



A time series investigation of the stability of nitramine and nitroaromatic explosives in surface water samples at ambient temperature

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ABSTRACT

We investigated the fate of nitramine and nitroaromatic explosives compounds in surface water to determine how surface water biogeochemistry affects the stability of explosives compounds. Five river water samples and 18.2 MΩ deionized water were spiked with 10 explosives compounds and the samples were held at ambient temperatures (20 °C) for 85 d. Surface water represented three rivers with a range of total organic carbon concentrations and two rivers draining glacial watersheds with minimal organic carbon but high suspended solids. 18.2 MΩ deionized water exhibited no explosives transformation. Nitroaromatic compound loss from solution was generally: tetryl > 1,3,5-TNB > TNT > 1,3-DNB > 2,4-DNT. The HMX, RDX, 2,6-DNT, 2ADNT, and 4ADNT concentrations remained somewhat stable over time. The surface water with the highest total organic carbon concentration exhibited the most dramatic nitroaromatic loss from solution with tetryl, 1,3,5-TNB and TNT concentrations decreasing to below detection within 10 d. The two water samples with high suspended solid loads exhibited substantial nitroaromatic explosives loss which could be attributable to adsorption onto fresh mineral surfaces and/or enhanced microbiologic biotransformation on mineral surfaces. An identical set of six water samples was spiked with explosives and acidified with sodium bisulfate to a pH of 2. Acidification maintained stable explosives concentrations in most of the water samples for the entire 85 d. Our results suggest sampling campaigns for explosives in surface water must account for biogeochemical characteristics. Acidification of samples with sodium bisulfate immediately following collection is a robust way to preserve nitroaromatic compound concentrations even at ambient temperature for up to three months.

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1. Introduction

Training with artillery, mortars, hand grenades and small arms is common at Department of Defense installations worldwide. These munitions contain nitroaromatic compounds like 2,4,6-trinitrotoluene (TNT) and nitramine compounds like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) that interact with the soils onto which they are deposited. These explosives and some of their transformation products are known to adsorb to surface soils and sediments where they can undergo reductive transformation or remain stored in soils (Brannon et al., 2002; Eriksson et al., 2004; Li et al., 2004). The off-site migration of explosives or their transformation products thus provides a long term contamination issue for the Department of Defense. Many explosive compounds transform in soil and water. For example, TNT photo transforms to 1,3,5-trinitrobenzene (TNB) and biotransforms to 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT). The transformation of

TNT would lead to a lower TNT concentration (and likely a higher 2ADNT or 4ADNT concentration) in a water sample. Since TNT transformation is time dependent it is paramount that holding times at typical room temperatures be established for explosives compounds to support the goals of environmental characterization, monitoring and fate investigations.

Training ranges are the focus of long term fate and transport investigations of explosives compounds. Most of these studies have focused on the transformation and absorption of explosives compounds in water and soils. Soils with high clay contents or small particle sizes (Larson et al., 2008) and high total organic carbon content (Myers et al., 1998) have been shown to promote TNT transformation. RDX and HMX are generally considered conservative in surface water (Selim et al., 1995; Tucker et al., 2002; Yamamoto et al., 2004; Dontsova et al., 2006). Presumably, water samples with high clay content, high organic content and/or small particle sizes pose the greatest risk of explosives compound transformation in the time between collection and explosive analysis.

Increasingly, autonomous sample collectors are being used to collect surface and shallow ground water samples during changing flow regimes. Automated collectors would be well suited for

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deployment on active training ranges where access can be limited by training schedules, remoteness or safety requirements associated with the presence of live or partially detonated ordnances. The objective of this study was therefore to determine how stable explosives compounds were in surface water samples stored at ambient temperatures. To address this, we investigated the long term stability of explosives compounds at ambient temperature (20 °C) in a variety of surface water samples that represented a range of organic and mineral particle contents. Five different surface water samples and a sample of 18.2 MΩ deionized water were spiked with a known concentration of explosive and transformation product analytes and samples were collected for 85 d. The surface water samples included three rivers with total organic carbon concentrations ranging from 3.4 to 14.5 mg L⁻¹. Two water samples from glacial outwash rivers containing little to no organic carbon but a high suspended sediment load were included. Sodium bisulfate was added to an identical set of six water samples to lower the pH to 2 to quantify how well sodium bisulfate functioned in preventing explosives analyte transformation.

2. Materials and methods

2.1. Water collection and batch sample preparation

Five 10 L high density polyethylene (HDPE) carboys were filled with river water from Interior Alaska. The carboys were cleaned with soap and triple rinsed with 18.2 MΩ deionized water prior to filling them with samples from the rivers. During sample collection personnel wore powder free latex gloves and each carboy was rinsed with river water from the collection site prior to collecting the river water sample. Three of the rivers, the Chena River, MacDonald Creek and Bear Creek, are clear water streams draining boreal forest watersheds. The Delta River and Jarvis Creek are dominated by glacial melt flow and thus contain a high silt and mineral content. An additional carboy was filled with 18.2 MΩ deionized water. A second set of 500 mL samples of each water body and deionized water was collected to establish background levels and they yielded no detectable concentrations of any explosives analytes.

