THE FATE OF NITROAROMATIC (TNT) AND NITRAMINE (RDX AND HMX) EXPLOSIVES IN FRACTURED AND WEATHERED SOILS

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ABSTRACT

We investigated the fate of explosives compounds in slurries containing fractured and weathered soil particles. Three soils were crushed with a piston to emulate detonation-induced fracturing. We used X-ray diffraction, scanning electron microscopy and gas adsorption surface area measurements to quantify the mineralogies and surfaces of the weathered and fractured soil particles. Soil batch slurries were prepared by spiking the soils with waters containing TNT, 2,4-DNT, HMX and RDX. Batch samples were collected 10 times over 92 days and the concentrations of the four spiked explosives compounds and TNT breakdown products 2ADNT and 4ADNT were measured. TNT, 2,4-DNT, RDX, and HMX exhibited substantially greater analyte loss batch solutions containing crushed soils compared to their uncrushed, weathered counterparts. This suggests explosives compounds breakdown more readily in the presence of fresh mineral and soil particle surfaces than in the presence of weathered surfaces. Concentrations of TNT breakdown products 2ADNT and 4ADNT were slightly greater in the slurries containing weathered soils than in slurries containing crushed soils. We suspect this is because these compounds are breaking down more rapidly to diamino and triamino compounds in the crushed soil batches than in the weathered batches. Following the batch runs the weathered, unfractured soils contained lower TNT, 2,4-DNT, RDX, HMX,2ADNT, and 4ADNT concentrations than their crushed counterparts. This suggests enhanced transformation of explosives compounds in the crushed soils is not associated with enhanced adsorption onto mineral surfaces but, rather, is associated with degradation to tertiary breakdown products.

INTRODUCTION

Artillery, mortars, hand grenades and small arms munitions contain nitroaromatic compounds like 2,4,6-trinitrotoluene (TNT) and nitramines like 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) and 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine (HMX) that interact with the soils onto which they are deposited. Explosives are known to adsorb to soil mineral surfaces and aquatic sediments (Brannon et al., 2002; Li et al., 2004; Eriksson et al., 2004). Training range soils with adsorbed explosives thus provide a long-term contamination issue at training, testing and manufacturing sites. The off-site migration of explosives either adsorbed to sediments or eluted from sediments provides a long-term risk.

Reactions on mineral and organic particle surfaces at a range of scales control nitramine and nitroaromatic compound adsorption and transformation. Previous investigations of the fate of explosives in sediments have used weathered clays, silts and sands in a series of column and incubation studies (eg. Price et al., 2000 and the references therein). These samples provide a substrate that is well characterized but the rounded grains and general lack of fresh mineral surfaces offered by these weathered substrates provide a less reactive surface for adsorption than fractured or unweathered mineral surfaces.

Explosives compounds are formulated based on their brisance, or ability to shatter materials which include targets and training range soil particles (Eremenko and Nesterenko, 1989; Pepekin and Gubin, 2007). These fractured soils are the primary transfer mechanism between explosives detonations and training range soils. It is widely known that fresh mineral

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surfaces (and newly created microparticles of them) are more reactive to geochemical species than weathered soil surfaces in river sediments (Stallard and Edmond, 1983) and soil solutions (Anbeek, 1992.

The focused objective of this study was to investigate the fate of explosives in the presence of fractured and pristine mineral particles from three different soils. Soils were manually crushed to create fresh, unweathered mineral surfaces. The fresh soils and their weathered counterparts were spiked with an aqueous solution containing nitramine and nitroaromatic compounds and the explosives compounds concentrations in soil slurries were measured over time. The results unequivocally suggest that explosives degradation is greater in slurries containing fresh mineral surfaces. This implies models of explosives retention and adsorption based on measurements from weathered soils likely underestimate the ability for soils to promote the degradation of explosives. However, the results also suggest that fresh mineral surfaces may contain adsorption sites that are more reactive for explosives compounds. These sites likely have active surface geochemical conditions that affect the long term fate of explosives compounds. This has ramifications for the adsorption, transformation and long term fate of other organic and metallic contaminants.

