing likely burns or volatilizes surface NG droplets so dissolution would be limited by molecular diffusion of NG from deeper within the NC matrix. 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 consumed during firing.

Triple base propellants are also used to fire artillery and contain NQ in addition to NG. Although there is more NQ than NG in the M31 propellant, and NQ is more soluble than NG (Table 4), both by mass and by percentage, more NG is dissolved (Fig. 8) [19]. This occurs because during manufacture of the propellant, NG is added as a liquid, whereas NQ is mixed in as a solid. The NQ, therefore, has to dissolve before it can leave the propellant.

Tests to measure how well the components in triple-based propellants were mixed [20] 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. Yazici et al. 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

Table 4 Some physicochemical properties of explosives

Compound	Formula	Mol wt.	Density (g cm^{-3})	S_w at 25 °C (g L^{-1})	Log K_{ow} at 25 °C
TNT	$C_7H_5N_3O_6$	227	1.65	0.10[c]	1.86–2.00[d]
2,4-DNT	$C_7H_6N_2O_4$	182	1.52	0.28[d]	1.98[d]
RDX	$C_3H_6N_6O_6$	222	1.82	0.060[e]	0.87[e], 0.81–0.87[d]
HMX	$C_4H_8N_8O_8$	296	1.81	0.0045[f]	0.17[f]
NG	$C_3H_5N_3O_9$	227	1.6	1.95[g]	1.62[g]
NQ	$CH_4N_4O_2$	104	1.71	2.6[i], 4.4[j]	−0.89[i], 0.148[i]

Data from [c]Ro et al. [75], [d]Rosenblatt et al. [76], [e]Banerjee et al. [77], [f]Monteil-Rivera et al. [78], [g]U.S. Army Materiel Command [79], [i]Haag et al. [80], [j]Van der Schalie [81]

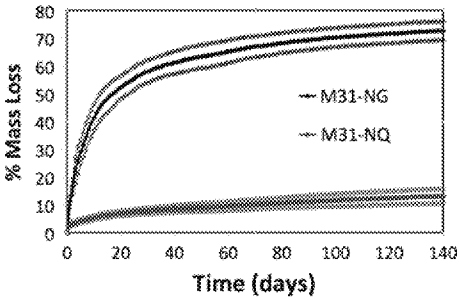

Fig. 8 Percent NG and NQ dissolved (Ave. ±1 sigma, n = 8) versus time for unfired M31 single-perforation propellants [5]

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.

A HYDRUS-2D simulation was able to model dissolution of NG and NQ from the M31 propellant using a combination of diffusion and adsorption of energetics to the NC matrix (Fig. 9). Diffusion only did not adequately describe the experimental results. However, adding kinetic adsorption significantly improved the fit (Fig. 9) and decreased the error for parameter estimates. For NG, adsorption to two types of kinetic sites (one slow and one fast) better described the data than one adsorption site only, but for NQ one kinetic site was sufficient. If no adsorption was modeled, fitted diffusion coefficients were lower than determined in simulations that included kinetic adsorption, as slow release was attributed to diffusion. If we included sorption, slow release was explained partially by slow desorption. The diffusion coefficients ($2.09 \times 10^{-8} \pm 4.39 \times 10^{-9}$ cm^2 s^{-1} for NG and $1.78 \times 10^{-9} \pm 3.74 \times 10^{-10}$ cm^2 s^{-1} for NQ) were higher than found for small arms propellants [8, 19] but in general agreement with numbers reported by Levy [21] for nitroglycerin in cellulose acetate, 5.2×10^{-9} cm^2 s^{-1}. The fact that HYDRUS-2D simulations require an

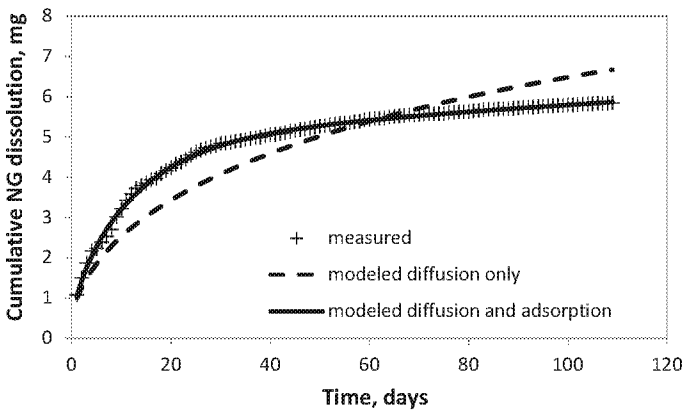

Fig. 9 Observed (*crosses*) and HYDRUS-1D generated cumulative dissolution curves for NG from M31 propellant particle in drip studies without soil: diffusion only (*dashed line*) and diffusion and adsorption on two kinetic sites in NC (*solid line*) [5]

adsorption term to describe energetic dissolution from propellants, supports observations by Yazici and Kalyon [22] that NG in propellant particles is adsorbed and held by NC preventing its movement within the particle.

3.2 High Explosives

The dissolution of pieces and particles of TNT, Comp B, and Tritonal was measured in the laboratory [17] and in the field [23]. Observations showed the TNT particles becoming smoother and smaller but retaining 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. 10a, b).

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 (Figs. 10c and 11b).

