

# A Conceptual Model of Fate and Transport Processes for RDX Deposited to Surface Soils of North American Active Demolition Sites

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## Abstract

The use of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) as an energetic material (EM) in ammunition constituents such as detonators, primers, mines, and rocket boosters and in plastic explosives has led to an international warning on possible soil, surface water, and groundwater contamination on military training sites. In Canada, the demolition sites of range training areas are known to be the second most contaminated sites by EM residues in terms of their concentrations in soil after anti-tank ranges. This research proposes a conceptual model of the presence of RDX at the field scale at demolition sites according to previous soil and water characterization studies. This model illustrates the origin of RDX contamination, the main RDX transport pathways and processes, and the main threatened receptors. This conceptual model is of importance to visualize and understand RDX's environmental fate and behavior and to ultimately enable the production of a detailed quantitative model that can help to manage those RDX-contaminated sites.

## Core Ideas

- RDX is mostly found in the form of aggregates of various sizes and shapes.
- A field-scale conceptual model of the source zone of RDX at Canadian demolition sites.
- We illustrate RDX's complex multiphysical phenomenon and its environmental behavior.

**B**ETTER site management or practices can reduce the accumulation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in the source zone to diminish the impact on soil and water. Testing and training with conventional weapons is necessary for maintaining armed services in combat readiness (Thiboutot et al., 2002). Unfortunately, ensuing from these activities is the energetic material (EM) and heavy metal contamination of military ranges, which is an internationally known problem (Dermont et al., 2008; Lewis et al., 2013). Reliable estimates on the extent of environmental contamination of training ranges by EMs are lacking. Currently, several US and Canadian federal and private agencies, such as the Strategic Environmental Research Development Program (SERDP) and US Army Environmental Command (USAEC), support and conduct research on site characterization to determine the fate and environmental impact of EMs. A selection of the most recent reports and reviews that describe contamination levels, distribution, and fate of explosives in the environment are available (Spain et al., 2000; Pennington and Brannon, 2002; Jenkins et al., 2006; Clausen et al., 2006; Clausen, 2011).

The use of RDX as an explosive first became common during World War II. Its relative stability is only slightly less than that of 2,4,6-trinitrotoluene (TNT), yet its explosive power is much greater. Since World War II, RDX has been used in detonators, primers, mines, rocket boosters, and plastic explosives (Yinon, 1990).

Military demolition sites are mostly used for training purposes to detonate various ammunitions and to destroy different structures; C4 is typically the choice explosive for this purpose. The published composition of C4 is 91% RDX and 9% of plasticizer and binder (Jenkins et al., 2002; Tringe et al., 2007). The contamination on demolition ranges comes mainly from RDX liberated by the detonation of C4 blocks (DLE, 2010; Ampleman, personal communication, 2014). RDX is a cyclic nitramine that is typically found in the soil after munitions have undergone a low-order (partial) detonation, or when unexploded ordnances (UXOs) are blown in place (Hewitt et al., 2007).

In Canada, military demolition sites are the second most contaminated site, after antitank ranges, in terms of EM residues

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**Abbreviations:** EM, energetic material; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; HPLC-UV, high-performance liquid chromatography–ultraviolet;  $K_d$ , partitioning coefficient; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine;  $t_{1/2}$ , half-life; UXO, unexploded ordnance.

and metal concentration within the soil (Ampleman et al., 2000, 2003, 2008, 2009; Ampleman, personal communication, 2014; Marois et al., 2004; Thiboutot et al., 2004, 2007; Diaz et al., 2007; Brochu et al., 2008). Canadian military demolition sites are a few hectares in size, and their designated areas are used periodically by military personnel to detonate multiple explosives. Spatially and temporally heterogeneous concentrations of EMs can be found in the soil (Martel and Lapointe, 2012, 2013; Pichtel, 2012). RDX concentrations in these ranges may reach 90 to 100 mg kg<sup>-1</sup> of soil (Ampleman et al., 2009; Ampleman, personal communication, 2014). RDX is mostly found in the form of aggregates of various sizes and shapes, which control its dissolution (Taylor et al., 2006). Consequently, significant quantities of RDX may remain at the surface of the soil several years after its use (Walsh et al., 2010). Hence, one of the major concerns is still offsite migration of dissolved RDX via percolation from the soil profile to the water table.