Each 10 L Carboy was spiked with a standard analyte solution (Restek Corporation Bellefonte, PA) that included equal amounts of RDX, HMX, TNT, tetryl, 2,4-DNT, 2,6-DNT, 2ADNT, 4ADNT, 1,3-DNB, and 1,3,5-TNB to achieve a final spiked concentration for each analyte of 50 μg L⁻¹. The six carboys containing water samples were shaken vigorously and each carboy was emptied into 20 500 mL amber glass bottles that were capped with no headspace. The carboys were shaken vigorously between filling each 500 mL bottle to ensure each bottle contained a representative portion of sediment. The 500 mL amber glass bottles were stored in a closet in the dark.

We added 0.8 g of sodium bisulfate to one set of ten 500 mL bottles representing each sample to reduce the sample pH to 2. This follows the protocols of Jenkins et al. (1995) to prevent the transformation of nitramine and nitroaromatic compounds in solution. All of the 500 mL bottles containing the batch samples were stored in the dark at 20 °C for 85 d and the explosives concentration of the samples (represented by one 500 mL bottle per surface water type) were measured over time. Explosives concentrations were measured from both the acidified and non-acidified samples over 85 d as follows: days 1, 3, 6, 10, 16, 27, 42, 64, and 85.

2.2. Biogeochemical characterization of the surface water samples

We measured the specific conductance and turbidity of the water bodies during collection. Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured following EPA method 415.1 (Analytical Resources Incorporated, Tukwila, Washington).

We collected a 10 L sample of water from the Delta River and Jarvis Creek and ~250 g of suspended sediment was separated from the water in a centrifuge. A 5 g sample of suspended sediment was placed in 200 mL of 18.2 MΩ deionized water to quantify the available cation and anion exchange from the particle surfaces over time. This material was sieved into seven size fractions between 10 and 200 mesh to characterize the soils following the protocols of the Department of Defense MIL-STD-621A “Unified Soil Classification System.”

Six grams of suspended sediment material from the Delta River and Jarvis Creek were placed into centrifuge tubes with 40 mL of 18.2 MΩ deionized water. The centrifuge tubes were placed on a shaker table at 140 revolutions per minute for 75 d. A 5 mL water sample was drawn off of the top of the centrifuge tube immediately after they were initially mixed (day 0) and following days 3, 9, 17, 24, 52 and 74 of mixing. Samples were stored frozen in pre-cleaned high density polyethylene centrifuge tubes until they were analyzed. Major cation and anion concentrations were quantified with a Dionex ICS-3000 ion chromatograph using an AS-19 anion column and a CS-12A cation column, each with a 10 μL injection volume. A gradient method using KOH eluent ranged from 20 μM to 35 μM in concentration for anion analyses while the cation analyses used methane sulfonic acid eluent with a concentration of 25 μM in isocratic mode. The flow rate was 1 mL min⁻¹ and the operating temperature was 30 °C. The ion chromatograph was calibrated using standards with a range of values from 0.5 to 50 mg L⁻¹. Repeat analyses of calibration standards from 0.5 to 50 mg L⁻¹ yielded a calculated precision for the analyses of ±4%. Peaks were identified using Chromeleon (Dionex) and verified visually.

2.3. Explosives concentrations in the batch samples

Explosive analytes were separated from the aqueous samples through solid phase extraction (SPE) following the procedures of Jenkins et al. (1995). Each 500 mL batch sample bottle was eluted through a Waters Sep-Pak Cartridge (Waters, Inc.) at a flow rate of 2 mL min⁻¹. The SPE procedure yields a 5 mL acetonitrile extract and these were stored frozen in 7 mL amber glass vials until analysis by high performance liquid chromatography (HPLC).

Concentrations of RDX, HMX, TNT, 1,3,5-TNB, 1,3-DNB, tetryl, 2,4-DNT, 2,6-DNT, 2ADNT and 4ADNT were determined in aqueous solutions following SW846 Method 8330: Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC; USEPA, 2006). A modular system from Thermo Electron Corporation composed of a Finnigan Spectra-SYSTEM Model P4000 pump and a Finnigan Spectra-SYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 254 nm (cell path 1 cm) was used. Samples were introduced with a 100 μL sample loop. Separations were achieved on a 15 cm × 3.9 mm NovaPak C8 column at 28 °C and eluted with 1.4 mL min⁻¹ of 15:85 isopropanol/water (v v⁻¹). Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference material was 8095 Calibration Mix A at 10 mg mL⁻¹ in acetonitrile of HMX, RDX, TNT, tetryl, 2,4-DNT, 2,6-DNT, 2ADNT, 4ADNT, 1,3-DNB and 1,3,5-TNB. Based on triplicate analyses of the laboratory spike solution the percent relative standard deviation of the explosives compound measurements was less than 2% for the compounds measured.

3. Results and discussion

3.1. Biogeochemical characterization of the surface water samples

The 18.2 MΩ deionized water, as expected, contained no measurable specific conductance, turbidity or organic carbon (Table

Table 1

Location and geochemical information for the water samples investigated in this study.

