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Dissolution and sorption of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) residues from detonated mineral surfaces

Ashley M. Jaramillo [a,b], Thomas A. Douglas [b,*], Marianne E. Walsh [c], Thomas P. Trainor [a]

[a] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, AK 99775, USA
[b] Cold Regions Research and Engineering Laboratory, P.O. Box 35170, Fort Wainwright, AK 99703, USA
[c] Cold Regions Research and Engineering Laboratory, 72 Lyme Road Hanover, NH 03755, USA

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ABSTRACT

Composition B (Comp B) is a commonly used military formulation composed of the toxic explosive compounds 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Numerous studies of the temporal fate of explosive compounds in soils, surface water and laboratory batch reactors have been conducted. However, most of these investigations relied on the application of explosive compounds to the media via aqueous addition and thus these studies do not provide information on the real world loading of explosive residues during detonation events. To address this we investigated the dissolution and sorption of TNT and RDX from Comp B residues loaded to pure mineral phases through controlled detonation. Mineral phases included nontronite, vermiculite, biotite and Ottawa sand (quartz with minor calcite). High Performance Liquid Chromatography and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy were used to investigate the dissolution and sorption of TNT and RDX residues loaded onto the mineral surfaces. Detonation resulted in heterogeneous loading of TNT and RDX onto the mineral surfaces. Explosive compound residues dissolved rapidly (within 9 h) in all samples but maximum concentrations for TNT and RDX were not consistent over time due to precipitation from solution, sorption onto mineral surfaces, and/or chemical reactions between explosive compounds and mineral surfaces. We provide a conceptual model of the physical and chemical processes governing the fate of explosive compound residues in soil minerals controlled by sorption–desorption processes.

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1. Introduction

High explosive (HE) compound contamination of soil and groundwater has been reported at many artillery training ranges (Jenkins et al., 2001; Pennington and Brannon, 2002; Clausen et al., 2004; Amaral et al., 2009; Zheng et al., 2009). The primary cause of this contamination is the incomplete detonation of military ordnance (Morley et al., 2006). Composition B (Comp B), a commonly used military formulation, is composed of two widely used HE compounds: 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). TNT and RDX have been found to pose a health risk to biological systems and humans due to their carcinogenic, mutagenic and toxigenic nature (Honeycutt et al., 1996; Bruns-Nagel et al., 1999; Steevens et al., 2002).

The dissolution of TNT and RDX residues and particles governs their entry into training range ecosystems and controls their migration to the subsurface (Taylor et al., 2009). Dissolution of explosive compounds is dependent on physical and chemical factors that include particle surface areas and solubility (Lynch et al., 2002; Pennington and Brannon, 2002; Phelan et al., 2002; Lever et al., 2005). While the solubility of pure TNT and RDX is well known, detonation processes often produce residues and undetonated particles of varying mass, size, and surface area mixed with, or coating, soil materials leading to complex and heterogeneous sample matrices (Ro et al., 1996; Lynch et al., 2001; Douglas et al., 2010).

Essential to the fate and transport of TNT and RDX in the subsurface are sorption and transformation processes which are highly dependent on soil and water biogeochemistry (Dontsova et al., 2006; Morley et al., 2006; Larson et al., 2008; Boparai et al., 2010). Nitramine compounds like RDX have lower affinities for sorption to inorganic soil components (soil mineralogy) compared to nitroaromatic compounds (NACs) like TNT (Singh et al., 1998; Lynch et al., 2002; Yamamoto et al., 2004; Dontsova et al., 2006). Clay minerals have been shown to provide effective substrates for TNT sorption in soils (Weissmahr et al., 1998; Eriksson et al., 2004; Charles et al., 2006). However, the complicated biogeochemical and mineralogical conditions present in natural soils, coupled with the alteration of the soil matrix during detonation, make it difficult to determine a priori the reactivity of specific mineral phases with respect to HE's associated with explosive residues.

* Corresponding author. Tel.: +1 907 361 9555; fax: +1 907 361 5142.
E-mail address: thomas.a.douglas@usace.army.mil (T.A. Douglas).

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Many previous studies investigating HE fate in training range soils introduced explosive compounds to soil media as aqueous solutions of pure explosives. Infrared (IR) spectroscopic measurements and High Performance Liquid Chromatography (HPLC) analysis have been used to study the sorption of HEs on an array of pure mineral substrates and native soils. While these studies provide important information about HE sorption and transformation in a controlled laboratory setting, this form of explosive loading is vastly different from the heterogeneous loading of residues that occurs during detonation events.