Mobilization of contamination is most likely to occur when (i) solid particles on the soil surface migrate with runoff toward surface water bodies, or (ii) when the solid particles come in contact with precipitation, dissolve, and then runoff or infiltrate the soil profile and migrate toward the water table (Bordeleau et al., 2008; Lewis et al., 2013). If RDX reaches the underlying aquifer, it can be carried considerable distances and has the potential to affect drinking water, as was seen at Massachusetts Military Reserve Camp Edwards (Clausen et al., 2004). The presence of RDX in the environment is of concern because it is a xenobiotic chemical known to be toxic to various terrestrial and aquatic organisms (Burton et al., 1994; Sunahara et al., 2009). An appropriate definition and understanding of the hydrogeological context of an active military demolition site is required to assess the risk of contamination of surrounding ecosystem receptors and to promote people's environmental awareness.

From the information available on training activities and from results of surface soil and surface and groundwater analyses, a conceptual model of the source zone of RDX at Canadian military demolition sites is proposed. The objective of this paper is to identify the basic causes of RDX contamination, main processes involved, and diverse RDX manifestation in nature including fate and transportation behavior. The model presented also accounts for the sorption of RDX and its degradation products within the soils via recent research reports on chemical, microbial, and enzymatic transformation pathways. The application of diverse mitigation methods at source zones is then carefully evaluated. Realistic remediation and management strategies are also proposed. This research is significant, as there have been few documented field-scale conceptual models on the presence of RDX within military demolition sites. This conceptual model is important to visualize and understand RDX's complex multiphysical phenomenon and its environmental behavior. Ultimately, this will enable the production of a detailed quantitative model for RDX-contaminated site management.

## Proposed Conceptual Model

Nine of twenty-three Canadian demolition sites were environmentally characterized between 1990 and 2014 by different agencies (Brochu et al., 2008; Lapointe et al., 2012; Ampleman, personal communication, 2014; Martel et al., 2014). From those reports and from the information obtained from the military, a

conceptual model was produced (Fig. 1). It shows details of the demolition site structures, summarizes demolition methods, and illustrates how and where RDX is deposited and found on site. Evidence supporting the development of this conceptual model is elaborated here.

Two types of demolition sites exist (Fig. 1) and will be described using this combined model in terms of dispersion, transportation, and attenuation. The first type of demolition site is essentially an open space with a relatively flat surface of 100 × 100 m where most of the military demolition exercises occur. Eight of the studied sites are configured in this way. At the locations under study, the total organic carbon content in the surface soil is between 0.56 to 3.6% and the clay content is very low, between 0.01 to 0.1%. Drilling logs confirm that the top part of the soil profile is predominantly composed of fine to coarse sand with pebbles. Lack of vegetation is also noticed. The water tables are located between 1 and 9 m below the ground surface. Eight of the nine sites are located along creeks or a lake.

The second type of demolition site is commonly referred to as a "demolition bay." It normally consists of multiple 6-m × 6-m bays, located side by side with each bay separated by a 3-m-high berm made of excavated soil. Each wall has a punched plastic net within the berm, 3 to 5 cm deep, preventing a land slide when detonation occurs. These bays are used by military engineers to instruct the basics of demolition to soldiers. Only one site of this kind is part of this study. The surface soil of each bay contains traces of organic matter (0.2%), and the clay content is also very small (<0.1%). The soil profile is composed of sand and gravel, and the groundwater table is situated 1 m below the ground surface.