Water body	Latitude (°north)	Longitude (°west)	Specific conductance ($\mu\text{S cm}^{-1}$)	Turbidity (NTU)	Total organic carbon (mg L^{-1}) ^a	Dissolved organic carbon (mg L^{-1}) ^a
Deionized water	N/A	N/A	0	0	<1.5	<1.5
Chena River	64.835	147.649	130	12.5	3.38	3.23
McDonald Creek	64.702	147.595	292	2.6	4.03	3.21
Bear Creek	64.705	147.604	298	1.2	14.5	11.3
Delta River	63.514	145.858	217	850	<1.5	<1.5
Jarvis Creek	64.023	145.723	322	650	2.53	<1.5

^a Measured by Analytical Resources Incorporated, Tukwila, Washington by EPA Method 415.1.

1). Water from the Chena River, McDonald Creek, and Bear Creek had a range of specific conductance, turbidity, TOC and DOC values that are typical of boreal forest fresh water rivers (Cai et al., 2008). Bear Creek had almost three times the TOC and DOC concentrations measured in the Chena River or McDonald Creek. The two glacial outwash rivers had elevated turbidities and no detectable DOC as would be expected. However, Jarvis Creek had a TOC value of 2.5 mg L^{-1} .

Suspended sediment from the Delta River and Jarvis Creek was classified by the Unified Soil Classification System as poorly graded sand. Major element concentrations of 18.2 M Ω deionized water mixed with the suspended sediment samples from the Delta River and Jarvis Creek are included as Fig. 1. Samples were prepared and analyzed in triplicate and the mean and standard deviation values of each triplicate analysis appear consistent for most samples. These aqueous samples serve as a proxy for the exchange of cations and anions between the newly created mineral surfaces in the glacial sediment and water. The Delta River cation values do not appear to be in equilibrium at the end of the 75 d batch while the anion values appear to settle to consistent values within 17 d. The Jarvis Creek cation and anion values appear to settle to consistent values after 75 d. Results from geochemical analysis of the suspended sediments are included in Table 2.

The sum of cations for Jarvis Creek sediments are roughly twice the value for Delta River sediments. Jarvis Creek sediments also have markedly higher cation exchange capacity, sulfur concentrations and soluble salts (Table 2). Calcium and magnesium are the two most prominent cations to exchange with the 18.2 M Ω deionized water while sulfate and nitrate are the most dominant anions measured. It is likely that bicarbonate (not measured) is the predominant anion in the aqueous phase and the samples should be charge balanced with bicarbonate (Anderson et al., 2000). We did not measure bicarbonate concentrations in these samples but the eight ions we did measure can adequately provide information on ionic exchange between the mineral particles and the 18.2 M Ω deionized water. Jarvis Creek sediments had greater cation exchange capacities and ammonium exchangeable magnesium and calcium concentrations. Jarvis Creek sediments also yielded higher sulfur concentrations and greater soluble salt values. Other investigations of surface water in glacial catchments have shown that they are geochemically reactive over short (days to weeks) timescales (Anderson et al., 2000). The effect of these unweathered mineral surfaces on explosives transformation is addressed in a companion study (Douglas et al., in press).

3.2. Explosives concentrations in the batch samples

In the solid phase extraction procedure the sample flows through resin columns to which explosives compounds are adsorbed and subsequently extracted with acetonitrile. The SPE method preconcentrates the samples by 100 times so we have divided the values measured on the HPLC by 100 for each sample (Jenkins et al., 1995) to correct for this. Fig. 2 includes a summary

of all of the explosive compound analyte concentrations measured over the 84 d exposure time. Most of the explosive analyte concentrations are initially slightly above the $50 \mu\text{g L}^{-1}$ aqueous spike concentration. The concentrations of most of the analytes decrease over time with tetryl, 1,3,5-TNB, and TNT decreasing markedly in