The purpose of this study was to investigate the dissolution and sorption of TNT and RDX residues loaded to pure minerals through controlled detonation. The mineral substrates used include biotite, vermiculite, nontronite, and Ottawa sand (quartz and calcite mixture). Detonated mineral substrates were mixed with water and solution phase concentrations of TNT and RDX were measured over a 42 d period. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, a surface sensitive spectroscopic technique, was used to investigate the partitioning of TNT and RDX in our detonated samples by monitoring the nitro (NO_2) stretching bands of the explosive residues.

2. Materials and methods

2.1. Chemicals

TNT and RDX standards and HPLC explosive calibration standards were obtained from Restek Corporation (Bellefonte, Pennsylvania) with a reported purity of 99%. The Comp B used for the preparation of detonation samples was obtained from the Defense Ammunition Center (McAlester, OK). HPLC grade acetonitrile and isopropanol were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). Ultrapure water was obtained using an ultrapure water system. All chemicals were used as received.

2.2. Minerals

The four pure minerals detonated were procured in 10 kg quantities. Vermiculite clay was obtained from Fisher Scientific (Pittsburgh, Pennsylvania). Nontronite, an iron rich smectite clay, came from the Uley Graphite Mine on southern Eyre Peninsula, South Australia (Keeling et al., 2000; Clay Mineral Society reference clay NAu-1). Magnesium biotite (phlogopite), a reddish brown mica, was chosen to represent a non-swelling phyllosilicate mineral and was procured from the Charles B. Chrystal Company (New York, New York). Ottawa sand, primarily quartz with minor calcite, was chosen as a common non-phyllosilicate substrate for comparison and was provided by US Silica Company (Berkeley, West Virginia). Mineral phase identification was verified with X-ray Diffraction (XRD). The mineral substrates were split into two portions; one intended for classic mineral preparation (suspension and fractionation) for use as Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy references, and the other left unaltered for detonation and batch experiments.

2.3. Mineral preparation for IR spectroscopy reference

Approximately 100 g of each mineral substrate was milled using a SPEXSample Prep 8000D Mixer/Mill (Metuchen, New Jersey) with a milling time of 10 min. To thoroughly suspend the milled minerals they were hydrated in 500 mL of ultrapure water and stirred for 24 h. After suspension, the <2 μm clay-sized particles were collected from solution following procedures outlined in McKay (1992). Mineral suspensions were stored in sealed containers in the refrigerator until use in acquisition of IR reference spectra.

2.4. Loading of explosives through detonation

A detailed description of our detonation process has been previously provided (Douglas et al., 2010), and is briefly discussed here. The four mineral substrates were proximally detonated in a $20 \times 40 \times 50$ cm steel can with a latching lid. Three meters of military detonation cord tied with an uli-style knot at one end was attached to a paper cup containing approximately 100 g of Comp B. The cup and cord were placed inside the steel can and between 450 g and 7 kg of each substrate was placed on top of the Comp B. The container lid was then closed but not latched. The steel can was placed into a 2 m by 2 m by 2 m shelter constructed of 8 cm thick steel. The detonation cord was initiated with a M21 shock tube initiator from a safe location 500 m away. Fig. 1 shows images from the detonation process. Following detonation, most of the sample remained in the steel can and a grey colored residue was visible on the surface of the sample. Samples were collected from each steel can using a pre-cleaned PTFE (Teflon) scoop and placed into pre-cleaned high density polyethylene (HDPE) bags.

2.5. Quantification of explosives loaded to mineral surfaces following detonation

Following detonation, acetonitrile-extractable explosives concentrations were determined in triplicate using HPLC following Method 8330B protocols (United States Environmental Protection Agency, 2006; Walsh, 2001). Each HDPE bag containing the detonated substrate was mixed manually and three 6 g portions were subsampled for extraction with 20 mL of HPLC grade acetonitrile. The mixture was placed on a platform shaker for 24 h and centrifuged at a relative centrifugal force of 805 times gravity for 10 min. One drop of each extract was tested with an Expray kit to determine the appropriate dilution to be within the calibration range of the analytical detector (Bjella, 2005). Subsequently, a 1 mL portion of the acetonitrile supernatant, or dilution, along with 3 mL of ultrapure water was placed into a 7 mL amber glass vial with a Teflon lid. Samples were stored in the freezer until HPLC analysis.

2.6. Batch experiments

Batch samples of detonated substrates were prepared in duplicate by placing between 2.5 and 5 g of each detonated mineral into 50 mL borosilicate vials fitted with Teflon-lined screw caps. Between 5 and 20 mL of ultrapure water was added to each vial. An individual vial was prepared for each sampling time. All samples were mixed in the dark using an end-over-end rotary shaker and samples were collected after the following elapsed times: 30 min; 4, 8, 24, and 32 h; 5, 7, 14, 21, 28, 35, and 42 d.