The cumulative mass losses for TNT pieces are shown in Fig. 11a. Data for Comp B, Tritonal and C4 are in Taylor et al. [24]. Except for the particles that split

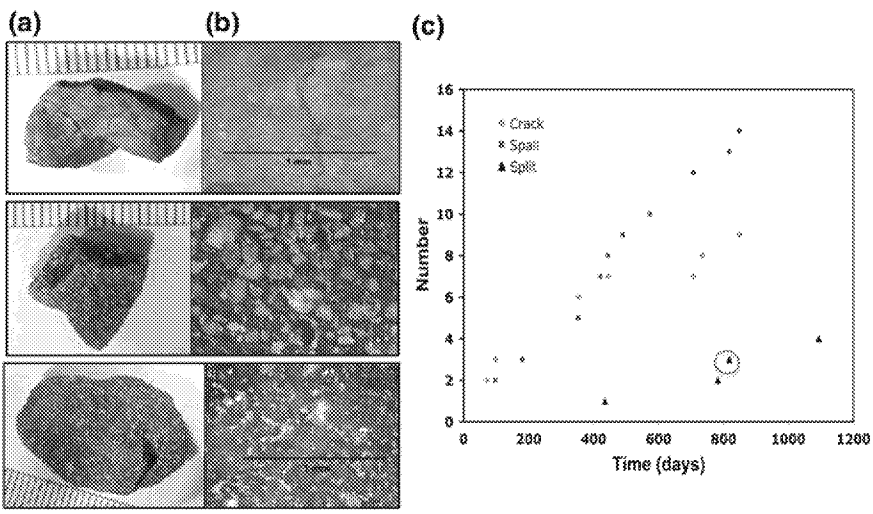

Fig. 10 **a** Photograph of particle and **b** close-up of its surface for TNT, Comp B and tritonal; **c** Number of HE chunks that cracked, spalled off a 1 mm piece, or split into multiple millimeter-sized pieces over the three-year test. For example, the *circled triangle* indicates that 3 of the 34 chunks had split by day 810 of the test

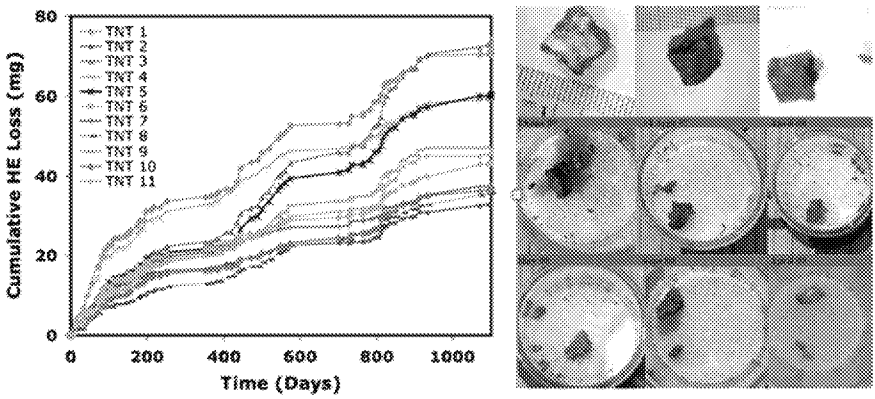

Fig. 11 *Left* cumulative mass loss of TNT (mg) versus time as measured by HPLC; *right* images of TNT particle # 3 over the course of the experiment

(TNT 3 and 5) the shapes of the cumulative mass loss curves are similar among all the particles. Although the largest particles 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.

A dissolution model for explosives was developed and validated using data from both the laboratory and outdoor experiments [18, 23, 24]. The key input parameters are particle size, HE type, annual rainfall, and average temperature. Given those parameters, the model offers a simple and accurate way to predict aqueous-phase HE influx into range soils (Fig. 12).

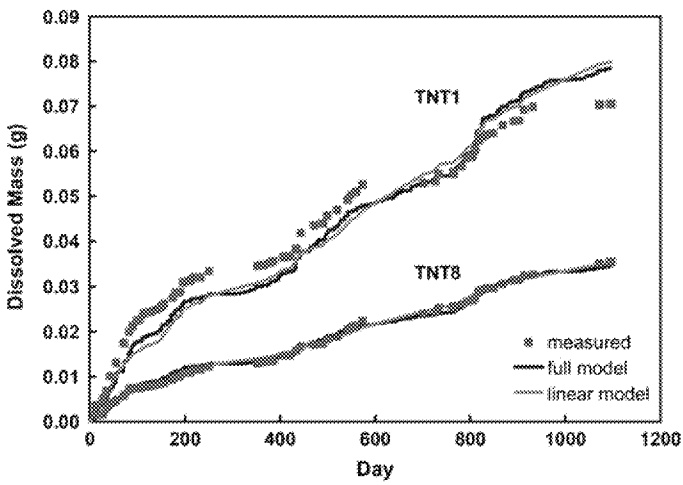

Fig. 12 Dissolved TNT mass measured for TNT 1 (1.9 g) and TNT 8 (0.36 g) along with predictions from full and linear drop-impingement models [24]

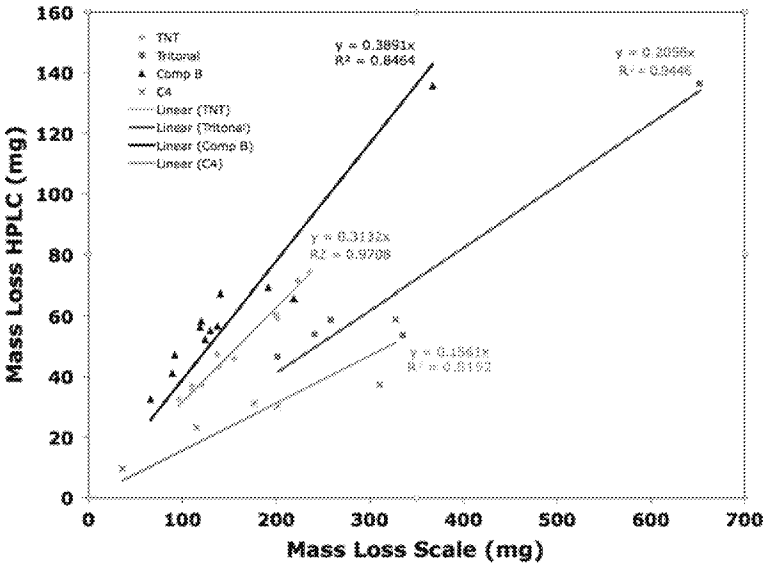

Fig. 13 Over 60% of the mass lost from the HE pieces, as measured by electronic balance, was not measured as dissolved explosives by the HPLC. The unaccounted for masses were larger than dissolved explosive masses, they scaled closely with surface area of each particle and increased with time

The mass loss for each HE chunk after three years is shown in Fig. 13. Note that two types of measurements are plotted against each other: mass loss measured by electronic balance, and cumulative dissolved mass obtained via high performance liquid chromatography (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 both measurement methods had low uncertainties, and there were very good mass balances for TNT, Tritonal, and Comp B in the laboratory tests [17, 18].