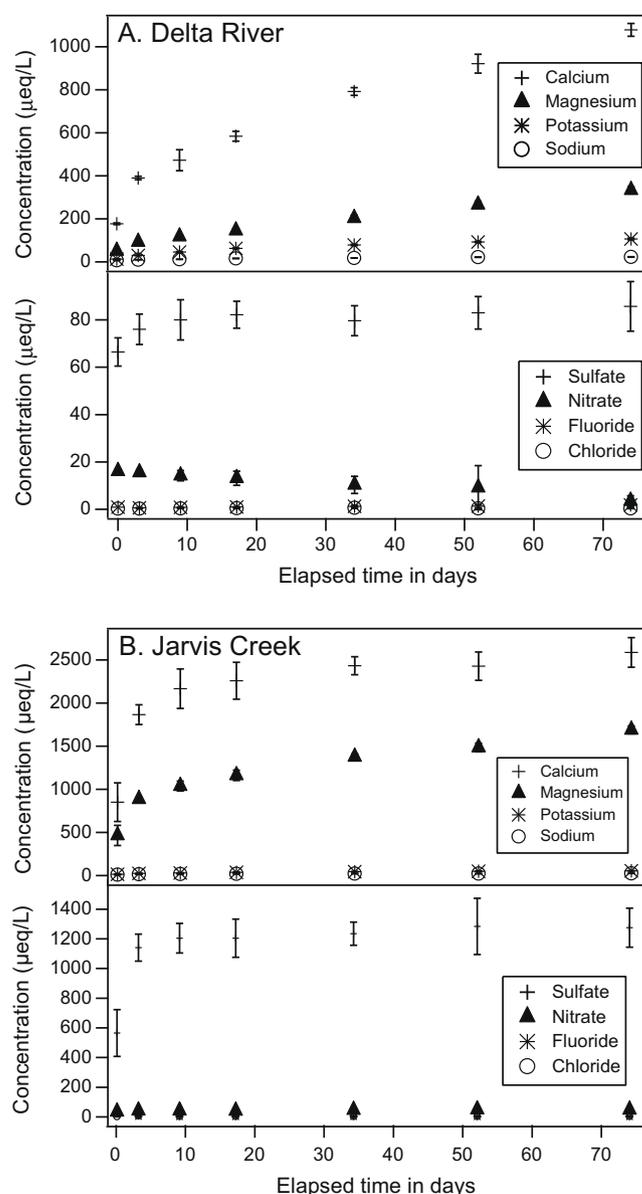


Fig. 1. Major element concentrations measured over time in the two glacial stream sediments. Triplicate batches were created and analyzed independently for each sample. The results presented here include a mean (horizontal line) \pm one standard deviation.

Table 2
Geochemical analysis results for the suspended sediments from the two glacial melt rivers.^a

Water body	Cation exchange capacity (meq/100 g)	% base saturation K	% base saturation Mg	% base saturation Ca	% base saturation Na
Delta River	3.8	1.3	8.6	88.6	1.5
Jarvis Creek	5.3	0.8	13.8	84.7	0.7
	Ammonium acetate exchangeable K (ppm)	Ammonium acetate exchangeable Mg (ppm)	Ammonium acetate exchangeable Ca (ppm)	Ammonium acetate exchangeable Na (ppm)	pH
Delta River	20	39	668	13	8.2
Jarvis Creek	17	88	893	9	7.6
	Sulfur (ppm)	Zinc (ppm)	Manganese (ppm)	Iron (ppm)	Soluble salts (mmhos/cm)
Delta River	73	0.8	4	15	0.2
Jarvis Creek	229	0.8	4	8	0.8

^a Measured by Midwest Laboratories, Omaha, Nebraska.