Following the specified reaction time the sample vials were centrifuged at a relative centrifugal force of 805 times gravity for 10 min and a 2 mL aliquot of the supernatant was collected and filtered through a 0.2 μm syringe filter. One mL of the filtered supernatant was placed into a 7 mL amber glass vial with a Teflon-lined screw cap along with 2 mL of ultrapure water and 1 mL of HPLC grade acetonitrile. These samples were stored in a freezer in the dark until analysis.

2.7. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Immediately following collection, ATR-FTIR spectra were recorded using a Nicolet 560 Magna Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific, West Palm Beach, Florida)

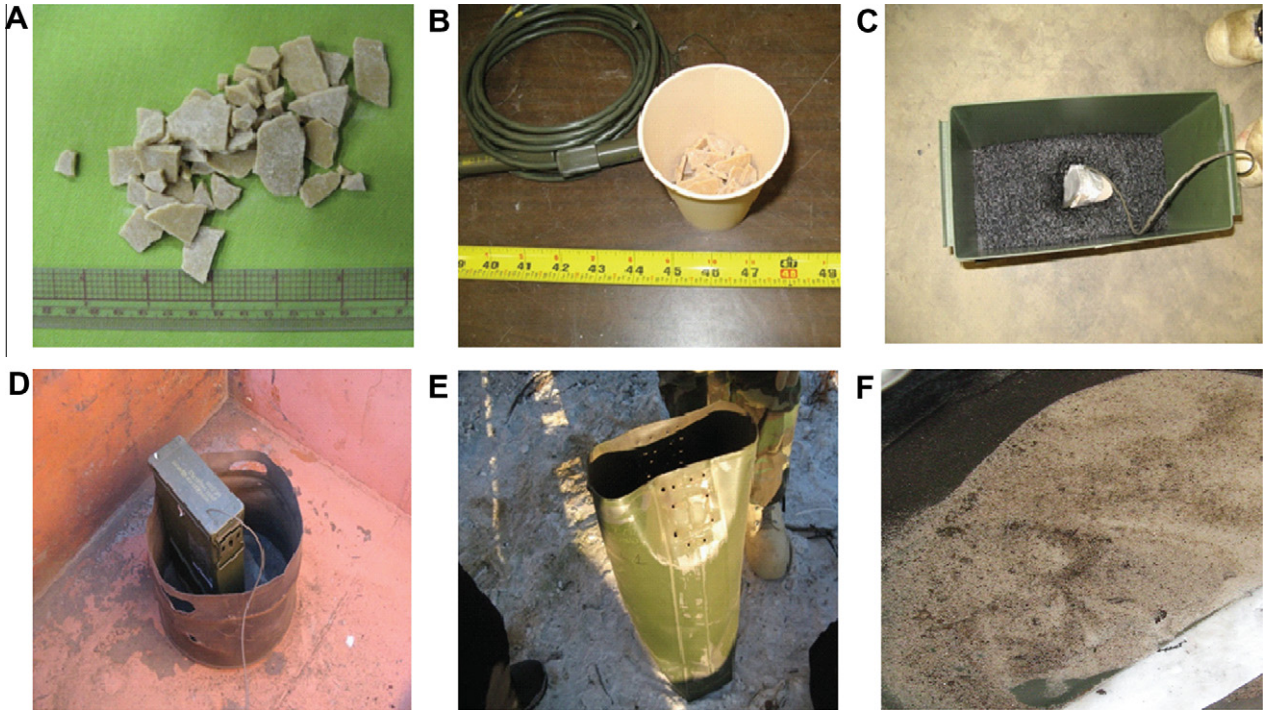

Fig. 1. Photos of: (A) Composition B used during detonations, (B) Composition B in the paper cup and detonation cord used in detonations with a reference scale in inches, (C) Biotite mica sample and explosives loaded into the detonation can, (D) Detonation can pre-detonation in the bombproof container, (E) a can following detonation, and (F) detonated Ottawa sand sample with visible explosive residue.

purged by dry air produced with a H_2O/CO_2 scrubber. All spectra were collected by repeating 240 replicate scans at a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1}. Thermo Nicolet software was used for data acquisition and processing. A SpectraTech (Oak Ridge, Tennessee) horizontal ATR accessory equipped with a ZnSe internal reflectance element with a 45° angle of incidence was used as the sample support for data collection. Approximately 1 g portions of each batch sample substrate was smoothed and then pressed firmly onto the ZnSe surface while wet to increase the optical quality of the interface between the crystal and the mineral substrate (Kubicki et al., 1997). After the spectra were obtained the remaining solid was stored in the freezer until solid fraction explosive compounds were quantified.