Mass balance discrepancies could be due to formation of transformation products unquantified by HPLC caused by photolysis of the particle's surface or by hydrolysis on the wetted surface of the particle. Photo-transformation is inherent to outdoor weathering of explosives. TNT containing explosives and aqueous solutions are known to turn red and RDX also degrades [25]. TNT was found to produce 2-amino-4,6-dinitrobenzoic acid and a red product, both of which are stable, soluble, polar and elute chromatographically in the pre-solvent peak [24]. The 2-amino-4,6-dinitrobenzoic acid was found in concentrations similar to those measured for TNT and could account for about half of the missing mass. The poor mass balance of RDX was attributed to its photo-destruction as formaldehyde and nitrate, which were detected in photo-degradation studies [24, 25]. On training ranges, these transformation products likely constitute additional HE-based contaminant influx into range soils.

4 Physicochemical Properties of Explosive and Propellant Constituents

Insight into the fate of energetic compounds in the environment can be derived from their physicochemical properties, including solubility in water (S_w), partitioning between water and non-polar solvents (octanol-water partition coefficient, K_{ow}), and acid dissociation constant (pK_a). Table 4 summarizes key physicochemical parameters of studied explosives. The aqueous solubility is a measure of how much of a compound can dissolve in water at a given 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. Some energetics in propellants, such as NG, and NQ, are soluble (Table 4) and have low health screening levels for drinking water. NG, for example, has a solubility limit of approximately 1500 mg L^{-1} at 20 °C in water [26] and a screening level of 1.5 μg L^{-1} in residential water [27]. Nitrocellulose, NC, on the other hand, is insoluble and has no known health or environmental risks, so its deposited mass is not estimated [28].

Energetic compounds in high explosives such as RDX, HMX and TNT have low solubility. HMX is almost insoluble in water (4 mg L^{-1}), adsorbs to soils, and does not migrate to the subsurface, while RDX and TNT, which are more soluble, have been detected in subsurface environments and in the groundwater of contaminated sites [29]. As Table 4 shows, solubility changes drastically between each of the following classes: nitroaromatics (TNT, DNT), cyclic nitroamines (HMX, RDX), nitrate esters (NG) and nitroimines (NQ).

Octanol-water partitioning coefficient is a measure of the polarity of the molecule, which affects its geo-biochemical interactions in the environment in a variety of ways. Less polar molecules have a higher affinity for octanol, a non-polar solvent, and for lipids, while more polar molecules have an affinity for water, a polar solvent. Therefore, compounds with high log K_{ow} values partition into lipids, while those with low log K_{ow} values partition into water. Because non-polar interactions are involved, explosives with high log K_{ow} values tend to partition into soil organic matter (OM). High partitioning to soil OM usually means high soil sorption and decreased migration through the subsurface to groundwater. High log K_{ow} also promotes diffusion through a cellular membrane potentially causing damage to the biological receptor. As environmental contaminants become more lipophilic (up to log K_{ow} of 3 to 4) their uptake increases [30].

Of the explosives, TNT with its three $-NO_2$ groups partitions into OM and is the most hydrophobic ($1.8 < \log K_{ow} < 2.0$). Transformation of TNT to its amine derivatives, i.e. replacing $-NO_2$ groups by $-NH_2$ groups, reduces its hydrophobicity and affinity for soil organic matter and increases its water solubility. Reduced TNT amine products, therefore tend to migrate through the subsurface soil unless their migration is slowed down by immobilization mechanisms, e.g. chemisorption by forming –NH–C(O)—covalent bonds with soil OM [31].

5 Soil Interactions

Explosives are N-based organics that are rich in functional groups, a property that promotes biogeochemical interactions in the environment. Soil constituents, including organic matter, phyllosilicate clays, iron and aluminum oxides and hydroxides, can all adsorb energetic compounds, due to their high surface areas and their various functionalities, or interfere with adsorption (e.g. [32]). The soil type can, therefore, drastically influence the extent of soil—contaminant interactions (Table 5). Interactions of explosive constituents with soil affect their environmental fate and the risk associated with their use in the field.

When the $-NO_2$ functional group(s) in explosives transform to the corresponding $-NH_2$ (amino-) group(s) under various environmental redox conditions [2, 37] different products have different physicochemical properties (S_w, pK_a, K_{ow}) influencing their soil adsorption [31, 38–40]. For example, Haderlein et al. [36] reported that reversible sorption to montmorillonite decreased with the number of nitro groups and followed the order TNT > DNT > NT (nitrotoluene).

Soil adsorption coefficient (K_d), a ratio between concentration of compound in the soil and solution, is used to characterize affinity of energetics for soil. As K_d values increase, the chemicals tend to reside mostly on the solid surface and little is transported downward in the moving pore water. Since the majority of adsorption of organic contaminants in soils is attributed to soil OM, K_d values are often normalized to soil organic carbon (OC) content. The resulting K_{OC} parameter (soil OC adsorption coefficient) can then be used to calculate adsorption of these compounds to other soils based on their carbon content. For example, RDX tends to partition to organic carbon [32, 33] and its behavior can be predicted using K_{OC}. However, TNT exhibits very complex sorption behavior. In addition to being adsorbed to both polar and non-polar regions of organic matter [34, 35], TNT can intercalate and be adsorbed between clay layers [36].

5.1 TNT, DNT and Their Transformation Products

Nitroaromatic compounds, such as TNT and DNT, interact both with organic matter and with phyllosilicate clays in the soil. Haderlein et al. [36] showed that K-saturated clays have very high affinities for both TNT and DNT but that their affinities decreased by several orders of magnitude when clays were saturated with other cations. Although K^+ is usually not a dominant cation in soils, experiments indicate that soil clays do adsorb nitroaromatics, but that adsorption is decreased by mixed clay mineralogy, the cation composition, and organic and oxide coatings on soil clays [32, 41].