## Origin of RDX at Demolition Sites

The RDX concentration found at Canadian demolition sites predominantly comes from C4 detonation (DLE, 2010; Ampleman, personal communication, 2014). A complete block of C4 weighs 567 g, and its dimensions are 28.6 × 5.2 × 2.7 cm. The total volume of the block is 404.3 cm<sup>3</sup> with a density of 1.40 g cm<sup>-3</sup>. The Bachmann process used for the preparation of commercially available RDX introduces 8 to 10% of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in the final product. The commercial composition is therefore 81.9% RDX, 9.1% HMX, and 9% plasticizer and binder. Consequently, some HMX might be found on demolition sites, as Supplemental Table S1 reveals. The detonator used is normally a RP-83 EBW. It contains 80 mg of pentaerythritol tetranitrate (PETN) as the initiator and 1 mg of RDX as a main explosive. Detonations are normally controlled remotely to ensure maximum safety of the personnel. Depending on how the detonator is inserted into the block of C4, or if the blocks are cut into pieces, an incomplete detonation may occur from the unconfined setup, distributing unconsumed RDX on the ground (Thiboutot et al., 2015).

Thiboutot et al. (2011), Jenkins et al. (2006), and Taylor et al. (2004) showed that significant quantities of explosives of heterogeneous nature can be deposited on the surface soil when the maximum detonation pressure and temperature of a munition is not reached and a deflagration occurs. This is also called a low-order detonation (Thiboutot et al., 2011). When such an event happens, solid EM particles are expelled (~100-m<sup>2</sup> to 10,000-m<sup>2</sup> sampled areas) and may vary from very fine dust (0.040 to <200 μm; Taylor et al., 2004) to large chunks of explosives, up