2. MATERIALS AND METHODS

2.1. Sample preparation

Roughly 15 kg of soil was collected from three different locations representing soils that we have found to be relatively common on impact ranges. The first, “Church,” is a poorly graded glaciofluvial sand collected from a bluff above the Connecticut River south of Norwich, Vermont (43.737˚N, 72.261˚W). The second, “Delta,” is a well graded sand with silt collected from a glacial moraine near Delta Junction, Alaska (63.854˚N, 145.732˚W). The third sample, “BBTS,” is an aeolian silty sand collected near Bovina, Mississippi near the Big Black River (32.273˚N, 90.719˚W). The soil samples were heated to 100 ˚C for 24 hours to drive off soil moisture. A 2 kg subset of each sample was sieved on a shaker for 20 minutes using sieves ranging from 10 to 200 mesh to characterize the soils by size fraction following the protocols of the Department of Defense MIL-STD-621A “Unified Soil Classification System.” Table 1 includes the results from the soil classification analysis.

TABLE 1. A summary of the size fractions retained on sieves during a test of the three samples investigated in this study prior to crushing and following crushing.

Mesh #	Mesh opening (mm)	Original Delta % by mass retained	Crushed Delta % by mass retained	Original Church % by mass retained	Crushed Church % by mass retained	Original BBTS % by mass retained	Crushed BBTS % by mass retained
>10	2.06	30.0	25.6	9.7	10.1	1.1	0.7
>20	0.853	29.6	27.5	16.1	15.8	8.2	1.7
>40	0.422	19.4	22.1	20.4	19.8	10.4	3.9
>60	0.251	8.1	9.5	18.9	18.5	7.3	5.8
>100	0.152	4.8	5.7	10.8	10.6	18.1	23.1
>200	0.076	3.3	3.9	8.0	8.9	15.1	18.5
<200	<0.076	4.8	5.7	16.1	16.4	39.8	46.2

A 5 kg subset of each of the three soil samples was crushed using a piston crusher at 146,000 kg/cm^2 (222 kN) following American Society for Testing and Materials (ASTM) Method D1557-02 “Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Modified Effort.” Roughly 300 g of each soil was placed in a 6 cm diameter steel tray and the downward force on the sample tray with the piston exerted a resistance load of 9100 kg. A square wave pulse of force was applied to the samples at a rate of one pulse per second for 60 seconds. Force sensors showed that the first three to four pulses generally yielded less than the maximum system force due to the initial redistribution and fracturing of grains into open pore spaces. By the fourth or fifth of the 60 piston pulses, the samples yielded the maximum resistance to the piston crusher. Following crushing the soils were scraped out of the sample tray with a spoon.

2.2. Batch experiment aqueous samples

All samples were prepared in triplicate so that an average and standard deviation of each analysis could be calculated. We placed 6 +/-0.002 g of each sample in a 50 mL glass centrifuge tube. A 20 mL spike solution containing 4.1 mg/L TNT, 4.4 mg/L 2,4-DNT, 0.49

mg/L HMX and 2.3 mg/L RDX in 18 M-Ω water were added to the centrifuge tubes at the start (March 27, 2007 at 11:17 AM). The TNT, 2,4-DNT, HMX and RDX used to prepare the aqueous spiking solutions were solid Standard Analytical Reference Materials from the U.S. Army Environmental Center, Aberdeen Proving Ground, MD.

The centrifuge tubes were placed on a platform shaker in the dark and shaken at 200 revolutions per minute continuously for three months. During this time, 10 samples of the batch slurry solution were collected from the batches at the following elapsed times: 30, 90 and 300 minutes and 1, 3, 6, 10, 17, 24 and 92 days. To collect a sample the centrifuge tubes were placed in a rotary centrifuge at 3,000 revolutions per minute for 10 minutes. A pipettor was used to collect 1 mL of each sample from the top of the tube. The sample was purged into a 7 mL amber glass vial with a PTFE (Teflon) lid. Two mL of 18 M-Ω water and 1 mL of HPLC grade acetonitrile were added to each sample to bring the total volume to 4 mL. Samples were stored frozen until they were analyzed for explosives compounds. Following each sample extraction the centrifuge tubes were shaken vigorously and returned to the shaker table.