Table 5 List of soil adsorption coefficients, K_d, for energetic compounds interacting with soils and minerals

Soils	Clay (%)	OC (%)	K_d (L kg^{-1})					
			TNT	2,4-DNT	RDX	HMX	NG	NQ
Newport	5.6	3.5	2.3[h]	–	–	–		
Lonestar	10.0	0.06	2.5[h]	–	–	–		
Cornhuskers	20.0	0.83	4.1[h]	–	–	–		
Crane	20.6	2.8	3.7[h]	–	–	–		
Joliet	23.8	3.6	6.8[h]	–	–	–		
Holston B	43.8	1.2	3.0[h]	–	–	–		
Sharkey Clay	54.4	2.4	11[h]	–	–	–		
K^+-LAAP D[a]	32	0.20	167[i]	12.5	0.66[i]	1.73[i]		
Aqua-gel	>87	ND[c]	130[j]	130[j]	6.6[j]	8.9[j]		
Sassafras loam	11[d] 16.4[l]	0.33[d] 1.30[l]	–	2.34[l]		0.7[d]	0.26[l]	0.60[l]
Catlin silt loam	15.7[l] 18[n]	3.75[l] 4.23[n]	17.9[n]	15.30[l]	2.03[n]		1.27[l]	0.24[l]
Kenner muck	55	35.4	285.2[n]		36.19[n]			
Benndale fine sandy loam	20	0.89	1.77[n]		0.78[n]			
Adler silt loam	4.5[m]	0.29	2.4[m]		0.48[m]	0.48[m]	0.08[p]	
Plymouth sandy loam	14.4[l] 5.0[m]	1.72[l]	1.6[m]	5.06[l] 0.28–2.01[o]	0.65[m]	0.43[m]	1.41[l]	0.44[l]
Yokena/Sharkey clay	48.7	2.4	10[q]	12.5[s] 9.43[g]	3.5[h]	12.1[t]		0.43[r]
Picatinny	5	0.63		2.06[g]		4.25[t]	3.8[f]	
Grange Hill	10	0.29		0.43[g]		0.12[t]		0.15[r]
Varennes	4	8.4	4.2[e]		1.9[e]	2.5[d]		
LAAP A[a]	6	0.31	1.09[i]			1[i]		
LAAP C[a]	12	0.08	1.06[i]					
LAAP D[a]	32	0.2	1.67[i]	1.67[s]	0.3[i]	2.4[i]		

(continued)

Table 5 (continued)

Soils	Clay (%)	OC (%)	K_d (L kg^{-1})					
			TNT	2,4-DNT	RDX	HMX	NG	NQ
Minerals								
K^+-montmorillonite	NA[b]	ND	21500[k]	7400[k]	1.2[k]			
K^+-illite	NA	ND	12500[k]	3650[k]				
K^+-kaolinite	NA	ND	1800[k]	690[k]				
Ca^{2+}-montmorillonite	NA	ND	1.7[k]					
Ca^{2+}-illite	NA	ND	1.2[k]					
Ca^{2+}-kaolinite	NA	ND	0.3[k]					
K^+-montmorillonite	NA	ND	414[i]		3.17[i]	22.1[i]		

[a]*LAAP* Louisiana army ammunition plant
[b]*NA* non applicable
[c]*ND* not determined
Data from [d]Monteil-Rivera et al. [78], [e]Sheremata et al. [82], [f]Pennington et al. [83], [g]Pennington et al. [84], [h]Pennington and Patrick [37]; [i]Price et al. [85], [j]Leggett [86], [k]Haderlein et al. [36], [l]Taylor et al. [5], [m]Dontsova et al. [47], [n]Dontsova et al. [32], [o]Dontsova et al. [56], [p]Dontsova et al. [52], [q]Townsend et al. [59], [r]Pennington et al. [53], [s]Pennington et al. [87], [t]Brannon et al. [88]

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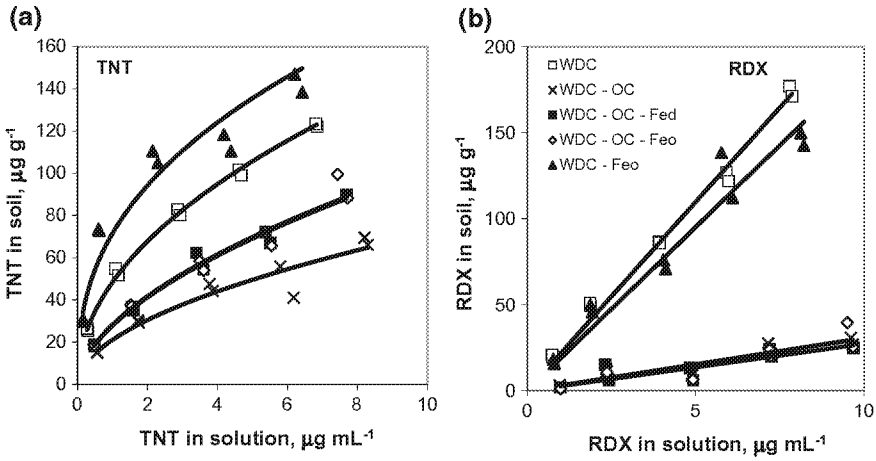

Fig. 14 Adsorption isotherms for TNT in Catlin (**a**) and RDX in Kenner (**b**) water-dispersible clay (WDC). WDC samples were then treated to remove carbonates, organic matter (–OM), non-crystalline aluminosilicates and hydrous oxides (–Fe_o), and free iron-aluminum oxides and hydroxides (–Fe_d) [32]

Organic matter also affects adsorption of TNT in soils (Fig. 14). Octanol-water partitioning coefficients for nitroaromatic compounds (Table 4) suggest nonspecific hydrophobic partitioning to OM [42]. This mechanism was thought to be important for particulate organic matter [34] while more polar soluble organic carbon interacts with TNT and its transformation products through bonds with functional groups present in humic substances [34, 42]. The non-linear shape of adsorption isotherms for TNT in soils (Fig. 14a) suggests that mechanisms other than OM partitioning are contributing to its retention.

