

DESORPTION OF NITRAMINE AND NITROAROMATIC EXPLOSIVE RESIDUES
FROM SOILS DETONATED UNDER CONTROLLED CONDITIONSTHOMAS A. DOUGLAS,*† MARIANNE E. WALSH,‡ CHRISTIAN J. MCGRATH,§ CHARLES A. WEISS,§
ASHLEY MARIE JARAMILLO,†|| and THOMAS P. TRAINOR||

†U.S. Army Engineering Research and Development Center, Fort Wainwright, Alaska

‡U.S. Army Engineering Research and Development Center, Hanover, New Hampshire

§U.S. Army Engineering Research and Development Center, Vicksburg, Mississippi

||Department of Chemistry, University of Alaska Fairbanks, Fairbanks, Alaska, USA

(Submitted 1 April 2010; Returned for Revision 25 June 2010; Accepted 3 September 2010)

Abstract—Potentially toxic nitroaromatic and nitramine compounds are introduced onto soils during detonation of explosives. The present study was conducted to investigate the desorption and transformation of explosive compounds loaded onto three soils through controlled detonation. The soils were proximally detonated with Composition B, a commonly used military explosive containing 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Gas-exchangeable surface areas were measured from pristine and detonated soils. Aqueous batches of detonated soils were prepared by mixing each soil with ultrapure water. Samples were collected for 141 d and concentrations of Composition B compounds and TNT transformation products 2-amino-4,6-dinitrotoluene (2ADNT), 4-amino-2,6-dinitrotoluene (4ADNT), and 1,3,5-trinitrobenzene (1,3,5-TNB) were measured. The RDX, HMX, and TNT concentrations in detonated soil batches exhibited first-order physical desorption for the first, roughly, 10 d and then reached steady state apparent equilibrium within 40 d. An aqueous batch containing powdered Composition B in water was sampled over time to quantify TNT, RDX, and HMX dissolution from undetonated Composition B particles. The TNT, RDX, and HMX concentrations in aqueous batches of pure Composition B reached equilibrium within 6, 11, and 20 d, respectively. Detonated soils exhibited lower gas-exchangeable surface areas than their pristine counterparts. This is likely due to an explosive residue coating on detonated soil surfaces, shock-induced compaction, sintering, and/or partial fusion of soil particles under the intense heat associated with detonation. Our results suggest that explosive compounds loaded to soils through detonation take longer to reach equilibrium concentrations in aqueous batches than soils loaded with explosive residues through aqueous addition. This is likely due to the heterogeneous interactions between explosive residues and soil particle surfaces. *Environ. Toxicol. Chem.* 2011;30:345–353. © 2010 SETAC

Keywords—Explosive residues TNT RDX HMX

INTRODUCTION

Active training on defense installations uses munitions containing 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) explosives. Nitramine (RDX and HMX) and nitroaromatic (TNT) compounds are known toxicants [1,2] that can be deposited onto range soils during training exercises. Nitramines are generally considered less reactive in soils than nitroaromatic compounds (NACs) that undergo sorption from aqueous solutions onto sediment surfaces, especially to clay minerals [3–5]. TNT can transform to 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) which can also sorb and bind to organic or mineral phases in soils. The deposition of explosive residues and their transformation products to soils poses a potential long-term contamination risk for the U.S. Department of Defense and industry. Understanding the extent of this risk requires detailed knowledge of the temporal fate of these compounds in training range soils.

The mass loading of explosive compounds to training range ecosystems is controlled by the degree to which detonation reactions reach completion. Partial (i.e., low-order) detonations

contribute a greater mass of explosive compounds to range soils than full (high-order) detonations [6,7]. However, uptake onto soil particle surfaces and transformation of explosive compounds depend strongly on soil and water biogeochemical parameters [4,8–15]. It has recently been shown that nitramine and nitroaromatic compounds exhibit greater transformation rates in aqueous solutions in the presence of fractured soil particles than in weathered soils [16]. This may be attributable to enhanced electron-reduction transformation in the presence of fresh, reactive mineral particle surfaces and/or to the presence of an active microbiological regime on fresh soil particle surfaces. The dissolution of Composition B (RDX and TNT with minor HMX) particles, and the desorption and dissolution of explosive detonation residuals, has been quantified and modeled based on particle sizes and the effect of rainfall to better simulate the temporal fate of explosive residues in training range ecosystems [17,18].

A majority of the previous work on the fate of explosive compounds in training range soils utilized batch reactors with pure compounds loaded to soil media as aqueous additions to soil slurries under controlled laboratory conditions. However, explosive compounds are designed for brisance, their ability to shatter materials [19,20]. Detonation events likely create fresh (unweathered) mineral surfaces which are coated with a combination of explosive residues (soot), undetonated explosive material, and other volatilized or remobilized range soil materials [6,7,21]. This type of real-world loading of explosive

* To whom correspondence may be addressed
(thomas.a.douglas@usace.army.mil).

Published online 29 October 2010 in Wiley Online Library
(wileyonlinelibrary.com).

residues to soil particles is difficult to recreate in a laboratory. To address this knowledge gap in our understanding of the temporal fate of explosive residues in soil solutions, we detonated dry soils using common explosives and then quantified the desorption (solution phase partitioning) and transformation of the explosive compounds as a function of time in aqueous batch reactors. The explosive Composition B, which contains roughly 60% RDX, 39% TNT, 1% wax filler, and minor HMX as an RDX impurity, was used. We proximally detonated three soils that represent typical training range soils.

MATERIALS AND METHODS

Soil composition, detonation, and collection

The location information, soil mineralogy, major- and trace-element chemical composition, and grain-size distribution of our three soil samples were presented in an earlier study [16], but are briefly summarized here. The three soil types detonated in the present study were extracted from river banks, represent soils that are thousands of years old, and likely were not previously exposed to soot or other potentially interfering chemical compounds. *Delta* is classified by the United Soil Classification System (USCS) as well-graded sand with silt. *Delta* was collected near Delta Junction, Alaska, USA (63.854°N, 145.732°W) and contains quartz, chlorite, calcium, and sodium feldspars, and illite clay. *Church*, classified by USCS as poorly graded glaciofluvial sand, is from Norwich, Vermont, USA (43.737°N, 72.261°W) and contains the same mineralogy as *Delta*. The BBTs, from the Big Black River test site, is classified by USCS as silty sand and was collected near Bovina, Mississippi, USA (32.273°N, 90.719°W). The BBTs contains quartz, sodium feldspar, potassium feldspar, and illite clay. A 2-kg subset of each sample was sieved into seven fractions between 10 and 200 mesh to characterize the soils following established protocols [22].