Concentrations of TNT, 2,4-DNT, HMX, RDX, 2-Am-DNT and 4-Am-DNT were determined in aqueous solutions following SW846 Method 8330B: Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC; USEPA 2006). Samples were filtered through a Millex-FH PTFE (Teflon) 0.45 µm filter unit prior to analysis.

Explosives compound concentrations in aqueous solutions were measured on a modular system from Thermo Electron Corporation composed of a Finnigan Spectra- SYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 210 (to detect NG) and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15 cm X 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).

Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference materials were 8095 Calibration Mix A (HMX, RDX, TNT, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, 2-Am-4,6-DNT, 4-Am-2,6-DNT, and tetryl). The concentration of each analyte was 10 mg/mL in acetonitrile in the solution used to calibrate the HPLC-UV.

2.3. Batch experiment soil samples

Soils from the batch experiment were air-dried at 20˚C for 24 hours. A 10 mL aliquot of HPLC grade acetonitrile was added to the soil to extract the energetic residues from the soil. Each sample was shaken vigorously to suspend the soil particles and then they were placed on a platform shaker for 18 hours at 200 revolutions per minute. The soil particles were allowed to settle, then 1 mL of the acetonitrile extract was mixed with 3 mL of 18 M-Ω water and the mixture was filtered through a Millex-FH PTFE (Teflon) 0.45 µm filter unit. Concentrations of TNT, 2,4-DNT, HMX, RDX, 2-Am-DNT and 4-Am-DNT from the soil extract solutions were determined following identical procedures outlined above for the aqueous samples.

3. RESULTS AND DISCUSSION

3.1. Batch experiment aqueous samples

We made 180 explosives compound concentration measurements from the batch experiment aqueous samples. All batches were constructed and sampled in triplicate and the values presented here include an average and standard deviation calculated from the triplicate measurements. The pristine and crushed soils from each sample were spiked with a solution containing TNT, RDX, HMX and 2,4-DNT. We collected a sample of the batch waters over time to monitor changes in the explosives composition in each sample.

The initial TNT spiked concentration was 4 mg/L. Over time, TNT exhibited a dramatic loss from the batch solutions with concentrations eventually dropping below detection in all samples (Figure 1A). This was expected as TNT has been shown to undergo reductive degradation in a variety of soil types (Weissmahr et al., 1998). The loss was almost instantaneous with TNT measurements 30 minutes following spiking of ~2 to 3 mg/L in all samples. In all three sample types the solutions collected from batches containing crushed samples yielded lower TNT concentrations than solutions from uncrushed batch samples. The TNT concentration for both the crushed and pristine BBTS samples decreased below detection within three days.

The rate of TNT loss from batch solutions was related to the sample particle size with the smallest particle size samples (BBTS) exhibiting the greatest TNT loss and the largest particle size samples (Delta) exhibiting the lowest rate of TNT degradation. This supports the results of a recent study of the fate of TNT in solutions containing a range of soil particle size that showed the sorption of aqueous TNT and RDX was greatest in samples with the smallest grain sizes (Larson et al., 2008).

We also measured two TNT breakdown products in our batch solutions: 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT). These two monoamines were not present in our initial spiked solutions but they began to appear in the batch samples within a few hours (4ADNT) or a few days (2ADNT) following spiking with TNT (Figure 1B). The 2ADNT and 4ADNT are present in the samples presumably due to the reductive transformation breakdown of TNT (Thorn et al., 2002; Jenkins et al., 2006). Concentrations of 4ADNT were greater than 2ADNT for the three different soil types and 4ADNT appeared in the samples before 2ADNT. In all cases both amines appeared in the crushed samples before they were detected in the pristine samples. For the BBTS samples the 4ADNT appeared within 6 hours for the crushed samples and 23 hours for the pristine. These two compounds appeared in the BBTS samples first but they reached their greatest concentrations in the Delta and Church samples. The 2ADNT concentrations remained low throughout the batch experiment (~0.2 mg/L for the greatest value) and in all samples they decreased between day 24 and day 92. The 4ADNT concentrations reached as high as 0.9 mg/L (Delta uncrushed), equal to almost 25% of the initial TNT concentration.