Pure iron oxides (e.g., magnetite, hematite, lepidocrocite, and goethite) do not adsorb TNT or other nitroaromatics [43]. Ainsworth et al. [44] showed a negative relationship between dithionite-citrate extractable iron (Fe_d) in soils and TNT adsorption. Removal of poorly-crystalline iron oxides (oxalate extractable) increased adsorption of TNT by soil clays (Fig. 14a). The likely reason for the negative effect of iron oxides on TNT adsorption is that they cover clay surfaces and interfere with adsorption onto the clay minerals.

Once the nitro groups in TNT and DNT are reduced to amino groups, the latter can irreversibly adsorb to OM through covalent bonds [31, 45]. The mechanism involves the amino-transformation products of TNT [2-ADNT; 4-ADNT; 2,4-DANT; 2,6-DANT and TAT (2,4,6-triaminotoluene)] undergoing nucleophilic addition reactions with quinone and other carbonyl groups in the soil humic

acid to form both heterocyclic and nonheterocyclic condensation products. Earlier studies also revealed that monoamino- and diamino derivatives of TNT, ADNT and DANT, experienced reversible adsorption in soils [46, 47]. The strongest indicator of TNT adsorption was the cation exchange capacity (CEC) that accounted for both OM and clay content in the soil, as well as clay mineralogy (Fig. 15). For 2,4-DNT, adsorption to the clays was lower (Table 5) and OC was a better predictor of adsorption to soils (Fig. 15).

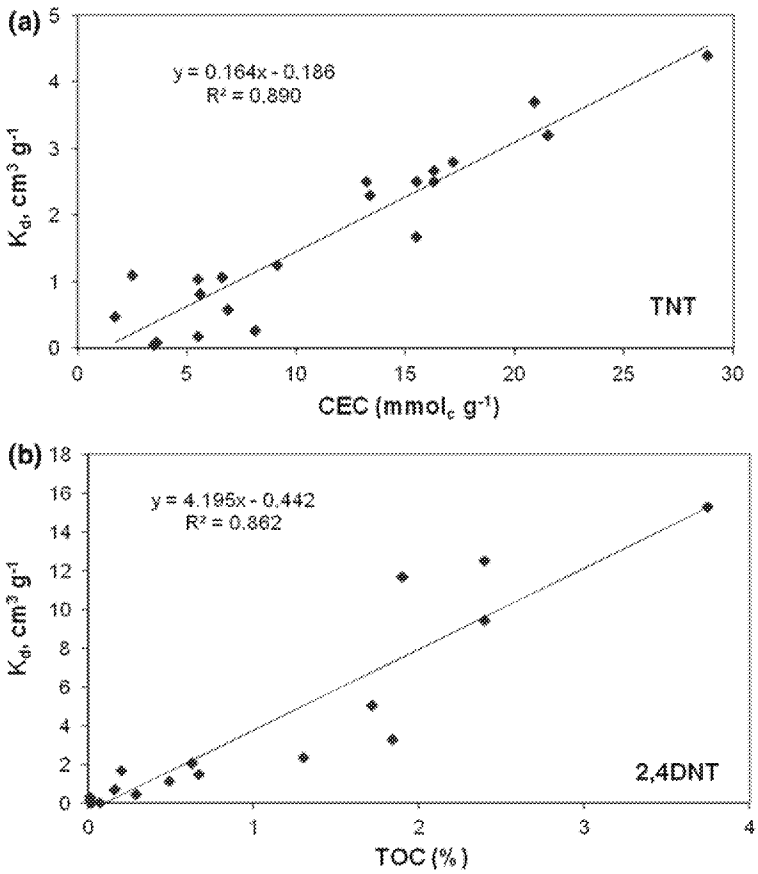

Fig. 15 Linear correlation between **a** measured TNT soil adsorption coefficients (K_d) and cation exchange capacity (CEC) that accounts for clay and OM in the soil ($P = 1.5 \times 10^{-10}$; data are from Brannon and Pennington [46]) and **b** measured 2,4-DNT K_d values and percent organic carbon (OC) in the soil ($P = 7.61 \times 10^{-8}$; data from Brannon and Pennington [46] and Taylor et al. [5]). P values smaller than 0.01 indicate a highly significant correlation

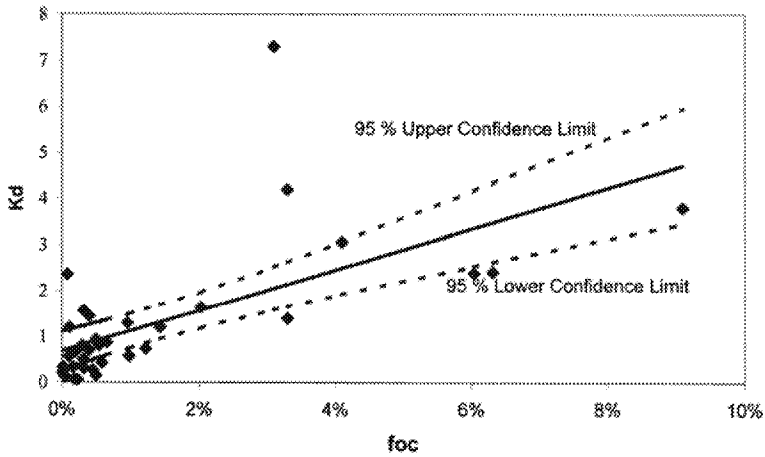

Fig. 16 Linear correlation between percent organic carbon in the soil and adsorption coefficients (K_d), L kg^{-1}, for RDX [33]

5.2 RDX and HMX

RDX and HMX are heterocyclic compounds. They are more polar and have smaller K_{ow} values than the nitro-aromatic TNT and DNT (Table 4). They do not adsorb to clay minerals [36], and have a lower affinity for soils that is determined primarily by OM (Figs. 14b and 16).