The three soils were proximally detonated in a 20-cm wide by 40-cm deep by 50-cm long steel can. A 3-m length of military detonation cord, cotton, and asphalt tubing filled with pentaerythritol tetranitrate, with a uli knot tied in one end, was placed into a paper cup containing 120 g of flakes of Composition B (Fig. 1A). The Composition B flakes were 0.5-cm thick and most flakes were less than 3 cm in length or width. The cup of Composition B was placed on the bottom of the can and roughly 6 kg of dry soil was placed in the can to cover the Composition B and detonation cord to a height of 15 cm. The can was isolated inside a 2-m² container constructed of 8-cm thick steel that was open at the top. The detonation cord was initiated remotely with a M21 shock tube initiator (lead, barium, antimony, and aluminum compounds with pentaerythritol tetranitrate and minor HMX) from a safe location 500 m away.

Figures 1B and C show samples before and after detonation. Following detonation, two types of samples were collected from each steel can and placed into precleaned high-density polyethylene bags. First, a precleaned polytetrafluoroethylene (PTFE, Teflon[®]) scoop was used to collect the upper 0.5 cm of soil from the can. This material was generally lightly soot-covered and contained aggregated chunks of soil material loosely bound together. These samples represent surface samples. After the entire surface 0.5 cm of sample was removed, the remaining material was collected to represent a bulk sample. Each detonation was recorded by video and no dudding (partial detonations) occurred. No Composition B particles were detected in any of the samples through visual or microscopic ($\times 10$ magnification) inspection.

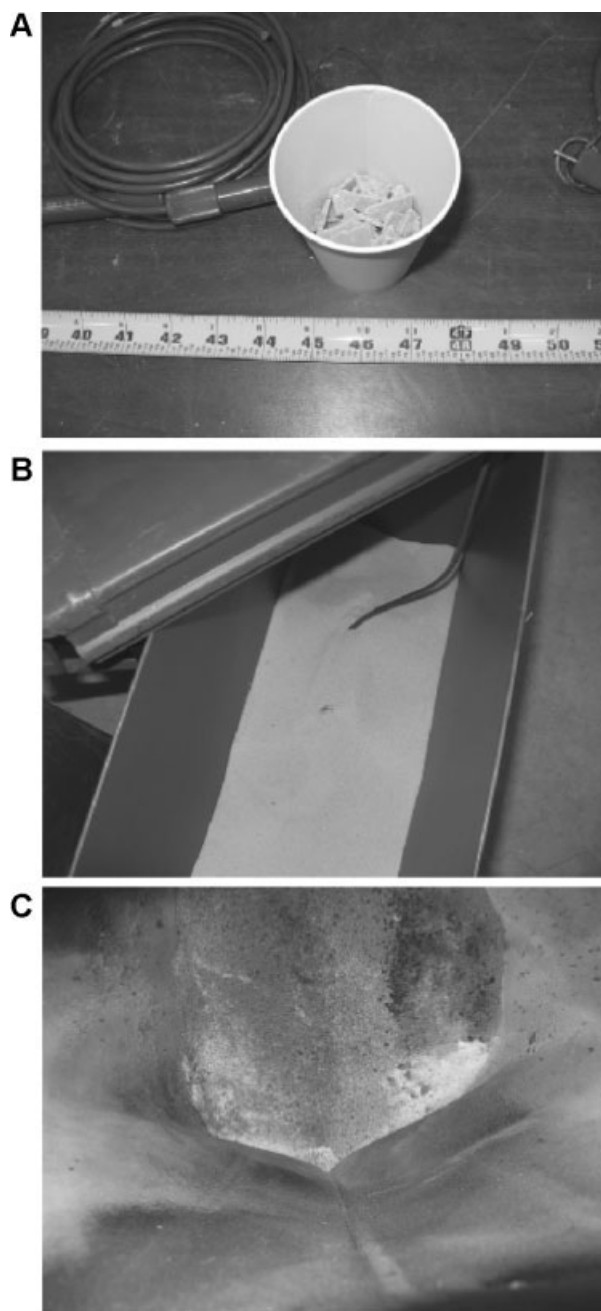


Fig. 1. (A) Flakes of Composition B in a paper cup, (B) a Big Black River test site (BBTS, USA) sample loaded into the detonation can, and (C) the BBTS sample following detonation.

Surface area measurements

We used the Brunauer-Emmett-Teller (BET) N₂ gas adsorption method to quantify the gas-exchangeable specific surface area of the pristine and bulk-detonated soil samples [23]. Measurements were made in triplicate from the surface and bulk material collected from each detonated sample. Multipoint surface area analyses were conducted from duplicate sample splits of approximately 2 g of each soil sample. Minerals were held under vacuum overnight at 105°C before surface area analysis with nitrogen gas (N₂) in a liquid nitrogen atmosphere (-194.8°C). Results from six relative pressure points were reduced to surface area values applying BET theory [23].

Quantifying explosive residue loading after detonation

Immediately following detonation, we quantified the acetonitrile-extractable explosive compound concentrations in triplicate samples of the surface and bulk soil materials (Table 1). A 20-ml aliquot of high-performance liquid chromatography (HPLC) grade acetonitrile was added to 6 g of each soil sample to extract energetic residues [24,25]. The soil and acetonitrile mixture was placed on a platform shaker for 24 h at 200 rpm, followed by centrifugation, with an 8-cm radius, at 3,000 rpm for 10 min. Following centrifugation, an aliquot of each acetonitrile extract was pipetted into a 7-ml amber glass vial with a PTFE lid. Samples were stored at -20°C until their explosive analyte concentrations were measured. Prior to analysis, each extract was tested using an Expray kit (Plexus Scientific) to estimate the dilution needed to be within the calibration range of the analytical method [25,26]. Then 1.0 ml of each diluted extract was mixed with 3.0 ml of 18 MΩ water, and nitroaromatic and nitramine compounds were measured following the analytical procedures outlined below for aqueous samples.

Batch experiments

Two sets of batch experiments were conducted, one to track the dissolution of pure Composition B over time, and the other to investigate the fate of explosive residues in detonated soils. The Composition B dissolution batch was constructed by crushing pure Composition B particles into a fine powder (<425 μm) and placing 0.02 g of the powder in 400 ml of 18 MΩ water. The batches were stored in amber glass bottles, capped, placed on a platform shaker, and shaken continuously at 200 rpm in the dark for 124 d. A 1-ml aqueous sample was collected from the batch at 1 h, and after 1, 5, 9, 19, 71, and 124 d.