To acquire a sample spectrum of adsorbed TNT and RDX two different reference spectra were subtracted from the sample spectra. These reference spectra included a water spectrum, taken immediately following the acquisition of the sample spectrum, and a prepared mineral substrate spectrum (in the absence of any explosive compounds). All reference spectra were acquired using the same ATR crystal used for sample spectrum acquisition and were collected using the same scan parameters: 240 repeat scans with a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1}. Prior to reference spectrum subtraction, all spectra were baseline corrected using the Omnic software package (Thermo Fisher Scientific, West Palm Beach, Florida).

2.8. Batch sample extractions

Following sample collection and ATR-FTIR analysis of each batch sample, the remaining solid was dried and weighed in aluminum tins. The remaining explosives were extracted by adding 20 mL of HPLC grade acetonitrile to the remaining mineral solid following the protocols presented earlier for the bulk samples in Section 2.5 (Sunahara et al., 1999; United States Environmental Protection Agency, 2006; Walsh, 2001).

2.9. HPLC analysis of explosives on mineral surfaces and batch samples

Explosive analyte concentrations from the acetonitrile extracts were quantified with a Finnigan SpectraSYSTEM Model P4000 liquid chromatograph (Thermo Finnigan, West Palm Beach, Florida) with a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VIS absorbance detector set at 254 nm (cell path 1 cm). Samples were introduced with a 100 μL sample loop. The samples were separated using a 15 cm × 3.9 mm (4 μm) NovaPak (Milford, Massachusetts) C8 column held at 28 °C and eluted with 1.4 mL min^{-1} of 15:85 isopropanol/water (v/v). Concentrations of RDX and TNT in the batch solution and batch solids extraction samples were measured with an Agilent (Santa Clara, California) 1100 series HPLC system with a UV–visible detector and a 15 cm × 3.9 mm (4 μm) Waters (Milford, Massachusetts) C8 reversed phase HPLC column. The UV absorption wavelength was 254 nm, and the mobile phase was 15:85 isopropanol/water (v/v) mixture with a flow rate of 1.25 mL min^{-1}.

Batch aqueous samples were collected in triplicate and filtered through a 0.45 μm filter. Explosive compound concentrations in the batch solution and batch solid extraction samples were measured with an Agilent (Santa Clara, California) 1100 series HPLC system with a UV–visible detector and a 15 cm × 3.9 mm (4 μm) Waters (Milford, Massachusetts) C8 reversed phase HPLC column. The UV absorption wavelength was 254 nm, and the mobile phase was 15:85 isopropanol/water (v/v) mix with a flow rate of 1.25 mL min^{-1}.

3. Results

3.1. Explosives loaded to detonated mineral surfaces

The acetonitrile-extractable TNT and RDX concentrations measured following detonation are given in Table 1. These values represent the total amount of explosive residues deposited to the pure

minerals through detonation. Significant variations in the TNT and RDX concentrations exist between the triplicate samples as indicated by high percent relative standard deviations (i.e. the errors are associated with sample to sample variation as opposed to analytical errors). Ideally, Comp B has a TNT/RDX ratio of 39/60 with 1% wax. After detonation the biotite samples retained this ratio while nontronite and Ottawa sand had slightly greater TNT values and vermiculite had a lower TNT content. These variable TNT/RDX ratios, as well as the large sample variances, are believed to be the result of both the heterogeneous manner in which explosive residues are loaded to target materials and the presence of undetonated or partially detonated particles of Comp B that are not well mixed in the sample matrices.

3.2. Batch sample HPLC analysis

The average aqueous concentrations of TNT and RDX over the 42 d period for duplicate batch samples of nontronite, vermiculite, biotite, and Ottawa sand are shown in Fig. 2. Also included in Fig. 2 is the maximum solubility of TNT at 5.06×10^{-4} M (128 mg L^{-1}; Sheremata and Hawari, 2000) and the maximum solubility of RDX at 2.03×10^{-4} M (45 mg L^{-1}; Dean, 1985; Phelan and Barnett, 2001; Zhang and Hughes, 2003) in water at 25 °C.

For nontronite, TNT and RDX reach their maximum concentrations within the first 5 h of mixing; biotite reaches its maximum TNT and RDX concentrations within 9 h of mixing, and Ottawa sand reaches the maximum dissolved explosive concentrations after roughly 5 d of reaction. In the vermiculite samples the RDX concentration reaches a maximum within 5 h of mixing but the TNT concentration maximum is present at the time the initial sample was collected. Taken in total, these results suggest the explosive compound residues in the detonated minerals dissolved rapidly in aqueous batch reactors, however there is distinct behavior among the various substrates.

It appears from Fig. 2 that during initial dissolution the maximum solution concentrations of TNT and RDX briefly exceed solubility in some instances. This is believed to be caused by the high apparent solubility of the HE compound residues present in the samples following detonation. If the TNT and RDX residues are not present as pure crystalline phases but rather as a mixture of components then it is possible that the residue form of TNT and RDX is more soluble than the pristine TNT and RDX phases present in Comp B. Comp B has been shown to behave as a simple mixture of the pure compounds achieving near ideal solubility limits relatively rapidly (Phelan et al., 2002; Douglas et al., 2010).