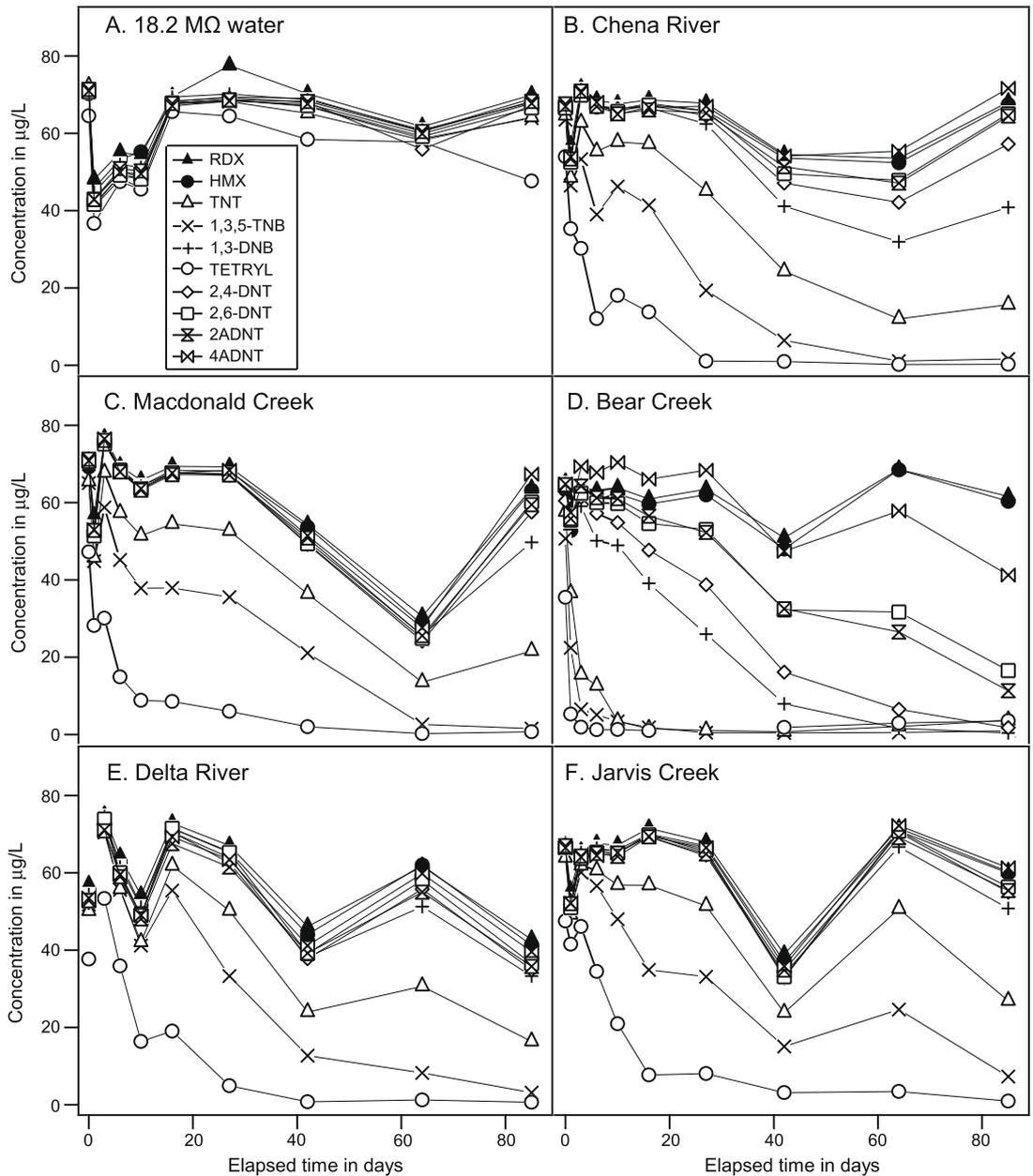


Fig. 2. Explosives compound concentrations from the spiked water samples.

the five river water samples. Explosives compounds exhibit minimal concentration changes for the 18.2 M Ω deionized water sample.

Slightly different flow rates (~20%) for the 10 different solid phase extraction runs likely account for the variations from the long term trends evident in the data. All six 500 mL samples representing each water body were run through the SPE procedure sequentially so variations from day to day are consistent across all samples. Concentrations of RDX and HMX are consistently among the greatest in all six water samples. The RDX:HMX ratio remained at 1 in all six of the batch solutions throughout the 85 d. Many studies have shown that these two nitramines do not readily transform in aqueous soil solutions (Selim et al., 1995; Tucker et al., 2002; Yamamoto et al., 2004; Dontsova et al., 2006) so this result is not surprising. Thus HMX provides a consistent analyte against which the others can be compared over time.

Fig. 3 includes a plot of the same concentration data as Fig. 2 but with the explosive compound analytes for each sample plotted as a ratio to the HMX concentration measured in that identical sample.

Explosives analyte concentrations from the aqueous solutions made from 18.2 M Ω deionized water exhibited minimal transformation during the 85 d batches (Fig. 3). In fact, only tetryl had a concentration that was significantly different than the initial spike concentration after 85 d. Explosives are attenuated through transformation, immobilization or biodegradation (Pennington et al., 2001). Transformation occurs either biotically (McCormick et al., 1981; Kaplan and Kaplan, 1982; Hawari et al., 2000) or abiotically (Brannon et al., 1998; Pennington and Patrick, 1990). The results from the 18.2 M Ω deionized water further imply that explosives transformation is driven only by organic and/or mineralogical compounds in a given water sample. Simply stated,