The detonated soil batch experiments were constructed with between 3 and 23 g of each detonated soil sample. Samples were prepared in duplicate, in amber glass bottles, and mixed with approximately 480 ml of 18 MΩ water (Table 1). The mass of detonated soil used in each batch experiment was determined such that the maximum aqueous concentrations of RDX and TNT (based on the acetonitrile-extractable concentrations) would be below the solubility limit in water at 20°C: 46.6 mg/L for RDX [27] and 150 mg/L for TNT [28]. The amber glass bottles were capped, placed on a platform shaker, and shaken continuously at 200 rpm in the dark for 141 d. An ambient air temperature of 20°C was maintained throughout the experiment. A 1-ml sample of slurry solution was collected from each batch at the following elapsed times: 30 min, and 3, 9, 17, 34, 52, 74, 115, and 141 d. The 1-ml sample aliquots were pipetted into a 7-ml amber glass vial with a PTFE (Teflon) lid. Two milliliters of 18 MΩ water and 1 ml of HPLC-grade acetonitrile were added to each vial. Samples were stored at -20°C until they were analyzed for explosive compounds.

Concentrations of RDX, HMX, TNT, 1,3,5-trinitrobenzene (1,3,5-TNB), 2ADNT, and 4ADNT were determined following extraction method SW846 and analytical method 8330B [29]. Samples were filtered through a Millex-FH PTFE (Teflon) 0.45 μm filter prior to analysis. Explosive compound concentrations were determined on a Finnigan SpectraSYSTEM Model P4000 liquid chromatograph (Thermo Electron) ultraviolet/visible absorbance detector set at 254 nm (cell path 1 cm). Samples were introduced with a 100-μl sample loop. Separations were achieved on a 15 cm × 3.9 mm (4 μm) NovaPak C8 column at 28°C and eluted with 1.4 ml/min of 15:85 isopropanol/water (v/v). Based on numerous analyses of 100 μl of a laboratory spike solution, the percent relative standard deviation of the explosive compound measurements was less than 2% for the analytes measured.

Table 1. The acetonitrile-extractable explosive compound concentrations measured from the detonated soil samples and the soil masses, water volumes, and maximum aqueous explosive compound concentration for the batches^a

Sample	Detonated soils					Batches			Expected concentrations (mg/L)				
	RDX (μg/g)	RDX mean (μg/g)	HMX (μg/g)	HMX mean (μg/g)	TNT (μg/g)	TNT mean (μg/g)	Sample mass (g)	Water volume (ml)	RDX	HMX	TNT		
Church surface	2,077	2,256	277	302	1,542	1,690	9.0	479.1	42.2	5.7	31.6		
	2,606		357		1,974				42.0			5.6	31.4
	2,085		273		1,554								
Church bulk	1,020	905	139	121	723	612	22.1	472.1	42.4	5.7	28.7		
	846		114		577				43.6			5.8	29.5
	849		111		537								
Delta surface	870	873	104	108	503	538	23.2	484.9	41.8	5.2	25.8		
	678		87		427				42.5			5.3	26.2
	1,071		134		685								
Delta bulk	3,073	3,577	394	446	2,031	2,344	5.6	467.2	42.8	5.3	28.1		
	4,090		497		2,683				45.2			5.6	29.6
	3,569		446		2,319								
BBTS surface	1,968	1,943	267	266	1,349	1,339	10.5	480.4	42.3	5.8	29.1		
	2,037		278		1,422				43.5			5.9	30.0
	1,825		252		1,245								
BBTS bulk	7,047	6,149	981	856	5,122	4,482	3.4	475.6	44.0	6.1	32.0		
	5,667		773		4,054				43.3			6.0	31.6
	5,732		813		4,270								

^aRDX = hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX = octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine; TNT = 2,4,6-trinitrotoluene; BBTS = Big Black River test site.

RESULTS AND DISCUSSION

Soil characteristics following detonation

The detonated soil particles were darker gray to black in comparison to the pristine soils (Fig. 1). An irregular dark sooty sheen covered some of the soil particles, and the detonated soils contained pockets of lightly cemented, clumped aggregates that were less than 1 cm in diameter. Gas-adsorption surface area measurements using BET theory (Fig. 2) indicate that the detonated soil material (both the surface and bulk samples) yields lower gas-adsorption surface areas than pristine, undetonated material. For the Church and BBTS soils, the surface samples yield gas-adsorption surface areas statistically significantly lower than their pristine soil counterparts (analysis of variance with $\alpha = 0.05$). For all three soils, the gas-adsorption surface areas measured from the bulk-detonated samples are statistically significantly lower than for the pristine soils (analysis of variance with $\alpha = 0.05$).

The lower gas-exchangeable surface areas measured from the detonated samples are likely attributable to the presence of an explosive residue coating on the detonated soils, shock-induced compaction [30], sintering, and/or partial fusion of soil particles under the intense heat associated with detonation reactions [31,32]. The detonation pressure (34 GPa) and temperature (2,400°C) for Composition B [33] are sufficient to provide significant shock forces and heating that would be expected to shatter, as well as melt and re-coalesce, soil particles. The Composition B material (and thus the main detonation force) was located at the bottom of our detonation cans, where the bulk samples were collected. As a consequence the explosive residues, shock pressures and temperatures would be expected to be greater for the bulk soil material than for the surface samples.

Dissolution of Composition B

Four batches of approximately 0.02 g of crushed Composition B particles (<425 μm) were placed in 400 ml of 18 M Ω water to quantify the dissolution of TNT, RDX, and HMX from the unaltered explosive materials over 141 d (Fig. 3). Other studies have provided similar Composition B dissolution infor-

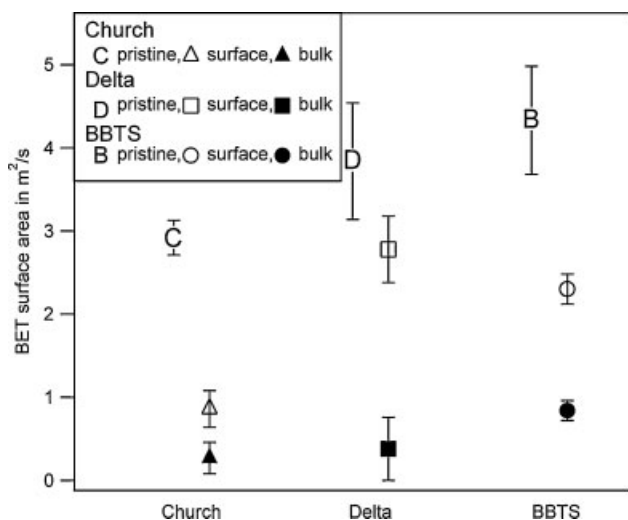


Fig. 2. Gas adsorption-specific surface area measurements of our samples measured using Brunauer, Emmitt, and Teller (BET) theory. All samples were analyzed in triplicate. Each symbol represents the mean, and the vertical bars represent one standard deviation above and below the mean, for each sample. BBTS = Big Black River test site.