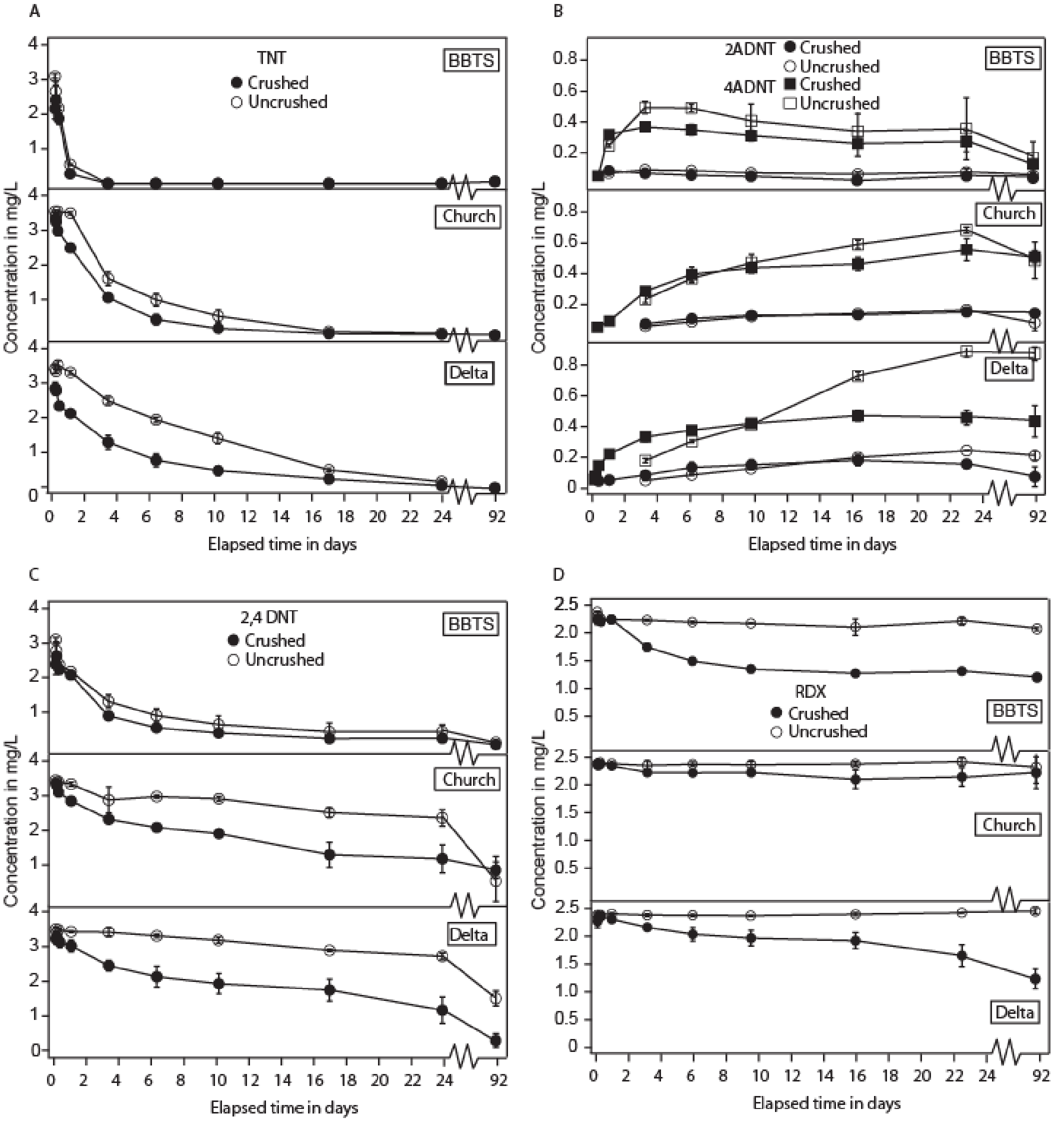

FIGURE 3. Explosives compound concentrations in waters from the batch spiking measurements. A 20 mL spike solution containing 4.1 mg/L TNT, 4.4 mg/L 2,4-DNT, 0.49 mg/L HMX and 2.3 mg/L RDX was added to 6 g of each soil sample.