Measured soil adsorption coefficients were reviewed by Brannon and Pennington [46] and Tucker et al. [33]. Significant linear regression between RDX K_d values and soil OC content was observed by Tucker et al. [33] (Fig. 16) indicating that adsorption to organic matter is the main way RDX interacts with the soils. Adsorption isotherms for RDX are generally linear and reversible [32, 33] (Fig. 14b) confirming partitioning as the principal sorption mechanism. Haderlein et al. [36] 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 [44]. Similarly to nitroaromatics, RDX does not adsorb to iron oxides. Szecsody et al. [48] observed no dependence of RDX adsorption on iron oxide content in studied sediments; and removal of iron oxides (both amorphous and crystalline) did not affect adsorption of RDX by soil fines [32]. HMX has a similar behavior to RDX but higher K_d values (Table 5).

5.3 Nitroglycerine

Reported nitroglycerin soil adsorption coefficients range from 0.08 to 3.8 cm^3 g^{-1} (Table 5), lower than the ones determined for 2,4-DNT. This agrees with a factor of

two lower K_{ow} values (Table 4), though a larger difference was measured in K_d values than in K_{ow} values for the two compounds. NG adsorption coefficients are not correlated with organic matter content (P = 0.4945), suggesting that other mechanisms are responsible for adsorption. NG is a polar molecule [49] and may form dipole-dipole and hydrogen bonds with polar moieties in the soils.

5.4 Nitroguanidine

NQ is a highly polar compound. However, reported pKa values (12.8) indicate that it is not protonated in environmental pH ranges [50]. It has low sorption and degradation in soils and is very mobile. Batch studies report K_d values between 0.15 and 0.60 $cm^3\ g^{-1}$ [5, 51]. Column transport studies also showed limited potential for NQ adsorption, with K_d values ranging from 0 to 0.14 $cm^3\ g^{-1}$ [52]. Calculated log K_{oc} values for NQ are similar: 1.25–2.12 for [53], 0.82–1.66 for [5] and 1.83–2.22 for [52]. However, NQ adsorption coefficients do not correlate with OC content in the soil (P = 0.1585) indicating a 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.

5.5 Reactive Transport

A number of studies have evaluated the transport of explosives and propellants compounds in soils [5, 47, 52, 54–60]. These studies measured both transport of prepared aqueous solutions and of solutions from dissolving particles. The latter combines dissolution and transport to observe leaching patterns and to evaluate the effect of varying concentrations of energetics, due to dissolution and compound interactions, on transport. Here we discuss solution-phase transport of explosives and propellants, combined dissolution and transport, and colloidal and particulate transport of explosive compounds.

Figures 17a, b show examples of breakthrough curves observed for aqueous solutions of TNT and RDX in a sandy soil. Note that RDX is little affected by interaction with the soil and elutes soon after the unreactive aqueous tracer, while TNT elutes later than the tracer and at a diminished concentration. Figure 17c, d show the transport behavior of Comp B when added as an aqueous solution (c) and as small particles on the surface of the column (d). The second scenario is representative of the particles dissolving on a soil surface as would be expected for the field conditions. When Comp B is added in solution, the RDX concentration in the leachate was much higher compared to all other solutes due to higher content of RDX in Comp B and the fast transformation of TNT in soil. In contrast, when Comp B particles are used, the concentrations of TNT and RDX are much closer in magnitude. The differences between these breakthrough curves exist because TNT

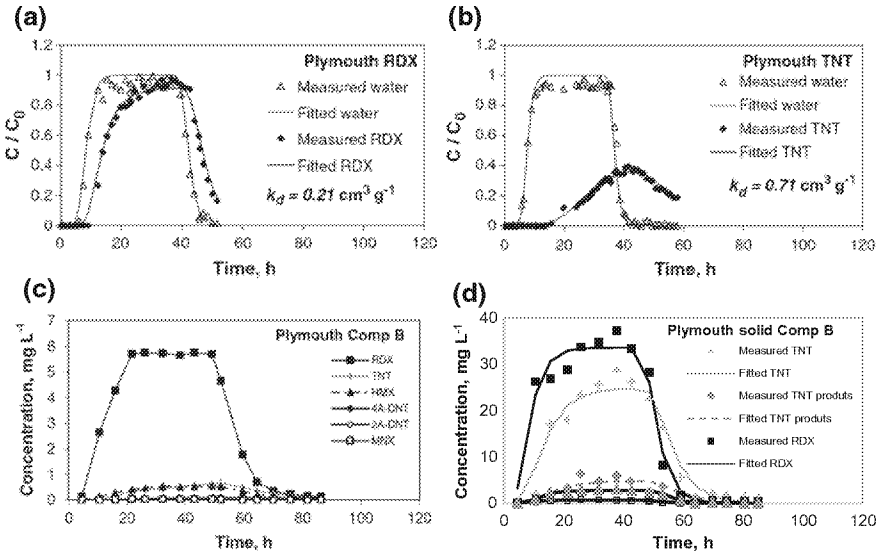

Fig. 17 Breakthrough curves for ^3H_2O tracer, as well as ^{14}C-RDX (**a**), ^{14}C-TNT (**b**), liquid phase Comp B (**c**), and solid phase Comp B (**c**) for continuous flow experiments. Tests used Plymouth loamy sand from Camp Edwards, MA and typical rainfall rate for the area [47]

dissolves faster than RDX. Overall for Comp B particles, dissolution was relatively steady and highly significant linear relationships were found among dissolution rates determined by HYDRUS-1D simulations for TNT, RDX and HMX eluting from the particles [47].