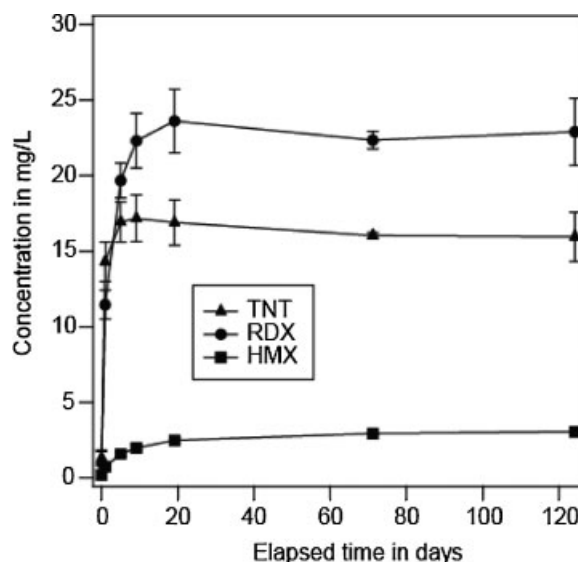


Fig. 3. Concentrations of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) measured in the Composition B batch samples over time. The batches were constructed in quadruplicate and analyzed as individual samples. Each symbol represents the mean, and the vertical bars represent one standard deviation above and below the mean, for each of the four samples collected at a given time.

mation [9,13,14,18]. However, because the RDX:TNT:HMX ratios in Composition B vary, we wanted to determine the formulation of Composition B that was used to detonate our samples. The results suggest that TNT dissolution reaches a steady state apparent equilibrium concentration in water within 10 d, while RDX and HMX require 20 d to reach apparent equilibrium. This is only a few days faster than the results reported from a similar Composition B dissolution study [18]. The TNT transformation products 2ADNT, 4ADNT, and 1,3,5-TNB were not detected in any of the aqueous samples collected during the Composition B dissolution measurements. It has been recently reported that TNT, RDX, and HMX will remain stable for many months in 18 M Ω water [15].

Desorption of explosive compounds in detonated soils

The acetonitrile-extractable explosive compound concentrations measured following detonation are included in Table 1 and are presumed to be a measure of the total loading of the compounds to the dry soil samples. A wide range in RDX, HMX, and TNT concentrations is evident in the triplicate analyses of the detonated soils. This reflects the heterogeneous nature of explosive compound loading during detonation events. The mass of detonated soil mixed with water to generate the batch reactor samples was chosen to ensure that the maximum possible aqueous RDX, HMX, and TNT concentrations were below solubility (i.e., assuming complete partitioning to the aqueous phase).

Five potential sources of explosive analytes exist within the batch reactors: explosive residues from detonation (sorbed and in the aqueous solution), undetonated Composition B crystals, undetonated explosive compounds in solution, undetonated explosive compounds adsorbed to soil particle surfaces, and transformation products of explosive compounds [15,34]. Hence, the accumulation of explosive compounds in solution during the course of the batch experiments is associated with a number of potentially competing processes including: dissolution of explosive compounds from any undetonated

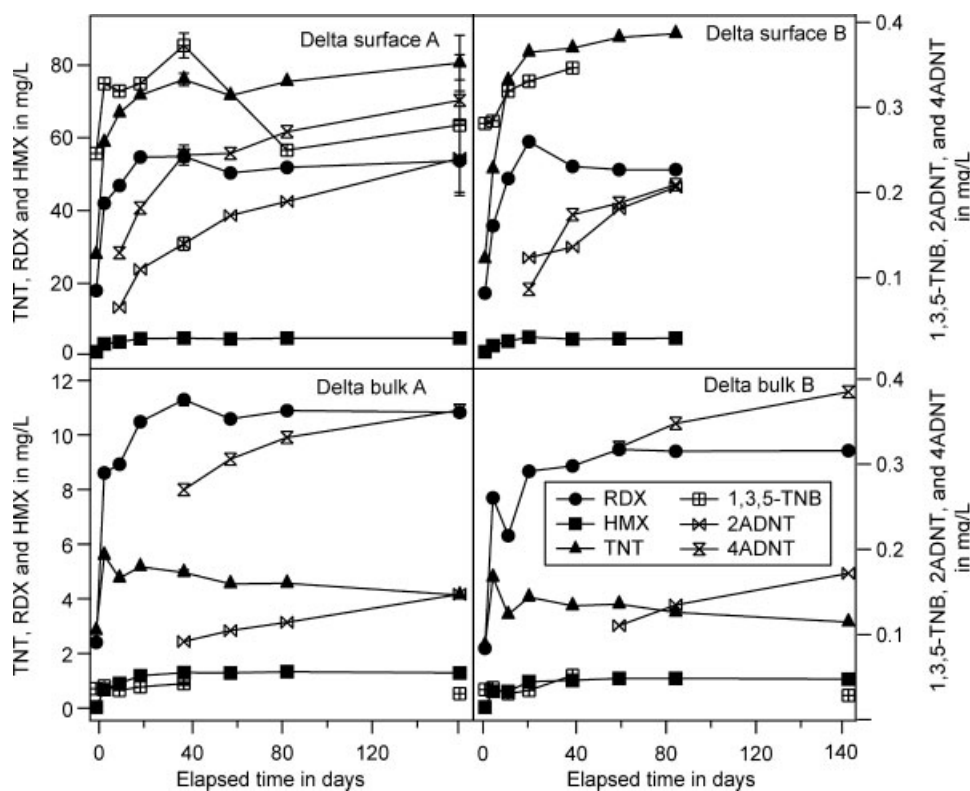


Fig. 4. Concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-amino-4,6-dinitrotoluene (2ADNT), and 4-amino-2,6-dinitrotoluene (4ADNT) measured in the Delta batch samples over time. For selected instances in which triplicate samples were collected on a given day, the symbol represents the mean, and the vertical bars represent one standard deviation above and below the mean, for each sample. The standard deviation values are within the vertical extent of the symbols for most of these triplicate samples.

Composition B in the soil samples, sorption–desorption reactions for explosive residues, and, in the case of TNT, transformation of the primary compound to secondary transformation products and their subsequent sorption–desorption.

Aqueous concentrations of the explosive compounds in the batch reactor solutions over the course of the 141-d experiments are given in Figures 4–6. Duplicate batches were constructed and sampled for each soil type and are labeled A and B. For each sample type, samples were collected in triplicate on some days, and their mean \pm one standard deviation is given. For most of these triplicate analyses, the range of standard deviation values are small enough to be contained within the symbols.