RDX is known to have a low sorption affinity for a variety of mineral phases including phyllosilicates (Yamamoto et al., 2004; Dontsova et al., 2006; Douglas et al., 2009, 2010). Three of our samples include phyllosilicates (vermiculite, biotite and nontronite). Ottawa sand (quartz and calcite) provides a non-phyllosilicate substrate for comparison. The RDX concentration oscillates around the solubility limit in all of our samples. This indicates that precipitation/dissolution likely controls the aqueous phase concentrations. TNT is known to strongly adsorb to phyllosilicate minerals (Weissmahr et al., 1998; Eriksson et al., 2004; Charles et al., 2006). In the nontronite, biotite, and Ottawa sand samples the aqueous phase concentration of TNT appears to level out at values below the solubility limit. This suggests that sorption reactions control the aqueous concentration in these samples following complete dissolution of the explosive residues.

Vermiculite has a significantly different TNT concentration profile than the other mineral substrates (Fig. 2). The TNT concentration in the detonated vermiculite batch reactor decreased throughout the reaction sampling period. The loadings of HE compounds to vermiculite were significantly lower than to the other substrates, and the time profile suggests that sorption and/or transformation processes dominate the overall TNT behavior. This is discussed in greater detail below.

Fig. 3 shows the total TNT and RDX recovered (sum of the aqueous and acetonitrile extracted values for each sample event) in our samples over time. At long time periods (>10 d), the nontronite, biotite, and Ottawa sand samples generally exhibit values that remain constant over time (within the error bars). At short time scales for nontronite and Ottawa sand the trend includes initially elevated values for the first few days followed by a decrease in values toward an apparent equilibrium. For biotite, the concentrations remain within the error bar values throughout the 45 d batch. In addition, the RDX and TNT concentration ratios remain roughly constant for these three substrates. However, for vermiculite the RDX values decrease slightly over time while the total TNT values are the lowest of any of the mineral batches and decrease markedly over time to values barely above detection.

The loss of TNT from solution could be due to either the adsorption of TNT onto the mineral surfaces or the loss of TNT from solution. TNT is known to undergo reductive transformation to 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT), especially in the presence of organic compounds (Douglas et al., 2009) and phyllosilicate minerals (Larson et al., 2008).

The amino-nitrotoluene transformation products of TNT further transform to diamino-nitrotoluenes and then to phenolic derivatives (Hawari et al., 2000) that we did not measure. Therefore, 2ADNT or 4ADNT produced from the transformation of TNT may be lost from solution due to further transformation, or via adsorption onto mineral surfaces (Weissmahr et al., 1999; Douglas et al., 2010). Fig. 4 shows 2ADNT and 4ADNT concentrations measured in the batch aqueous samples over time. 2ADNT was present in barely detectable concentrations in all samples. However, 4ADNT shows some striking trends. First, biotite and vermiculite samples show significant 4ADNT concentrations even after relatively short reaction times despite the fact that the initial TNT concentrations in these two batches were markedly different. However, the trend in 4ADNT concentrations in the vermiculite samples is slightly downward toward the end of the batch, either from the adsorption of 4ADNT onto the vermiculite grains or the transformation of the 4ADNT. Initially, nontronite yields comparatively low 4ADNT concentrations but there is a distinct trend of increasing 4ADNT in solution over time. Ottawa sand is associated with barely detectable 4ADNT concentrations throughout the reaction period. The lack of expected sites for adsorption and/or reductive transforma-

Table 1
Acetonitrile-extractable TNT and RDX concentrations with corresponding percent relative standard deviation values measured following detonation.

Mineral	RDX mean (μg g^{-1})	RDX %RSD	TNT mean (μg g^{-1})	TNT %RSD	Approx. TNT/RDX %ratio
Biotite	7970	30	5530	28	40/60
Vermiculite	310	18	110	14	26/74
Nontronite	23,400	8	20,950	7	47/53
Ottawa sand	900	8	900	10	49/51

[1]RSD: Relative standard deviation.