For the most part the concentrations of 2ADNT and 4ADNT were greater in the batches of uncrushed samples compared to crushed samples. 2ADNT and 4ADNT also undergo breakdown to other products (Schmidt and Butte, 1999) and it is highly likely that these compounds broke down in the batch solutions following their being converted from TNT. This is supported by the fact that the 2ADNT and 4ADNT concentrations were lowest in the crushed soils and appeared first (and in greater initial concentrations) in the finest soils (BBTS). We did not measure the concentrations of the varied 2ADNT and 4ADNT breakdown products in our batch solutions or final soil samples so we can only speculate that these species are breaking down themselves.

The results from 2,4 DNT measurements in the batch samples (Figure 1C) are similar to what we report for TNT- the crushed sample aqueous solutions have lower concentrations than the pristine soil aqueous solutions, the finer grain samples (BBTS) have the greatest rate of breakdown and breakdown is evident for all sample types within the first 24 hours. It has been established that 2,4-DNT undergoes a reductive transformation process similar to TNT (Leungsakul et al., 2005) however there have been far more investigations of the fate of TNT in soils than the fate of 2,4-DNT.

The results from our batch experiments with RDX (Figure 1D) suggest that the pristine soils do not exhibit any degradation with the values consistently close to the 2.3 mg/L spike solution concentration. However for the BBTS and Church crushed soils there is a marked decrease in the RDX concentration over time to roughly half of the initial spike solution concentration. Our batch results for HMX (not shown) are similar to RDX- a decrease in the crushed BBTS and Delta aqueous solution values to almost half of the initial spike solution concentration. These results suggest that nitramines such as RDX and HMX, generally thought to behave somewhat conservatively in soils, may undergo adsorption to mineral surfaces or degradation in the presence of fresh mineral surfaces. However, the mineralogical and geochemical conditions that promote nitramine degradation are not largely understood.

2.2. Batch experiment soil samples

Following the 92 day batch mixing experiments we air dried the soils and quantified the explosives compounds extractable in acetonitrile in the soils. The results are presented in Figure 4. For TNT (Figure 2A) the soils with the largest fine grained fraction (BBTS) yield the highest concentrations but they are substantially lower than the 82 μg concentration expected from the 20 mL spike solution with a 4.1 mg/L concentration mixed into a 6 g sample. The Church samples yield no detectable TNT concentrations and the Delta samples yield low values (less than 0.04 μg/g). Unlike the aqueous solutions there is no statistically significant difference in TNT values for the soil extracts between crushed and uncrushed samples.

The TNT breakdown products 2ADNT and 4ADNT exhibited greater concentrations in the pristine soil extracts than the crushed ones (Figure 2B). In the Church and Delta samples the 2ADNT and 4ADNT values were statistically significantly greater in the uncrushed samples (analysis of variance with $\alpha=0.05$). For all samples the 4ADNT concentrations are greater than 2ADNT which was also the case in the aqueous samples. There does not appear to be a relationship between the soil particle size and the 2ADNT or 4ADNT concentration. Based on the timeline of values from the batch aqueous samples it appears that the 2ADNT and 4ADNT concentrations initially increase and then slowly decrease over time. These soil sample extractions represent the final values at the end of the batch. If the 2ADNT and 4ADNT underwent further degradation to tertiary TNT breakdown products then their concentrations would decrease in the aqueous samples and thus in the final soils. Though we cannot be certain that the 2ADNT and 4ADNT underwent breakdown in the batches the aqueous solution results suggest their concentrations decreased markedly between days 24 and 92.