The explosive compound concentrations measured in the duplicate sets of analyses for each sample type show good reproducibility with the exception of the Church bulk sample pairs. While clear differences exist between the bulk and surface samples of each sample split, the shapes of their desorption curves are generally similar. This suggests that the dominant processes controlling desorption of explosive compounds are consistent between each of the batch reactors. The ratios of TNT, RDX, and HMX to one another are not consistent across the three soil types or with the values measured during the Composition B dissolution batches (53.5% RDX, 39.5% TNT, 7% HMX). This may be explained by the heterogeneous nature of the detonation events whereby inconsistent fractions of the three primary explosive compounds underwent full detonation.

Delta surface samples exhibited roughly twice the expected TNT concentration in the batch solutions, and yield the highest TNT concentrations of any samples. This may be attributable to an unexpectedly elevated TNT load present in the soils used for the Delta surface batches, given that the TNT:RDX and TNT:HMX ratios in the Delta surface samples are roughly

twice what would be expected based on the Composition B dissolution and based on the TNT:RDX:HMX values in all the other batch samples. However, the Delta bulk samples yield the lowest explosive analyte concentrations of any of the soils.

We performed a best fit analysis of the desorption curves for RDX, HMX, and TNT in the batch samples for all three soil types. The logarithmic fit equation

$$C = k_1 \ln(t) + k_2$$

where C is the analyte concentration in mg/L, k is a correction factor, and t is the time in decimal days, yielded the best coefficient of determination values among linear (second-, third-, or fourth-order), power, or exponential curve fittings. Results from the curve fit analysis for the 12 batches are included as Table 2. The r^2 values are above 0.9 for RDX and HMX for all but one sample. Plots of logarithmic concentration versus linear time were generally linear for the initial two or three samples collected from the batches (i.e., for the first 9 d) and then trended toward a steady state apparent equilibrium value from roughly 20 d to 141 d. This implies that, initially, explosive residues are represented by a first-order physical desorption process. The dissolution of pure Composition B is first-order for the initial 10 d (Fig. 3). Though we did not find any pristine Composition B particles in our detonated samples, it is possible that small undetonated or partially detonated particles of Composition B were present in our sample batches. The first-order state of explosive compound desorption and dissolution is potentially limited by the available surface area and/or exposure of soluble residues or undetonated compounds, as well as surface area-controlled kinetics of sorption–desorption.

Nitramines RDX and HMX are generally considered conservative under common biogeochemical conditions

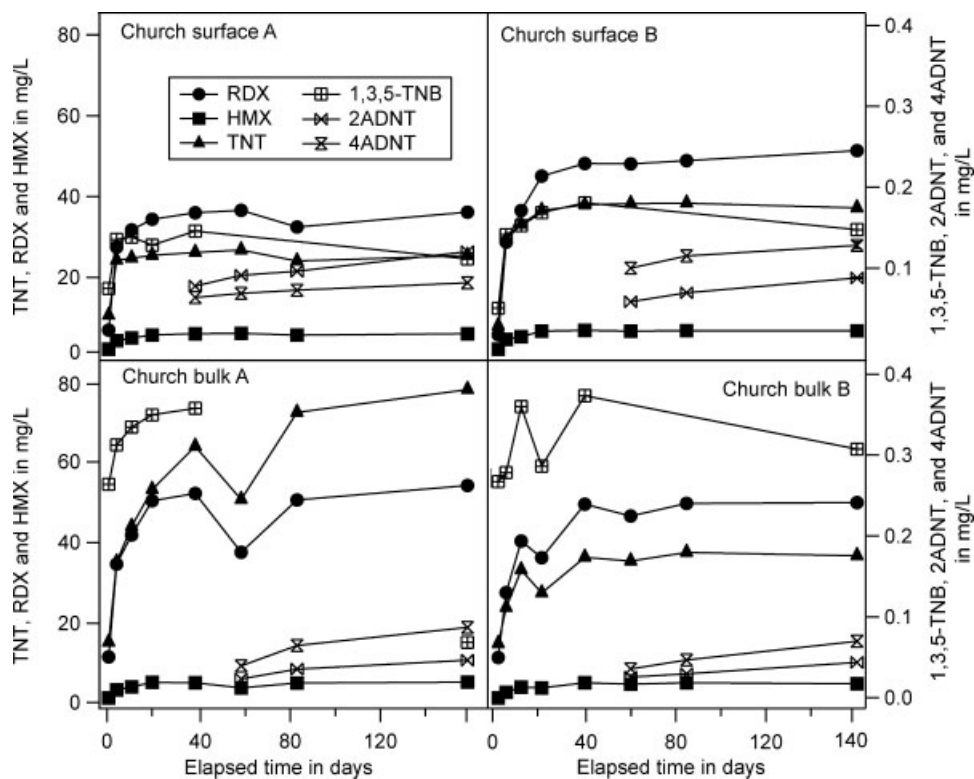


Fig. 5. Concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-amino-4,6-dinitrotoluene (2ADNT), and 4-amino-2,6-dinitrotoluene (4ADNT) measured in the Church batch samples over time. For selected instances in which triplicate samples were collected on a given day, the symbol represents the mean, and the vertical bars represent one standard deviation above and below the mean, for each sample. The standard deviation values are within the vertical extent of the symbols for most of these triplicate samples.