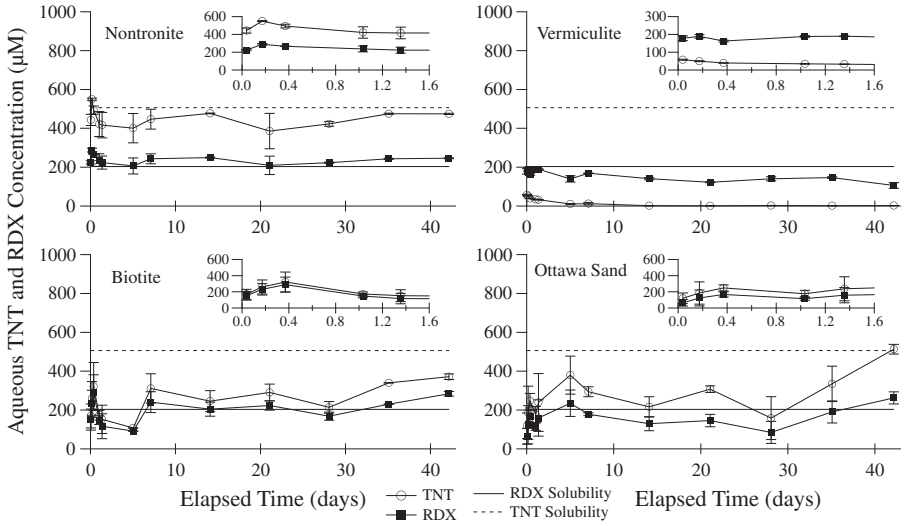

Fig. 2. TNT and RDX concentrations measured in nontronite, vermiculite, biotite and Ottawa sand batch samples over time. The horizontal lines represent the solubility of TNT (dashes) and RDX (solid) in water at 25 °C.

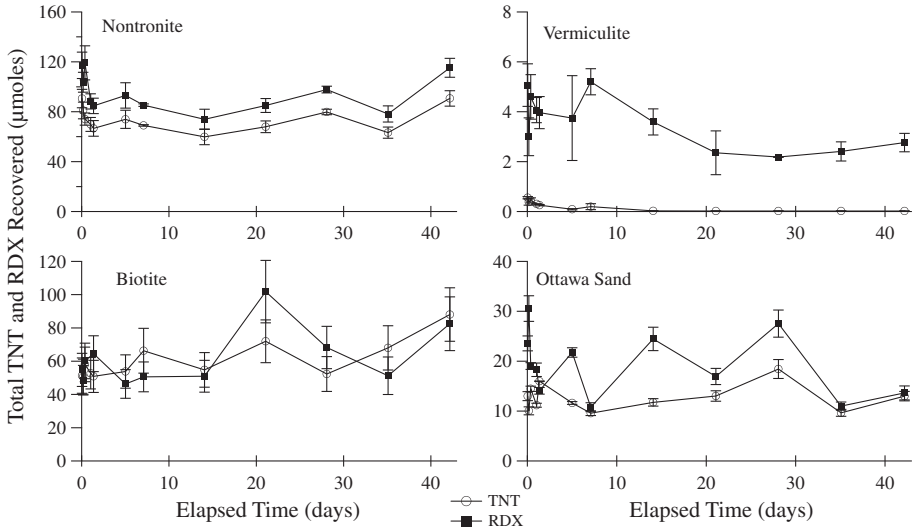

Fig. 3. Total moles of TNT and RDX in the samples over time. Each data point represents the sum of the batch aqueous concentrations and the acetonitrile-extracted concentration for each sampling event.

tion of TNT in this mineralogy (quartz and calcite) supports the previous finding that Ottawa sand does not provide a substrate that would promote transformation of TNT (or its transformation products 2ADNT and 4ADNT).

3.3. ATR-FTIR analysis

The HE compounds in the detonated mineral samples can be associated with a number of molecular environments, including their presence within residues, in solution, sorbed to mineral surfaces/interlayers and/or due to the dissolution of particles of undetonated Comp B. ATR-FTIR analysis was chosen to determine the extent of TNT and RDX sorption onto the mineral surfaces based on well known spectral characteristics from numerous model system studies (Weissmahr et al., 1996; Johnston et al., 2001). The ATR-FTIR measurements are semi-quantitative but provide novel information on the sorption of TNT and RDX to the sample substrates. Fig. 5 shows the integrated NO_2 stretching band absorbance values at 1350 cm^{-1} for TNT and 1260 cm^{-1} RDX in the detonated minerals. NO_2 stretching band absorbance values were not detected for TNT or RDX in the vermiculite samples, likely due to the low TNT and RDX concentrations in the vermiculite batch samples, consistent with the mass balance results noted above.