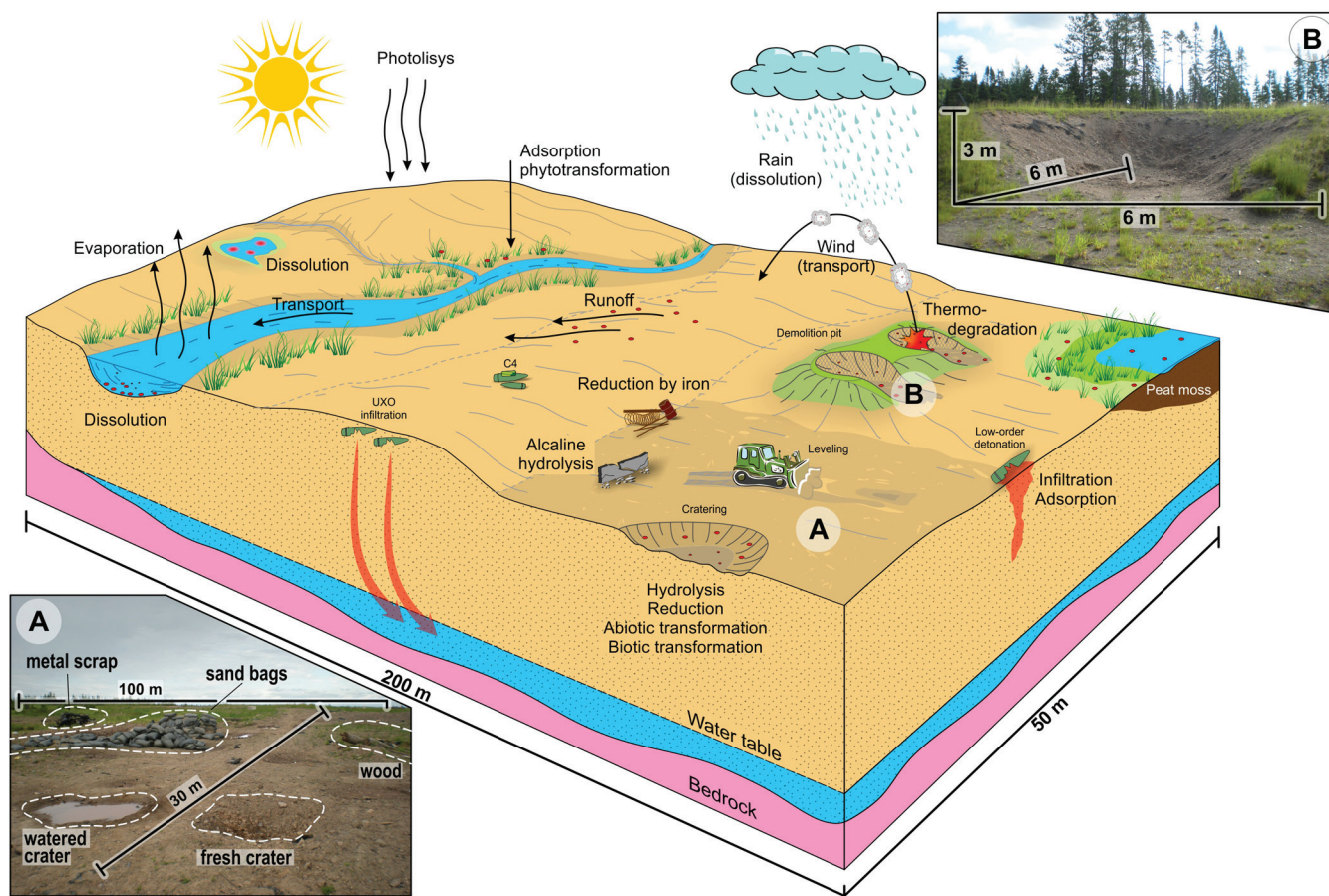


Fig. 1. Conceptual model of a typical military demolition site in North America showing the dispersion and transportation of energetic materials (hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX] in this case): (A) Canadian open demolition site; (B) Canadian demolition bay.

to centimeter size, and the pattern of dispersion on the soil surface is never the same (Jenkins et al., 2006). Malfunctioned ordnance are disposed of by military personnel using blocks of C4 (Pennington et al., 2001, 2002, 2003, 2004, 2005, 2006, 2008a, 2008b). Since the UXO may partially be buried or in a position that does not allow its complete detonation, there is a high probability that it will disperse RDX and other EM within the surrounding area.

Small quantities of explosives are also deposited to the ground when a complete detonation occurs, also known as a high-order detonation (Thiboutot et al., 2011). The quantities are spread over large areas ( $\text{km}^2$ ) and vary from no detectable trace of explosives to micrograms of fine explosive dust, which are more often measured. Moreover, depending on the detonation practices of various ammunitions, different contaminant concentrations are found in the soil, ranging from not detected to  $143,000 \text{ mg EM kg}^{-1} \text{ soil}$  (Supplemental Table S1). As demonstrated in Supplemental Table S1, many studies have reported RDX concentrations in the order of nondetectable to  $678 \text{ mg EM kg}^{-1} \text{ soil}$  in top soil (0–5 cm) after detonation.

Canadian demolition sites are normally cleaned up by the military personnel and checked by Range Control after each demolition exercise. Therefore, few cracked or corroded UXOs are found; however, some do end up buried at various depths and are missed during clean up. Exposure to the elements as well as soil conditions and physicochemical characteristics of soil play a determinant role in the corrosion of UXOs. This can lead to

their perforation over time. If UXO perforation occurs, EM can leach in the environment.

## Materials and Methods

This section details the sampling methods used to collect surface and subsurface soil samples and surface and groundwater samples. Nine Canadian demolition sites were characterized using the following methods.