The transport behavior of propellants in solution is a function of their affinity for the soils. 2,4-DNT and NG are adsorbed and transformed in soils and therefore are retarded during transport, while NQ, which does not adsorb to soils and is very persistent, tends to travel through the soils with the water. Dissolution and therefore elution patterns of propellants are very different from explosives. While explosives followed approximately zero-order kinetics of dissolution, propellants are characterized by very high initial dissolution from the particles followed by steady state or quasi steady state dissolution. The pattern is explained by diffusion-limited dissolution from the insoluble NC matrix as discussed in Sect. 3.1. If the flow is interrupted and then restarted (as may happen between rainfall events), the effluent concentrations increase again (Fig. 18). Both the peak and the steady-state concentrations are highly dependent on the compound. For NQ there is a very sharp spike in concentration followed by low steady-state concentrations, while NG does not have a sharp peak but tends to maintain a higher concentration in the effluent over time (Fig. 18c) even when the concentration of NQ in the propellant is higher than for NG (19.5% NG and 55% NQ in M31 propellant). Very large changes in concentration result in non-linear adsorption behavior with soils having lower affinity for the propellants initially as the first elution wave moves through the soil

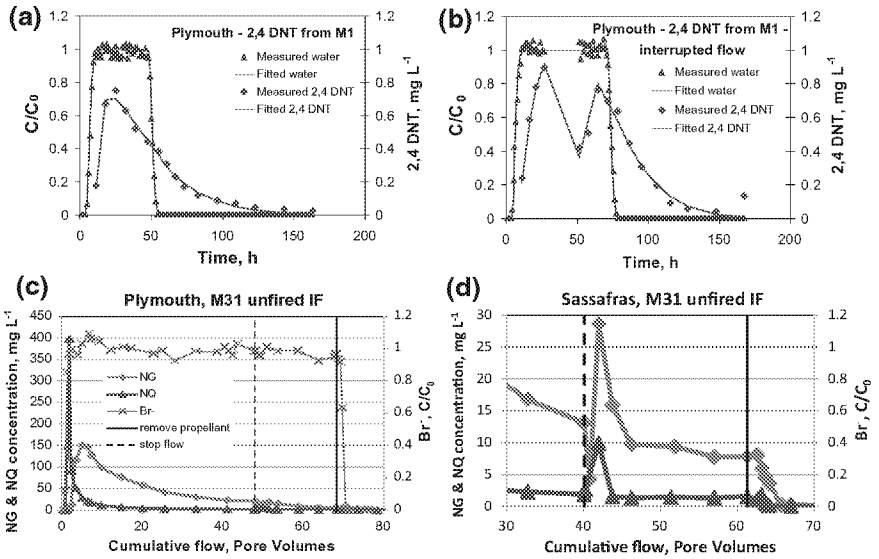

Fig. 18 Breakthrough curves for ^3H_2O tracer, as well as NG, NQ, and 2,4-DNT for continuous flow experiments in Plymouth and Sassafras soils and interrupted flow (segment) using solid propellants. The decrease in concentration of NG upon flow interruption is attributed to transformation, followed by an increase in concentration due to time-limited dissolution. NQ experiences only the increase in concentration when flow is interrupted because it does not transform

profile and higher affinity when the concentrations are lower later. Little 2,4-DNT was observed in the effluent of columns with M1 propellant [5, 56] due to low dissolution rates and high adsorption and transformation in soils. For all studied propellants higher effluent concentrations were observed for unfired propellants compared to the fired residues. Increase in the flow rate resulted in a decrease in the NG concentration indicating dissolution limitation on the propellant constituent flux. Slow dissolution of energetics in propellants results in their long residence in NC particles and lack of ground water contamination [61].

A mechanism of transport that is not often considered but can influence movement of energetics in soils is colloidal or facilitated transport. Colloids are 0.001–1 μm particles that are potentially mobile and have a high affinity for dissolved explosives due to their high surface areas. If an energetic is strongly adsorbed by the colloid, colloid-facilitated transport can become a significant part of the overall movement of this chemical. Because water samples are routinely filtered through 0.45 μm filters when analyzed for explosives, a part of colloid-adsorbed explosives could be included in water analyses. The fraction >0.45 μm represents explosives that are potentially mobile but not routinely analyzed, while the fraction <0.45 μm are explosives included in routine water analysis. However, the behavior of colloid-adsorbed explosives in the water would differ from the behavior of pure explosives in solution. Since the mobility of the

colloids is influenced by the ionic strength of the solution, these and their HE "passengers" could be moved by low electrolyte rainwater. The HE might also be precipitated out by any salt in the aqueous solution.

To determine the contribution of colloidal transport the effluent from soil columns receiving solutions of TNT and RDX was analyzed. The effluent was either filtered (0.45 μm), not filtered, or flocculated using alum and filtered to remove colloids. No difference was found between the filtered and unfiltered samples, indicating that the explosives are either attached to colloids <0.45 μm in size or are fully dissolved. However, the results of filtering after addition of alum to flocculate colloids indicated that there was a significant amount of explosives in the filtered material that was transported with colloidal particles or dissolved organic matter (Fig. 19; Table 6).

The contribution of colloidal transport to the total transport of energetics depended on soil type and on solution chemistry (Table 6). High electrolyte concentration resulted in a smaller contribution of colloidal transport. For RDX in all soils and conditions and for TNT without salt in all soils and with salt in Benndale