At the initiation of the batches (i.e. following the addition of the ultrapure water to the detonated minerals) it is likely that the explosives present were in the form of detonation residues and undetonated Comp B particles. The lowest absorbance values were detected in these samples. Over time, the absorbance values increased; this is likely due to the redistribution of TNT and RDX from residue films/particulates to a more homogeneous distribution on mineral particle surfaces/interlayers. This redistribution is expected to enhance the ATR-FTIR signal since more compounds would be within the sampling depth of the probe. This conclusion is supported by the HPLC results showing consistent total TNT mass balances (except for vermiculite) and solution concentration

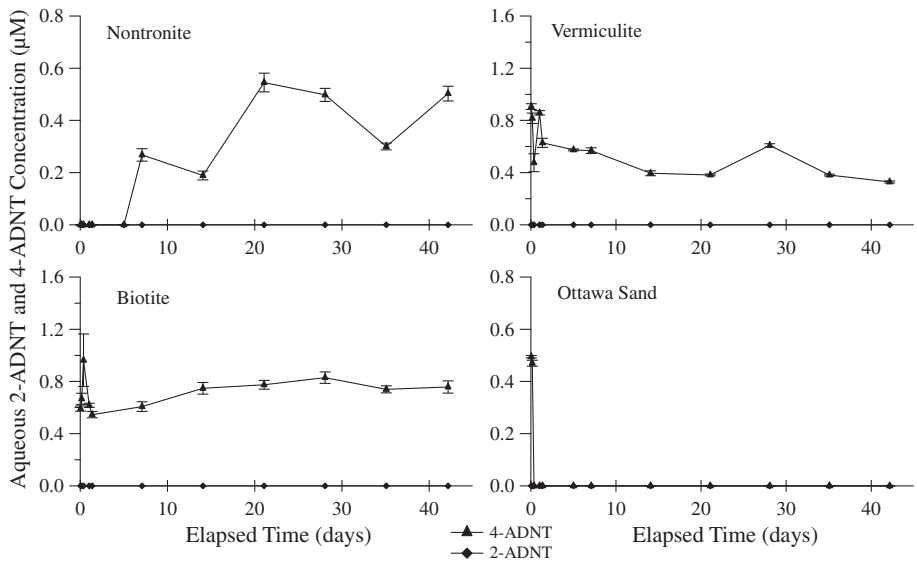

Fig. 4. Concentrations of 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) measured in the aqueous batches over time.

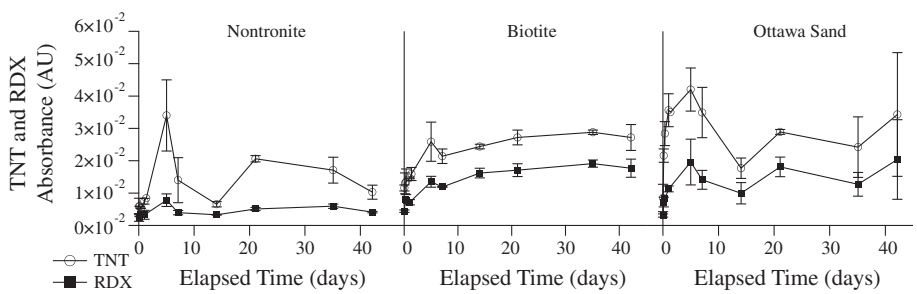

Fig. 5. TNT and RDX integrated NO_2 stretching band absorbance values at 1350 cm^{-1} for TNT and 1260 cm^{-1} for RDX in arbitrary units (AU) over time for the batch samples.

profiles showing rapid initial dissolution coupled with apparent sorption. The similarity of the TNT and RDX results indicate there is a redistribution of both species, with RDX controlled by saturation with respect to the solid phase.

4. Discussion

The objective of this study was to determine the fate of explosive residues loaded to pure minerals during a detonation event. It is well known that explosive residues are loaded to detonated materials heterogeneously (Jenkins et al., 2006; Pantea et al., 2006). As a consequence, even in laboratory based batch reactors, identifying equilibrium values of solution and substrate concentrations from detonated substrates is difficult (Douglas et al., 2010). For the present study the identification of steady state concentrations for aqueous and solid samples is made more difficult because each time series represents the values represented in a unique batch reactor. Thus cross sample (or in the case, cross residue) heterogeneity limits our ability to calculate adsorption coefficients (K_d) using the methodology followed by previous work where controlled laboratory spiking methods were used to "load" explosives to soil and mineral substrates (i.e. Weissmahr et al., 1998; Dontsova et al., 2006, 2008; Larson et al., 2008).

Despite the aforementioned limitations in calculating adsorption coefficients from our data we feel that the results from this study provide important insight into how, conceptually, explosive residues and pure minerals interact in an aqueous environment. After the initial dissolution of the explosive residues RDX and TNT are redistributed via sorption and precipitation. Transformation is another pathway high explosive compounds may follow which is exhibited by the rapid loss of concentration from solution with time, as is the case for the behavior of TNT in the vermiculite samples. During the initial dissolution of Comp B the TNT and RDX concentrations in the mineral samples exhibit a slight increase followed by a decrease, which is followed by "apparent equilibrium" concentrations (see Douglas et al., 2010), the exception being the behavior of TNT in the vermiculite sample.