The results for RDX measurements from the soil extracts support the results from the aqueous analyses, namely that RDX is present in roughly twice the concentration in the uncrushed samples compared to the crushed ones (Figure 2D). Based on an analysis of variance with $\alpha=0.05$ the RDX concentrations in all three of the crushed soil aqueous solutions are statistically significantly lower than in their uncrushed counterparts. The Church crushed samples showed no degradation in the aqueous solutions but in the soil samples the crushed Church samples had less than half the RDX concentration that was measured in the uncrushed samples.

The results for HMX concentrations measured in soil extracts are similar to what was measured for RDX- in all three soil types the crushed samples yielded statistically significantly lower HMX concentrations than the uncrushed samples. The uncrushed sample extract HMX concentrations were 0.35 μg/g (BBTS), 0.12 μg/g (Church), and 0.15 μg/g (Delta) while the crushed sample extract HMX concentrations were 0.46 μg/g (BBTS), 0.25 μg/g (Church), and 0.29 μg/g (Delta). The RDX and HMX results suggest that nitramine explosives compounds are breaking down in our soils but the presence of fractured mineral surfaces is associated with enhanced degradation.

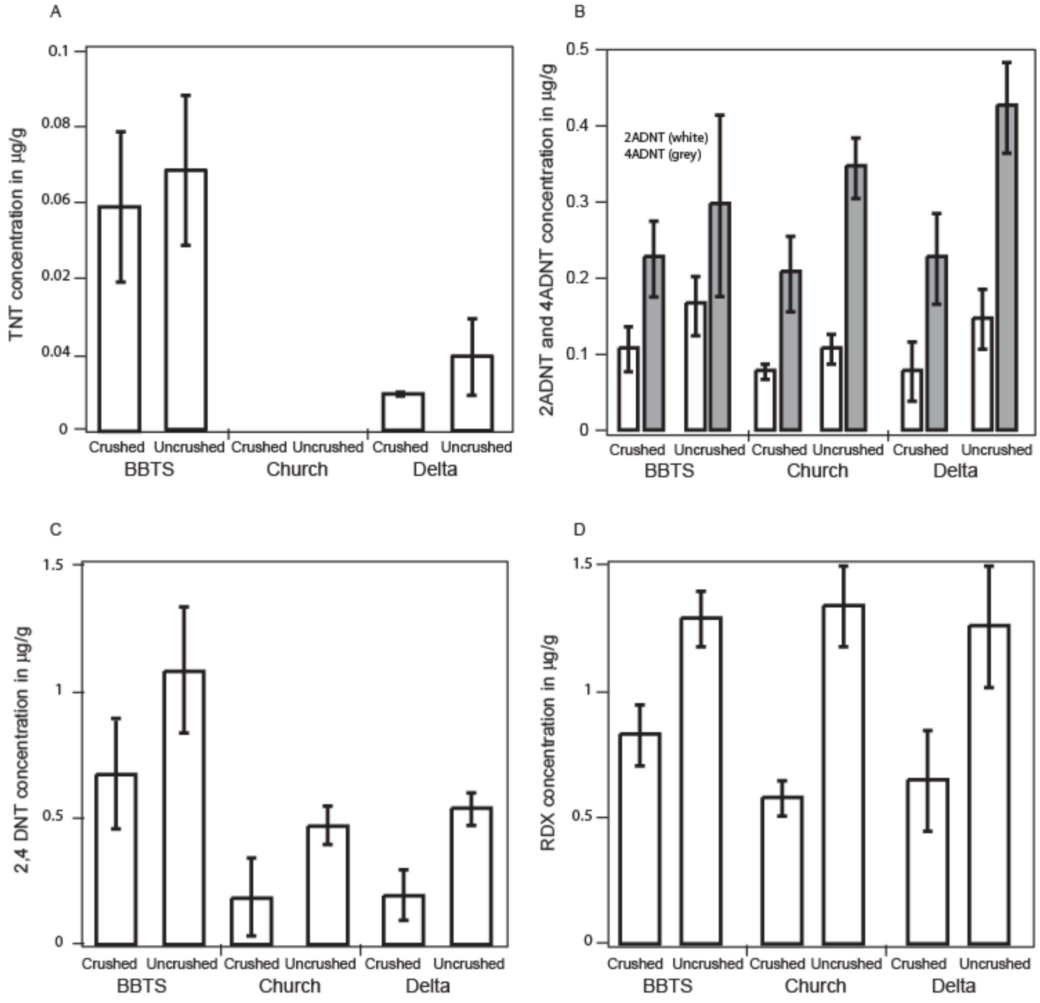

FIGURE 4. Explosives compound concentrations in the soils that were remaining at the end of the batch spiking measurements. A 20 mL spike solution containing 4.1 mg/L TNT, 4.4 mg/L 2,4-DNT, 0.49 mg/L HMX and 2.3 mg/L RDX was added to 6 g of each soil sample.

4. SUMMARY AND CONCLUSIONS

Taken in total, the results from this study suggest that fresh, unweathered soil particle surfaces are associated with the enhanced degradation of nitroaromatic (TNT and 2,4-DNT) and nitramine (RDX and HMX) explosives compounds. In all the compounds we investigated the primary product solution concentrations were lower in aqueous batch solutions containing crushed samples than with aqueous batch solutions containing uncrushed samples. Little TNT was recovered from the aqueous solutions or the final soils. This is not a surprise as TNT is known to degrade rapidly in nature to 2ADNT and 4ADNT (Thorn et al., 2002; Jenkins et al., 2006). TNT degradation is greatest in the soils with the smallest particle size fractions supporting recent work where TNT degradation was correlated to particle size distributions (Larson et al., 2008 and references therein). 2ADNT and 4ADNT also yielded the highest concentrations in uncrushed soil batches. It is established that TNT degrades to 2ADNT and 4ADNT and these aminodinitrotoluenes, in turn, degrade to phenolic derivatives (Hawari et al., 2000). We did not measure TNT tertiary breakdown products but suspect the 2ADNT and 4ADNT are breaking down more rapidly in the crushed soil solutions than in the presence of pristine soil solutions.