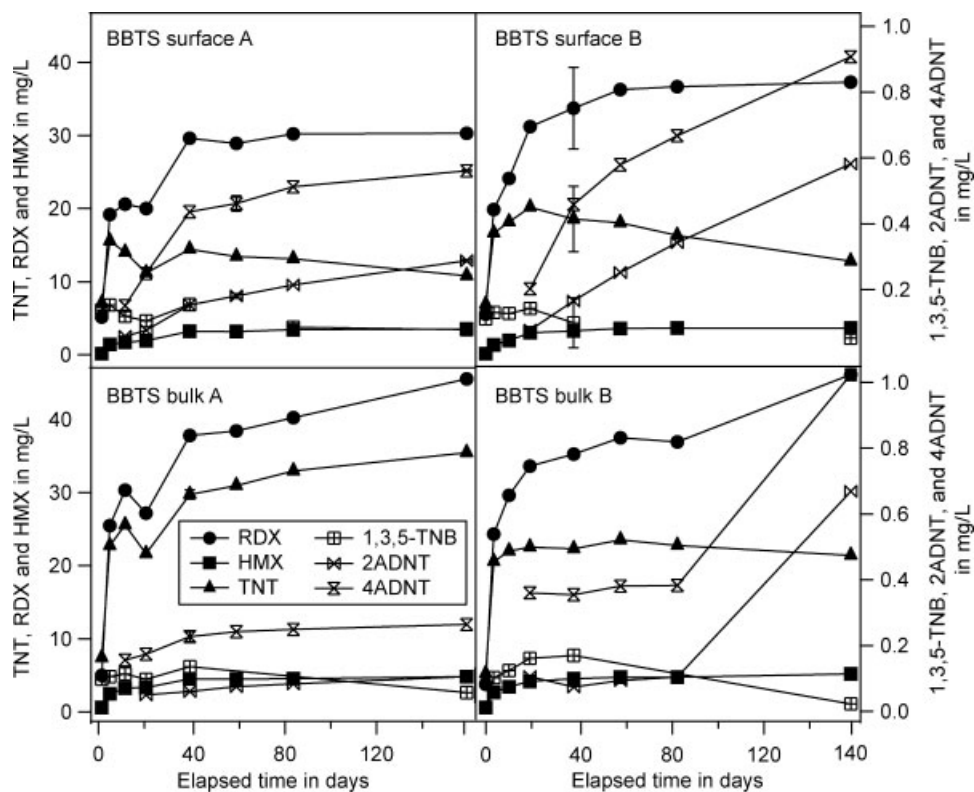


Fig. 6. Concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-amino-4,6-dinitrotoluene (2ADNT), and 4-amino-2,6-dinitrotoluene (4ADNT) measured in the Big Black River test site (BBTS) batch samples over time. For selected instances in which triplicate samples were collected on a given day, the symbol represents the mean, and the vertical bars represent one standard deviation above and below the mean, for each sample. The standard deviation values are within the vertical extent of the symbols for most of these triplicate samples.

Table 2. Results from the logarithmic curve-fitting analysis of the batch aqueous sample concentrations^a

Sample	RDX equation	r^2	HMX equation	r^2	TNT equation	r^2
Church surface A	$C = 3.1 \ln(t) + 21.1$	0.94	$C = 0.4 \ln(t) + 2.5$	0.95	$C = 1.6 \ln(t) + 17.9$	0.86
Church surface B	$C = 4.9 \ln(t) + 25.5$	0.97	$C = 0.5 \ln(t) + 2.7$	0.93	$C = 3.3 \ln(t) + 22.6$	0.96
Church bulk A	$C = 4.2 \ln(t) + 31.1$	0.86	$C = 0.4 \ln(t) + 3.0$	0.84	$C = 6.0 \ln(t) + 36.7$	0.83
Church bulk B	$C = 4.2 \ln(t) + 28.4$	0.92	$C = 0.4 \ln(t) + 2.8$	0.90	$C = 2.4 \ln(t) + 24.4$	0.87
Delta surface A	$C = 3.8 \ln(t) + 37.3$	0.93	$C = 0.4 \ln(t) + 3.4$	0.96	$C = 5.4 \ln(t) + 53.1$	0.99
Delta surface B	$C = 4.2 \ln(t) + 36.8$	0.86	$C = 0.4 \ln(t) + 3.4$	0.90	$C = 7.2 \ln(t) + 56.8$	0.92
Delta bulk A	$C = 0.9 \ln(t) + 7.1$	0.96	$C = 0.1 \ln(t) + 0.8$	0.95	$C = 0.2 \ln(t) + 4.3$	0.35
Delta bulk B	$C = 0.8 \ln(t) + 6.0$	0.93	$C = 0.1 \ln(t) + 0.7$	0.94	$C = 0.1 \ln(t) + 3.5$	0.21
BBTS surface A	$C = 2.7 \ln(t) + 16.8$	0.92	$C = 0.4 \ln(t) + 1.8$	0.86	$C = 0.5 \ln(t) + 11.5$	0.35
BBTS surface B	$C = 3.4 \ln(t) + 19.8$	0.94	$C = 0.4 \ln(t) + 2.0$	0.89	$C = 0.9 \ln(t) + 13.7$	0.45
BBTS bulk A	$C = 4.0 \ln(t) + 21.5$	0.95	$C = 0.4 \ln(t) + 2.3$	0.95	$C = 2.8 \ln(t) + 18.9$	0.93
BBTS bulk B	$C = 3.5 \ln(t) + 19.0$	0.99	$C = 0.4 \ln(t) + 2.1$	0.97	$C = 1.7 \ln(t) + 14.0$	0.87

^aRDX = hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX = octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine; TNT = 2,4,6-trinitrotoluene; C = concentration in mg/L; t = time in decimal days; BBTS = Big Black River test site.

[10,15,34–37]. At considerably lower initial concentrations (i.e., 2–3 ppm) than the samples in the present study, RDX was lost from solution in batches created by spiking explosive compounds into the same three soils investigated here [16]. In the present study, RDX (and HMX) appear to be stable in solution in all three batches.

For TNT, the logarithmic fit of desorption over time was also the optimum fit, but the r^2 values for curve fitting for the TNT measurements varied widely. The greater variance is likely due to desorption of TNT residues from soil surfaces, dissolution of any available undetonated Composition B, and the transformation of TNT to 2ADNT, 4ADNT, and 1,3,5-TNB. Pure Composition B dissolution reaches an equilibrium after 20 d (Fig. 3). However, in deionized water, with an absence of biogeochemical surfaces, TNT does not undergo transformation [[16]; the present study]. The 2ADNT, 4ADNT, and 1,3,5-TNB were not detected in the Composition B used to detonate our soils. As a consequence, their presence in our aqueous soil solutions can be attributed solely to TNT transformation. However, the 2ADNT, 4ADNT, and 1,3,5-TNB concentrations are quite low compared to the TNT values, so the transformation of TNT to these products would not be expected to greatly affect the equilibrium of TNT in the batch solutions.

The three TNT transformation products generally increase with time from values below detection to values in the 0.1 to 1 mg/L range. In all of the samples, 1,3,5-TNB appears within the first day of initiation of the batches; 2ADNT and 4ADNT

were detected instantly in the BBTS samples, but not for the first 7 d (Delta surface), 20 d (BBTS samples), or 40 to 60 d (Delta bulk, all Church samples). The presence of 2ADNT and 4ADNT in the aqueous solutions is likely limited by both their production through the electron-reduction transformation of TNT [7,38] and by their subsequent transformation (i.e., loss from solution) to phenolic derivatives [39,40] that we did not measure. However, in all samples, the 2ADNT and 4ADNT concentrations are stable or increasing after 141 d. This is most dramatic in the BBTS samples that have the highest 2ADNT and 4ADNT concentrations.

The logarithmic fit equations were used for each sample to compare its apparent equilibrium RDX, HMX, and TNT concentrations to the maximum expected concentrations calculated when the batch reactors were constructed. The results, presented in Table 3, suggest that the apparent equilibrium desorption concentrations of RDX in aqueous solutions are somewhat predictable for most batches (calculated and steady state values are generally within 30%). This supports previous work suggesting that RDX is conservative in soil solutions [10,15,34–37]. It also implies the desorption of RDX in water, over long timeframes (141 d), is nearly complete (i.e., concentrations are comparable to those from the acetonitrile extractions).