The dissolution, sorption, and precipitation controls on the aqueous concentration of explosive compounds in our batch reactors over time are shown schematically in Fig. 6. In all cases it appears there is a rapid (irreversible) dissolution of explosive residues introducing HE compounds to solution (possibly at levels exceeding the solubility of the homogeneous precipitates). If, following initial dissolution, sorption sites become rapidly saturated and there is still excess HE compound such that the solution concentrations exceed solubility, precipitation will occur and the equilibrium will approach solubility limits (Fig. 6A). If the system is dominated by sorption reactions the profile will likely look similar to one for precipitation control but the effective equilibrium will be below solubility (Fig. 6B). If the system is dominated by transformation reactions the profile will look drastically different from profiles with either precipitation or sorption control. This case is

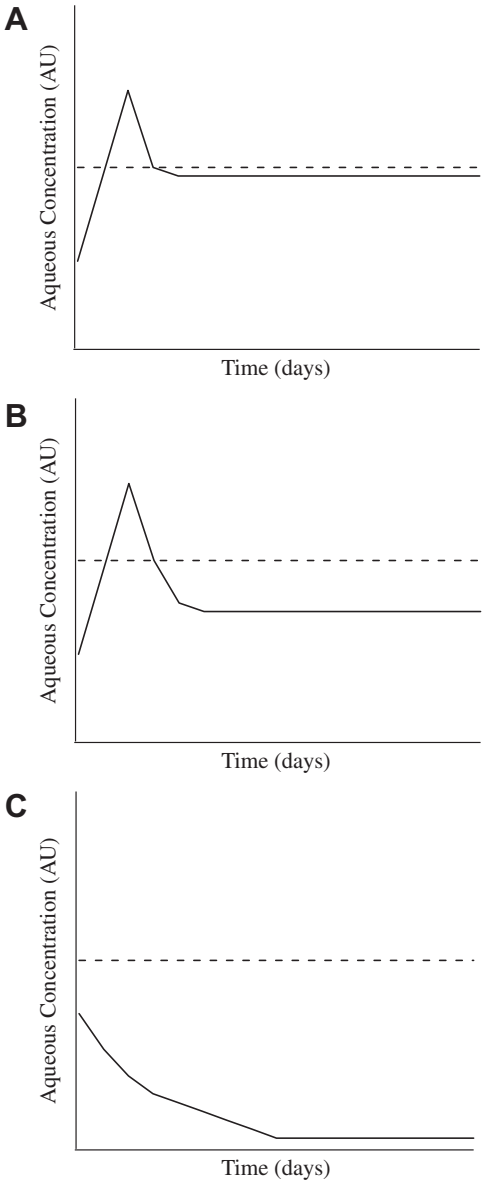

Fig. 6. Example plots illustrating: (A) dissolution followed by precipitation/solubility equilibrium, (B) dissolution followed by sorption/solubility equilibrium, and (C) rapid dissolution followed by transformation. Aqueous concentration values are in arbitrary units (AU). Dashed lines indicate the solubility of the analyte in water at 25 °C.

depicted in Fig. 6C in which explosive residues initially dissolve rapidly and undergo rapid transformation like the profile observed for the TNT concentrations in the detonated vermiculite samples.

The profiles observed experimentally (by our research and the numerous other studies of the fate of explosive compounds in batch reactors) are more complex than the simple conceptual models presented in Fig. 6. However, the results for the non-vermiculite minerals are consistent with rapid dissolution of explosive residues followed by sorption/precipitation controlling the RDX concentrations and sorption dominating solution concentrations of TNT. The significant sample to sample variation observed is largely attributable to the heterogeneous nature of the starting materials (each sample was prepared independently). The exceptional case is the behavior of TNT in the vermiculite system. In this case the results suggest TNT transformation is the dominant process. Whether this is intrinsic to the vermiculite substrate (i.e. its exchangeable cation and hydration properties relative to the other substrates or its ability to provide a reductant for TNT transformation), or is associated with simply a lower initial concentration requires additional study.

5. Conclusions

Explosive detonation processes are inherently heterogeneous. Once explosive compound residues or undetonated explosive particles are loaded to soils dissolution processes rapidly introduce TNT and RDX into the aqueous phase. These dissolution processes occurred rapidly with dissolved concentration maximums reached within 9 h for all four of our detonated pure mineral phases. Once dissolved, the fate and transport of explosive compounds are controlled by precipitation and sorption processes and, potentially, transformation to other compounds. In this study, both adsorption and precipitation were found to control the aqueous phase explosive compounds in detonated nontronite, biotite, and Ottawa sand. Vermiculite had a unique behavior with respect to TNT transformation. Based on the results from our study vermiculite presents a potential substrate that could be used in training ranges or impact areas to promote TNT transformation. However, further investigation of the TNT transformation rates and surface chemical interactions between vermiculite and explosive compounds are warranted.

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