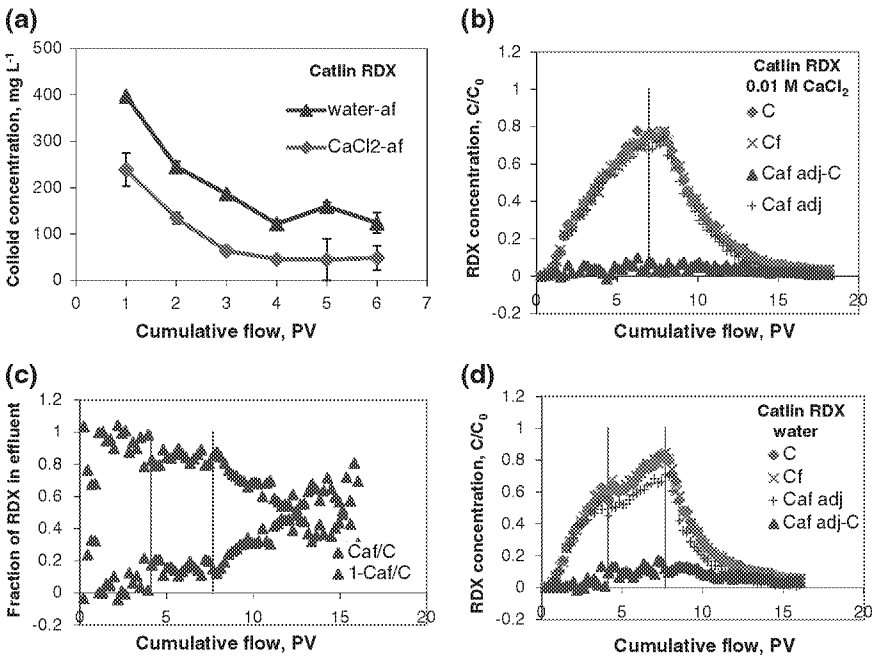

Fig. 19 Colloid concentration in solution (**a**), and breakthrough curves for RDX in Catlin soil in the presence of 0.01 M $CaCl_2$ (**b**) and in water (**d**), as well as a fraction of RDX in solution and adsorbed to colloids (**c**). *Vertical lines* indicate timing of flow interruption and when the RDX solution was switched back to the background solution without RDX. C–^{14}C-RDX in unfiltered samples, C_f–^{14}C-RDX in samples filtered through 0.45 μm filter, C_{afadj}–^{14}C-RDX in samples that were filtered through 0.45 μm filter after addition of alum. "*Adj*" refers to correction for dilution of the sample through alum addition

Table 6 Percent of total explosives in solution moved through soil with colloidal particles

	Catlin silt loam 4.2% OC 18% clay 16% WDC[a]		Benndale fine sandy loam 0.9% OC 20% clay 8% WDC[a]		Kenner muck 35.3% OC 55% clay 7% WDC[a]	
	Mean	CI	Mean	CI	Mean	CI
TNT						
0.01 M $CaCl_2$	1.37	1.65	0.49	0.16	0.43	0.54
Water	2.08	1.07	1.43	1.05	0.70	0.01
RDX						
0.01 M $CaCl_2$	4.11	1.20	0.97	0.31	1.34	0.05
Water	6.56	0.84	1.36	0.00	2.61	0.38

[a]*WDC* water-dispersible clay

soil, colloidal transport was significantly different from zero. For RDX but not TNT there was a significant difference between the mass of explosive transported with 0.01 M $CaCl_2$ and without salt. At low electrolyte concentrations, the contribution of colloidal transport to the transport of explosives is greater because at higher concentrations colloids are flocculated and immobilized (Fig. 19a).

The largest amount transported (6.56%) was for RDX in mineral soil with high organic matter content (4.2% OC). Natural rainfall has a low salt content so no salt treatment realistically represents field conditions. The significant colloid transport observed for high OM soil may be exaggerated due to the use of repacked columns as repacking could mobilize more colloids. However, if we consider that the HE particles that serve as the source of energetics are deposited in impact areas, disturbances of the soils would be expected.

The contribution of colloidal transport varied during the course of the experiment (Fig. 19c). The largest quantity contributed was expected in the beginning of the tests because this is when colloid concentrations in the effluent were the largest (Fig. 19a). However, the colloid transport was largest during the desorption stage of the isotherm and colloidal transport is responsible in large part for the tailing observed in transport experiments.

Another way explosives can be transported is if micron-sized explosives residues, resulting from detonations or particle weathering, move through soils [62]. Fuller et al. [63] showed that 20–45 μm sized particles of Comp B moved through sand resulting in increased transport compared to mm-sized particles. Similar results were obtained for transport of 2,6-DNT particles ground to 2–50 μm size in sand and glass beads [64]. The contribution of particulate transport of explosives should be more significant in coarse sediments with large pores and fast pore water velocities, while in finer soils micrometer sized particles would likely dissolve before they are transported due to their high surface area per mass.

5.6 Conclusions

A critical problem facing range managers is determining if live-fire training is likely to contaminate groundwater under their ranges. Off-base migration of energetic contaminants may trigger federal regulatory actions that can close bases or restrict training. To predict the likelihood of off-base contamination, one needs to know the following:

- the mass, type and spatial distribution of explosives on the range;
- the dissolution rates of each HE type as a function of piece size, rainfall and temperature;
- the interaction of aqueous-phase HE with different types of soil; and
- the amount of transport through the vadose zone to the groundwater.

Good progress has been made in quantifying and characterizing the residues deposited by live fire training. The key environmental physicochemical parameters (dissolution, the octanol-water partitioning coefficient, and soil adsorption coefficient) have also been measured for TNT, RDX, HMX, 2,4-DNT, NG, and NQ and a robust dissolution model developed for TNT and RDX, if their particle sizes are known.

In regards to groundwater contamination, TNT bio- and photo-degrades and is less likely to reach groundwater than RDX, which is stable and has a low affinity for soils. The energetics in propellant residues, 2,4-DNT, NG and NQ, tend to dissolve slowly from their nitrocellulose matrix and the NG/NC ratio appears to control the amount of NG dissolved. Because 2,4-DNT and NG interact strongly with soils and have high adsorption and transformation rates, they are unlikely to reach groundwater. NQ, on the other hand, has a low soil adsorption and does not degrade or transform in the soil and could travel to groundwater.

Probably the largest source of uncertainty in estimating HE aqueous influx into range soils results from poorly quantified mass of HE residues on ranges. The number and sizes of these particles depends on many factors including the munitions used, their firing rates, their detonation probabilities (high-order, low-order, or dud) and weathering and mechanical disaggregation. If we had a better estimate of the mass of HE particles, this information could be used to predict the HE aqueous influx to soils. When coupled to a vadose transport model, these data would provide a first-order estimate of the HE mass reaching groundwater.

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