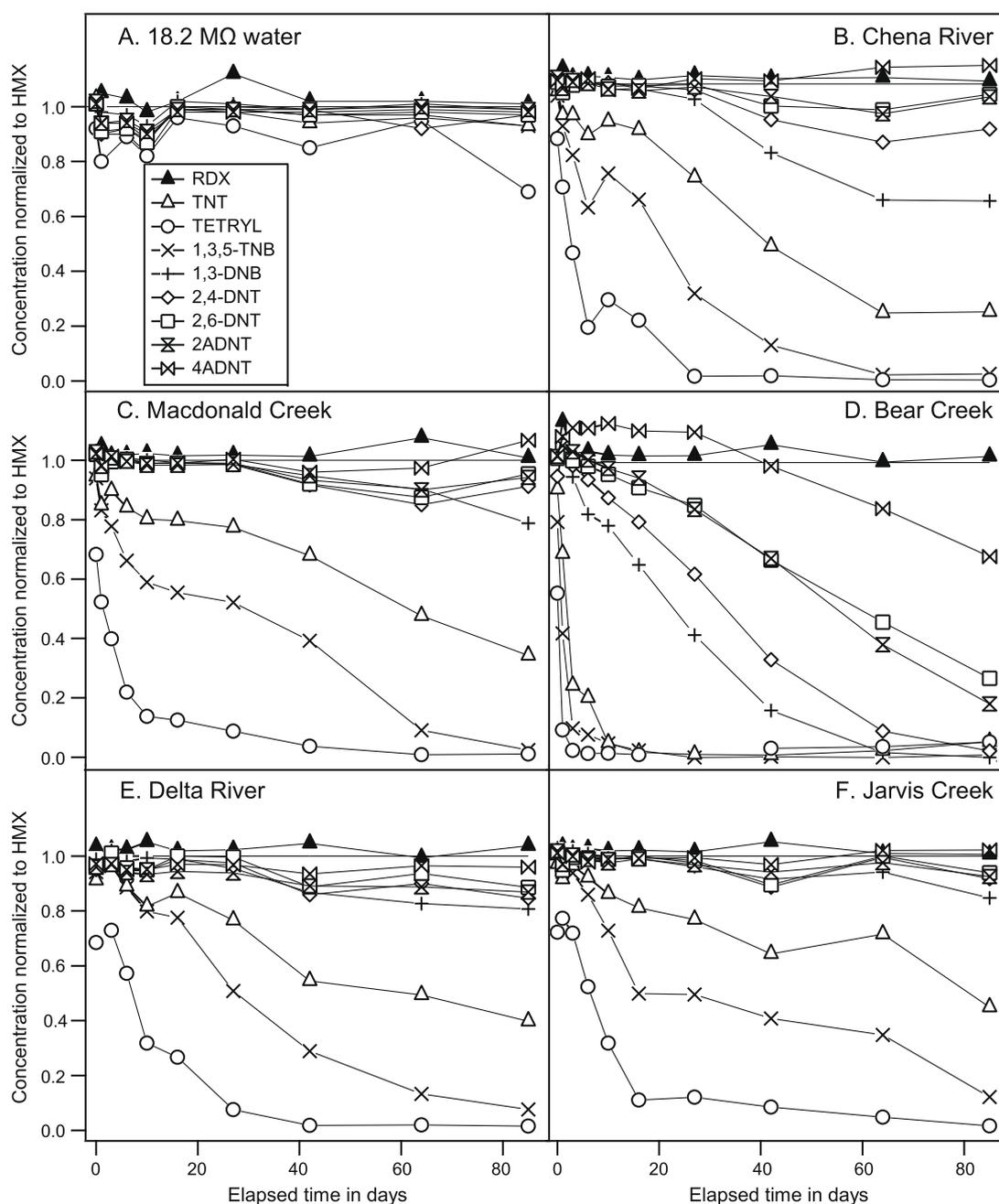


Fig. 3. Explosives compound concentrations from the spiked water samples normalized to the HMX concentration of a given sample.

biogeochemical characteristics control the fate of explosives in water samples. In addition, the results from the 18.2 M Ω deionized water batches suggest that laboratory analytical standards or spike solutions prepared with ultraclean water are stable for at least three months or perhaps longer.

Nitroaromatic (TNT, 1,3,5-TNB, 1,3-DNB, tetryl, 2,4-DNT, 2,6-DNT, 2ADNT and 4ADNT) concentrations varied extensively in the different aqueous samples. In general, the rate of decrease in concentrations compared to HMX in the aqueous samples was as follows: tetryl > 1,3,5-TNB > TNT > 1,3-DNB > 2,4-DNT. The 2,6-DNT, 2ADNT, and 4ADNT concentrations generally remained stable over time in most samples, although 2ADNT and 4ADNT may have formed from TNT transformation in some samples. This is discussed in greater detail below.

The Chena River yields the lowest specific conductance but the highest turbidity of the three clear water surface water samples (Table 1). The most striking difference between these three surface water samples is the far greater total organic carbon and dissolved organic carbon concentrations in Bear Creek. The Bear Creek batch samples exhibited the greatest rate of analyte decreases with tetryl, 1,3,5-TNB and TNT concentrations decreasing to below detection within 10 d of spiking (Fig. 3). It is well established that organic material including soil humic acid (Thorn and Kennedy, 2002), soil organic matter (Tucker et al., 2002; Eriksson et al., 2004; Crocker et al., 2005) and microbes (Hallas and Alexander, 1983; Hawari et al., 2000) promote the transformation of nitroaromatic compounds. The high DOC and TOC concentrations in the Bear Creek water likely represent a high degree of organic activity.