The modeled and predicted values for HMX are within 20% for the Church batches, but the modeled values are up to three times lower than the predicted values for the Delta and BBTS soil samples (Table 3). The Delta bulk samples yielded far

Table 3. Calculated and apparent equilibrium RDX, HMX, and TNT concentrations in the batch samples^a

Sample	Calculated maximum RDX (mg/L)	Apparent equilibrium RDX (mg/L)	Calculated maximum HMX (mg/L)	Apparent equilibrium HMX (mg/L)	Calculated maximum TNT (mg/L)	Apparent equilibrium TNT (mg/L)
Church surface A	42.2	37.5	5.6	4.7	31.6	26.4
Church surface B	42.0	49.9	5.6	5.3	31.4	38.9
Church bulk A	42.4	54.6	5.7	5.2	28.7	76.5
Church bulk B	43.6	50.2	5.9	4.9	29.5	37.2
Delta surface A	41.8	56.8	5.2	5.4	25.8	78.5
Delta surface B	42.5	54.9	5.3	5.3	26.2	88.0
Delta bulk A	42.8	11.7	5.3	1.5	28.1	5.1
Delta bulk B	45.2	10.1	5.6	1.3	29.6	4.0
BBTS surface A	42.3	31.1	5.8	3.7	29.1	14.3
BBTS surface B	43.5	37.2	5.9	3.9	30.0	18.4
BBTS bulk A	44.0	42.3 ^b	6.1	4.5 ^b	32.0	33.6 ^b
BBTS bulk B	43.3	38.5 ^b	6.0	4.3 ^b	31.6	22.3 ^b

^aRDX = hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX = octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine; TNT = 2,4,6-trinitrotoluene; BBTS = Big Black River test site.

^bApparent equilibrium not reached after 141 d.

lower explosive compound concentrations than was expected. The reasons for this are not clear. For the bulk samples, it is either that the acetonitrile extractable explosive compound concentrations measured following detonation represented soil samples with an anomalously elevated concentration, or that the soils in the batch reactor contained an anomalously low explosive compound concentration, or some combination of both.

As stated earlier, the TNT values varied within and across the batches, and this is reflected in the modeled and predicted values for TNT equilibrium. For all but the Church bulk samples, the two apparent equilibrium TNT values for each sample pair are within 40% of one another. The Church surface samples present the only sample type for which the modeled and predicted values for TNT equilibrium are similar. The rest of the sample sets yield values with as much as a fivefold difference between the modeled and predicted TNT values.

Desorption and dissolution of explosive residues, and dissolution of undetonated explosive compounds from the soil samples into the 18 M Ω water begins to reach apparent equilibrium within roughly 40 d for all of the sample types (Figs. 4–6). In addition, the desorption rates of the bulk explosive compounds are consistent among the sample pairs (Delta surface A and B, etc.). This is longer than it takes to reach the dissolution equilibrium for Composition B (roughly 20 d for RDX, HMX, and TNT), and suggests that either the detonation process and/or the presence of soil material affects the fate of explosive compounds in the soil slurries.

Results from a laboratory-based adsorption investigation, using the same three soils spiked with explosive compounds in solution [16], suggest that both the loss of explosive compounds from solution and the creation of TNT transformation products in batch slurries were greatest in the BBTS soil, followed by the Church and Delta soils. In the present study, the BBTS samples consistently yield the lowest solution explosive analyte concentrations and the highest TNT transformation product concentrations. This suggests that adsorption and/or transformation is greatest in the BBTS soil. However, no consistent relationship between explosive compound and TNT transformation product concentrations is evident in the Church or Delta samples.

CONCLUSIONS

The range in explosive compound concentrations we measured in surface versus bulk samples suggests that, even under controlled conditions, detonation events heterogeneously load soils with explosive compounds. Bulk samples were collected from the region closest to the location of the detonated Composition B. However, bulk soil samples are not consistently associated with higher explosive analyte concentrations than surface soils. As a consequence, it is difficult to draw conclusions from our results on how proximity to a detonation event controls the loading of explosive compounds in the training range soil environment.

For both the laboratory-spiked [16] and field-detonated situations, the BBTS soils are associated with higher TNT transformation product concentrations. The BBTS soil contains a greater clay and organic matter content that likely promotes TNT transformation [16]. In addition, the time to apparent equilibrium for detonated soils (roughly 40 d) is far longer than in soils spiked with explosive compounds in a laboratory (2 to 20 d for TNT; 2 d for RDX; compare Figs. 4–6 with Fig. 3 from Douglas et al. [16]). This is probably the most important result from the present study: Laboratory measurements may overestimate the rates at which explosive compounds reach

sorption–desorption equilibrium. Taken in total, our results support previous research showing desorption and dissolution of explosive residues, and dissolution of undetonated explosive compounds in soils, is largely dependent on soil biogeochemical conditions. At an impact site, the heterogeneous nature of detonation events likely plays a large role in the deposition, and thus the overall fate, of explosive compounds on training ranges.

Acknowledgement—Charles Collins, Terry Sobocki, Alan Hewitt, and Katerina Dontsova provided insightful comments throughout the incubation and development of the project. Anna Wagner assisted with the field detonations. David Hoffman and his colleagues at the Cold Regions Test Center, Donnelly Training Area, Alaska are gratefully acknowledged for assistance with designing and implementing the soil detonation campaign. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the U.S. Army Environmental Quality Technology Basic Research Program by the U.S. Army Engineer Research and Development Center. The use of trade, product, or firm names in this article is for descriptive purposes only and does not imply endorsement by the U.S. Government. Permission was granted by the Chief of Engineers to publish this information.