RDX and HMX exhibited loss from solution over time in two of the crushed soils but not in any of the weathered soils. This nitramine degradation did not appear to be related to particle size (the samples representing the smallest and largest sizes exhibited loss from solution). The degradation of RDX and HMX is somewhat surprising because these compounds are generally considered conservative (Selim et al., 1995; Singh et al., 1998; Tucker et al., 2002; Yamamoto et al., 2004; Dontsova et al., 2007). Based on the results of this study we cannot definitively address what soil geochemical or surface conditions favor the preservation or breakdown of RDX or HMX. Regardless, the results suggest that these explosives compounds are not as conservative in the presence of fractured soil particles as they are in the presence of weathered soil particles.

Our results are the first to compare the fate of explosives compounds in the presence of fractured and pristine soil particles. We cannot say that the piston crushed samples represent the impact forces of any specific explosive detonations. However it is apparent that there are marked differences in the fate of explosives compounds in the presence of the fractured (piston crushed) samples and their pristine counterparts. Based on our research the available models used to assess the fate of explosives in impact ranges likely underestimate the rate of degradation of nitroaromatic and nitramine compounds in some soil types. As a consequence the partition coefficient (Kd) values for impact area soils that are heavily fractured from explosives detonations are likely larger than for similar soils in their weathered (pristine) state.

Clearly more research is needed to quantify why enhanced degradation occurs in the presence of fractured minerals. This research should integrate surface geochemical investigations with batch scale measurements to better determine whether specific geochemical or surface chemical situations favor the breakdown or retention of nitroaromatic and nitramine compounds in soils. Future investigations should pair piston crushed samples with those blasted with explosives to better assess the similarity in using these two methods to create fresh mineral surfaces. Finally, the fresh mineral surfaces may present active surface geochemical conditions that affect the long term fate of explosives and other environmental contaminants such as organic and metallic compounds.

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