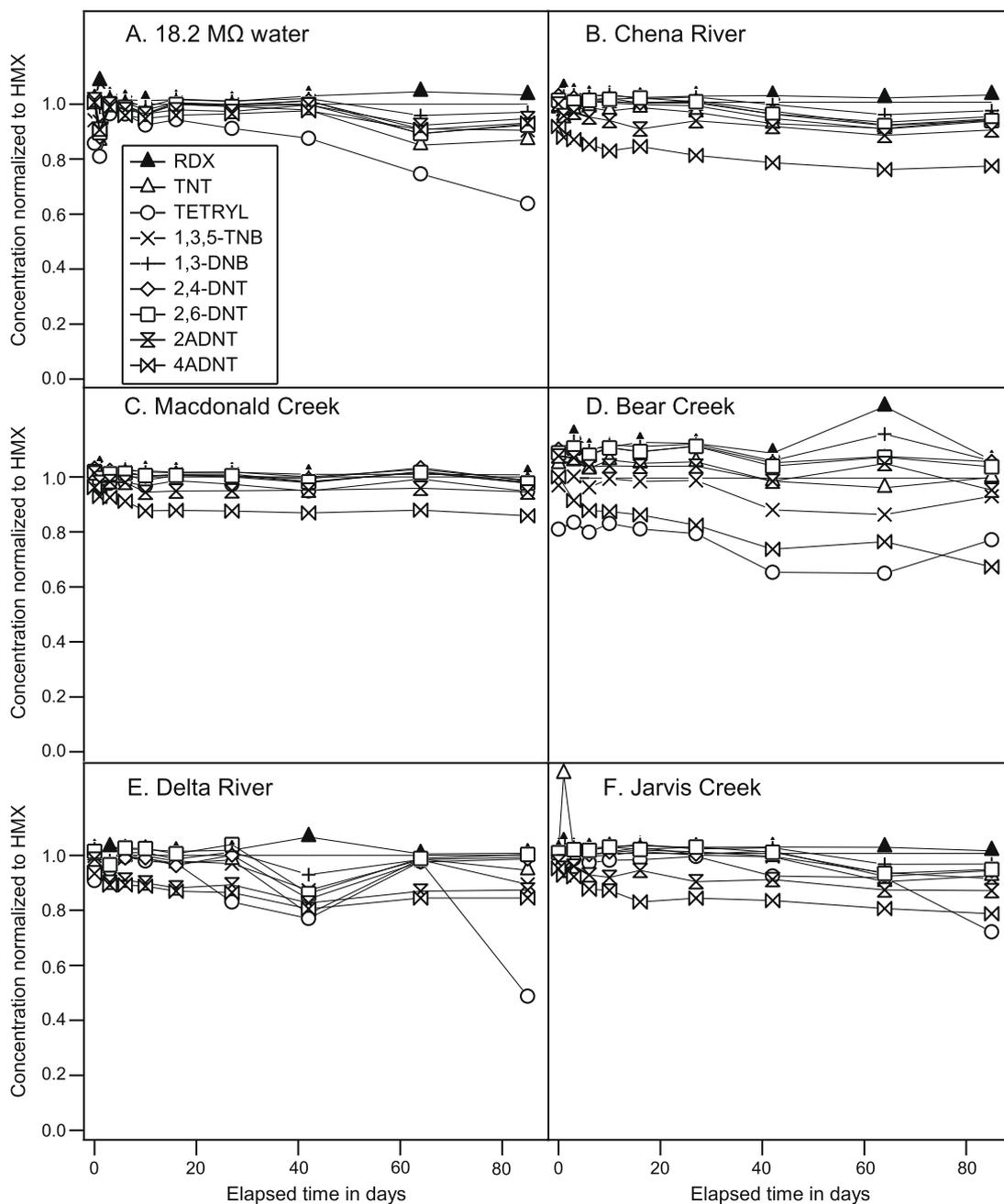


Fig. 4. Explosives compound concentrations from the spiked water samples acidified with sodium bisulfate normalized to the HMX concentration of a given sample. Samples are presented as their concentration compared to the concentration of HMX.

The Bear Creek water samples exhibit dramatic decreases in the TNT concentration within the first 10 d. This is accompanied by elevated 2ADNT and 4ADNT concentrations during the first 27 d followed by a major decrease in the 2ADNT and 4ADNT concentrations. These two monoamines were part of the initial spike solution but they are also formed through reductive transformation of TNT (Thorn and Kennedy, 2002; Jenkins et al., 2006). 2ADNT and 4ADNT undergo transformation to phenolic derivatives (Schmidt and Butte, 1999; Hawari et al., 2000; Leungsakul et al., 2005). It is likely these compounds initially increased above the spike concentration while TNT was being transformed to provide added 2ADNT and 4ADNT in solution. After a few weeks the 2ADNT and 4ADNT subsequently underwent transformation or reacted with organic matter to form an amide. A similar trend was seen in an accompanying study of the interactions between soils and aqueous explosives compounds whereby 2ADNT and 4ADNT concentrations initially increase as TNT is decreases in solution and then after ~30 d the 2ADNT and 4ADNT concentrations decrease as well (Douglas et al., in press). The concentrations of the 2ADNT and 4ADNT transformation products (amides) were not measured in any of our batch solutions so we can only speculate that these species also transformed based on their concentration patterns during the 85 d batch tests.

The two glacial melt surface water samples (the Delta River and Jarvis Creek) exhibited substantial nitroaromatic explosives loss from solution (compared to HMX) over time (Fig. 3). These surface water samples yielded no detectable dissolved organic carbon and only the Jarvis Creek water had detectable total organic carbon. It is thus likely that the fresh mineral surfaces present in this water plays a role in explosives loss from the batch solutions over time. Fresh mineral surfaces (and newly created microparticles of them) are more geochemically reactive than weathered surfaces (Anbeek, 1992). In addition, organic compounds exhibit a greater affinity for fresh reactive surfaces than for weathered ones (Braidia et al., 2002). We cannot say whether the loss of nitroaromatic compounds in these water samples is due to transformation to other organic compounds or to adsorption onto mineral surfaces, or a combination of both. Further, it is possible that the fresh mineral surfaces present in these samples provide a substrate on which biological activity can thrive. Thus, the loss of nitroaromatic compounds from these solutions could be a combination of biologic and geologic processes. Regardless of the mechanism(s) involved it is apparent that surface water with high suspended sediment loads is associated with substantial explosives loss from solution.