REFERENCES

1. Rickert DEE. 1985. *Toxicity of Nitroaromatic Compounds*. Hemisphere, Washington, DC.
2. Weissmahr KW, Haderlein SB, Schwarzenbach RP. 1997. In situ spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals. *Environ Sci Technol* 31:240–247.
3. Haderlein SB, Weissmahr KW, Schwarzenbach RP. 1996. Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. *Environ Sci Technol* 30:612–622.
4. Li H, Teppen BJ, Johnston CT, Boyd SA. 2004. Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. *Environ Sci Technol* 38:5433–5442.
5. Charles S, Teppen BJ, Li H, Laird DA, Boyd SA. 2006. Exchangeable cation hydration properties strongly influence soil sorption of nitroaromatic components. *Soil Sci Soc Am J* 70:1470–1479.
6. Hewitt AD, Jenkins TF, Walsh ME, Walsh MR, Taylor S. 2005. RDX and TNT residues from live-fire and blow-in-place detonations. *Chemosphere* 61:888–894.
7. Jenkins TF, Hewitt AD, Grant CL, Thiboutot S, Ampleman G, Walsh ME, Ranney TA, Ramsey CA, Palazzo AJ, Pennington JC. 2006. Identity and distribution of residues of energetic compounds at army live-fire training ranges. *Chemosphere* 63:1280–1290.
8. Pennington JC, Patrick WH Jr. 1990. Adsorption and desorption of 2,4,6-trinitrotoluene by soils. *J Environ Qual* 19:559–567.
9. Lynch JC, Brannon JM, Delfino JJ. 2002. Dissolution rates of three high explosive compounds: TNT, RDX and HMX. *Chemosphere* 47:725–734.
10. Dontsova KM, Yost SL, Simunek J, Pennington JC, Williford C. 2006. Dissolution and transport of TNT, RDX, and Composition B in saturated soil columns. *J Environ Qual* 35:2043–2054.
11. Morley MC, Yamamoto H, Speitel GE Jr, Clause J. 2006. Dissolution kinetics of high explosives particles in a saturated sandy soil. *J Contam Hydrol* 85:141–158.
12. Hofstetter TB, Neumann A, Schwarzenbach RP. 2006. Reduction of nitroaromatic compounds by Fe(II) species associated with iron-rich smectites. *Environ Sci Technol* 40:235–242.
13. Furey JS, Fredrickson HL, Richmond MJ, Michel M. 2008. Effective elution of RDX and TNT from particles of Comp B in surface soil. *Chemosphere* 70:1175–1181.
14. Larson SL, Martin WA, Escalon BL, Thompson M. 2008. Dissolution, sorption, and kinetics involved in systems containing explosives, water and soil. *Environ Sci Technol* 42:786–792.
15. Douglas TA, Walsh ME, McGrath CJ, Weiss CA. 2009. Investigating the fate of nitroaromatic (TNT) and nitramine (RDX and HMX) explosives in fractured and weathered soils. *J Environ Qual* 38:2285–2294.
16. Douglas TA, Johnson L, Walsh ME, Collins CM. 2009. Time series investigation of the stability of nitramine and nitroaromatic explosives in surface water samples held at ambient temperature. *Chemosphere* 76: 1–8.
17. Lever JH, Taylor S, Perovich L, Bjella K, Packer B. 2005. Dissolution of Composition B residuals. *Environ Sci Technol* 39:8803–8811.

18. Taylor S, Lever JH, Fadden J, Perron N, Packer B. 2009. Simulated rainfall-driven dissolution of TNT, Tritonal, Comp B and Octol particles. *Chemosphere* 75:1074–1081.
19. Kuznetsov VM, Shatsukevich AF, Romanov AR. 1979. Ejection explosion in sand. *Combustion, Explosion, and Shock Waves* 15:240–245.
20. Pepekin VI, Gubin SA. 2007. Heat of explosion of commercial and brisant high explosives. *Combustion, Explosion, and Shock Waves* 43:212–218.
21. Pantea D, Brochu S, Thiboutot S, Ampleman G, Scholz G. 2006. A morphological investigation of soot produced by the detonation of munitions. *Chemosphere* 65:821–831.
22. U.S. Department of Defense. 1964. Subgrade, subbase, and test method for pavement base-course materials. Military Standard, MIL-STD-621A. Washington, DC.
23. Brunauer S, Emmett PH, Teller E. 1938. Adsorption of gases in multimolecular layers. *J Am Chem Soc* 60:309–319.
24. Sunahara GI, Dodard S, Sarrazin M, Paquet L, Hawari J, Greer CW, Ampleman G, Thiboutot S, Renoux AY. 1999. Ecotoxicological characterization of energetic substances using a soil extraction procedure. *Ecotoxicol Environ Saf* 43:138–148.
25. Walsh ME. 2001. Determination of nitroaromatic, nitramine, and nitrate ester explosives in soil by gas chromatography and an electron capture detector. *Talanta* 54:427–438.
26. Walsh MR, Walsh ME, Hewitt AD. 2010. Energetic residues from field disposal of gun propellants. *J Hazard Mater* 173:115–122.
27. Monteil-Rivera F, Paquet L, Deschamps S, Balakrishnan VK, Beaulieu C, Hawari J. 2004. Physico-chemical measurements of Cl-20 for environmental applications comparison with RDX and HMX. *J Chromatogr A* 1025:125–132.
28. Prak DJL, O'Sullivan DW. 2006. Solubility of 2,4-dinitrotoluene in seawater. *J Chem Eng Data* 51:448–450.
29. U.S., Environmental Protection Agency. 2006. Nitroaromatics, nitramines and nitrate esters by high performance liquid chromatography (HPLC). Method 8330B. SW846. Office of Solid Waste, Washington, DC.
30. Gohl WB, Jefferies MG, Howie JA, Diggle D. 2000. Explosive compaction: Design, implementation and effectiveness. *Geotechnique* 50:657–665.
31. Abdulazeem MS. 1998. Condensed media shock waves and detonations: Equation of state and performance. *High Temperatures-High Pressures* 30:387–422.
32. Keshavarz MH, Nazari HR. 2006. A simple method to assess detonation temperature without using any experimental data and computer code. *J Hazard Mater B* 133:129–134.
33. Donnet JB, Lemoigne C, Wang TK, Peng CM, Samirant M, Eckhardt A. 1997. Synthèse par explosive et par choc de nanodiamant. *Bull Soc Chim Fr* 134:875–890.
34. Yamamoto H, Morley MC, Speitel GE, Clausen J. 2004. Fate and transport of high explosives in a sandy soil: Adsorption and desorption. *Soil Sediment Contam* 13:459–477.
35. Selim HM, Xue SK, Iskandar IK. 1995. Transport of 2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine in soils. *Soil Sci* 160:328–339.
36. Singh J, Comfort SD, Hundal LS, Shea PJ. 1998. Long-term RDX sorption and fate in soil. *J Environ Qual* 27:572–577.
37. Tucker WA, Murphy GJ, Arenberg ED. 2002. Adsorption of RDX to soil with low organic carbon: Laboratory results, field observations, remedial implications. *Soil Sediment Contam* 11:809–826.
38. Thorn KA, Kennedy KR. 2002. ¹⁵N NMR investigation of the covalent binding of reduced TNT amines to soil humic acid, model compounds, and lignocellulose. *Environ Sci Technol* 36:3787–3796.
39. Kaplan DL, Kaplan AM. 1982. Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions. *Appl Environ Microbiol* 44:757–760.
40. Hawari J, Beaudet S, Halasz A, Thiboutot S, Ampleman G. 2000. Microbial degradation of explosives: Biotransformation versus mineralization. *Appl Environ Microbiol* 54:605–618.