It has been previously shown that acidification of surface and ground water samples to a pH of 2 using sodium bisulfate (NaHSO_4) prevents explosives analyte transformation in surface water samples for up to 28 d (Jenkins et al., 1995). However, Jenkins et al. (1995) only investigated one surface water sample and it was for a river draining a watershed in northern New England. We expanded on this work by investigating whether acidification also preserves explosives in water samples collected from boreal forest and glacial melt watersheds.

Overall, acidification does enhance the stability of explosives analytes in our surface water samples (Fig. 4). Tetryl, 4ADNT, and 1,3,5-TNB appear to be the only analytes that consistently exhibit some loss from solution over time. Jenkins et al. (1995) showed some examples of tetryl and 4ADNT loss from aqueous solutions acidified with sodium bisulfate. Jenkins et al. (1995) hypothesize since the losses were evident within the first several days and then ceased the loss mechanism was of finite capacity. They ultimately conclude that colloidal or suspended matter is responsible for the loss of amines from acidified solutions. We do not have adequate information to fully address the potential amine loss. However, we note, like Jenkins et al. (1995) that most of our amine loss is within the first few days (Chena River, Bear Creek and Jarvis Creek samples in Fig. 4). The Jarvis Creek samples exhibit loss and they

are rich in suspended sediment (particles). However, the Delta River water also contains a high suspended sediment load and the samples from the Delta River do not exhibit similarly substantial amine loss. Bear Creek water samples exhibited the greatest amine loss (~30%). Bear Creek water also exhibited the greatest rates of explosives analyte loss from unacidified water samples (Fig. 3). The Bear Creek water samples exhibit the widest range of analytes compared to HMX. We can only speculate that the large organic matter present in the Bear Creek water leads to enhanced explosives recovery for some analytes in acidified samples and/or high rates of loss of other explosives compounds from the unacidified samples. Further work on the relationship between DOC and explosives transformation and acid preservation is warranted.

4. Summary and conclusions

Three important results emerge from this investigation of the stability of explosives compounds in surface water samples. First, it is evident that when a surface water sample is collected for the purpose of quantifying explosives analytes a “transformation clock” starts immediately following collection. For tetryl, 1,3,5-TNB and TNT the concentrations may decrease markedly within a week following collection. The 4ADNT concentrations showed some increases above their initial spiked concentrations in Chena River, McDonald Creek, and Jarvis Creek samples which is likely due to the transformation of TNT to 4ADNT.

Second, acidification with sodium bisulfate appears to be a robust preservation method for explosives samples in five of the six water samples we investigated. There is some evidence for the loss of tetryl, 4ADNT, and 1,3,5-TNB in solution for some acidified water samples but for the majority of explosives compounds acidification allows for longer sample holding times (a few weeks at least). Jenkins et al. (1995) conclude that most explosives analyte concentrations are stable in acidified samples for up to a month. Our results suggest that for many explosives compounds proper acidification may maintain their original concentrations for at least three months and perhaps longer.

The third and most important result from this study is that biogeochemical characteristics of surface water drive the rates of explosives transformation. All explosives compounds were stable for the entire 85 d investigative period in the 18.2 M Ω deionized water which suggests that in the absence of biochemical or geochemical reaction surfaces explosive compounds are stable. The results from the three boreal forest surface water samples suggest total organic carbon may be a proxy for the rate of explosives transformation in water samples that are low in suspended sediment but high in organic carbon.

The effects of humic acid, bacteria and mineralogy on explosives transformation have been the focus of numerous previous aqueous batch studies. We have added to these studies by investigating the fate of explosives compounds in the presence of suspended sediments with little to no organic carbon and in the presence of a range of DOC concentrations. Our explosives analyte batch results, combined with the results of the major element concentrations measured in 18.2 M Ω deionized water exposed to the Delta River and Jarvis Creek suspended sediments, suggest the presence of mineral surfaces (suspended sediment particles) can promote explosives compound transformation in the absence of biochemical species. An accompanying study of the fate of explosives compounds in aqueous batches that contain fractured soils (Douglas et al., in press) further suggests that mineral particle surfaces alone can provide geochemical conditions through which explosive compounds are transformed. Taken in total, the results from our two studies suggest that mineral surfaces can provide either sites for explosives compounds to adsorb or a substrate onto which explosives transforming humic acids or bacteria can grow or both.

Clearly more work needs to be done before a capability can be developed using surface water biogeochemical parameters to predict the stability of explosives compounds in surface water samples following their collection. However, sampling and monitoring campaigns for explosives compounds in surface water must account for explosives transformation processes in their design. At many active and closed ranges where explosives have been used, access to sample collection sites may be limited resulting in barrier to collecting surface water samples. This makes it difficult to collect surface or shallow ground water samples during specific flow regimes. One way to support project goals where timely water collection is required would be to deploy automated sample collectors. Based on our results, it appears that automated sampling campaigns designed to collect surface water samples should integrate sample acidification into their design protocols. The simplest way to achieve this would be to preload sodium bisulfate into the sample bottles prior to installing the collectors and have surface water samples added to the pre-acidified bottles over time.

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