### Soil Sampling

Composite surface soil samples (top 5 cm) were collected using the multi-increment sampling (MISS) approach (Esbensen, 2004). For small areas of  $6 \times 6 \text{ m}$  such as demolition bays,  $10 \times 10 \text{ m}$ ,  $25 \times 25 \text{ m}$ , or  $50 \times 50 \text{ m}$  ( $36\text{--}2500 \text{ m}^2$ ), composite samples of 50 increments were made. For larger areas of  $100 \times 100 \text{ m}$  ( $10,000 \text{ m}^2$ ), such as open demolition sites, 100 increments were collected. Increments were acquired using a discrete corer (2.5-cm diameter, 5-cm depth) or with stainless steel trowels when the soil was noncohesive. Subsurface soil samples up to 50 cm deep were collected along a massive crater located on one of the sites. Subsurface samples consisted of a combination of 12 increments collected at 0 to 5 cm, 5 to 10 cm, 10 to 15 cm, 15 to 20 cm, 20 to 30 cm, 30 to 40 cm, and 40 to 50 cm deep. In this case, sampling was done with a stainless steel spoon from the bottom to the top of the wall of a handmade trench. Two different craters on two different sites were also sampled. Fifty top soil subsamples collected at 25-cm, 50-cm, 1-m, 2.5-m, and 5-m radius from the center of



the crater with a stainless steel trowel comprised each sample. All equipment used was cleaned with acetone, hydrochloric acid (10% HCl) and distilled water between samples.

The samples from the handmade trench were used for the analysis of RDX in the different grain size fractions. For each of those samples, a mass of ~500 g of soil was collected and dried at room temperature in darkness before being sieved by manual shaking using the following mesh sizes: 4, 2, 1, 0.5, 0.25, 0.125, and 0.063 mm. The metallic sieves were thoroughly cleaned with running water, acetone, and compressed air between each sample. A total 108 samples were collected.

## Surface and Groundwater Sampling

Surface water from creeks and lakes located within 1 km of the demolition sites were sampled. Samples were collected by submerging (top down) a 1-L amber glass bottle into the water and letting water flow inside by turning it up under 10 cm of water to avoid collecting dust particles from the surface of water bodies. Two grams of sodium bisulfate (excess) was then added to each bottle to ensure the stability of EM samples with respect to microbial degradation (Jenkins et al., 1995). Samples were kept in coolers at 4°C until the analysis was completed.

A total of 36 groundwater samples located within 1 km of the demolition sites were taken via a peristaltic or a bladder pump using the low-flow technique as described in the supplemental material.

## Chemical Analyses

### Soil Sample Preparation and Analysis

Soil samples were air dried at room temperature in darkness and sieved through a 10-mesh sieve (<2 mm) and the oversize fraction was discarded. The sub-2-mm fraction was ground in three cycles of 30 s, with a 1-min cooling period between cycles, using a LM2-P mechanical grinder (ESSA). Ground sample was mixed thoroughly, spread to form a 1-cm-thick layer, and a 10-g subsample was then collected in amber glass vials by combining >30 random increments. Soil samples were extracted by adding 20 mL of acetonitrile into the vial, followed by a sonication period of 18 h in an 18°C cooled ultrasonic bath. After sonication, the samples were left to settle for 30 min. Two aliquots were then filtered at 0.45 µm and analyzed for their chemical content as per high-performance liquid chromatography–ultraviolet (HPLC-UV) Method 8330B (USEPA, 2006) and Paquet et al. (2011).

### Water Sample Preparation and Analysis

Water samples (0.5 L) were preconcentrated on Porapak RDX 6CC/500 mg cartridges (Waters). The EMs were then eluted from the cartridge using 5 mL of acetonitrile. A 1-mL sample volume was mixed with 1 mL of ultrapure water. The solution was vortexed, and filtered at 0.45 µm. These samples were then analyzed for their chemical content as per HPLC-UV Method 8330B (USEPA, 2006).

## Results and Discussion

### RDX in Surface and Subsurface Soil Samples

Figure 2 illustrates the range of concentrations of RDX in water and soil that have been found at different locations within the studied Canadian demolition sites. Within the surface soil

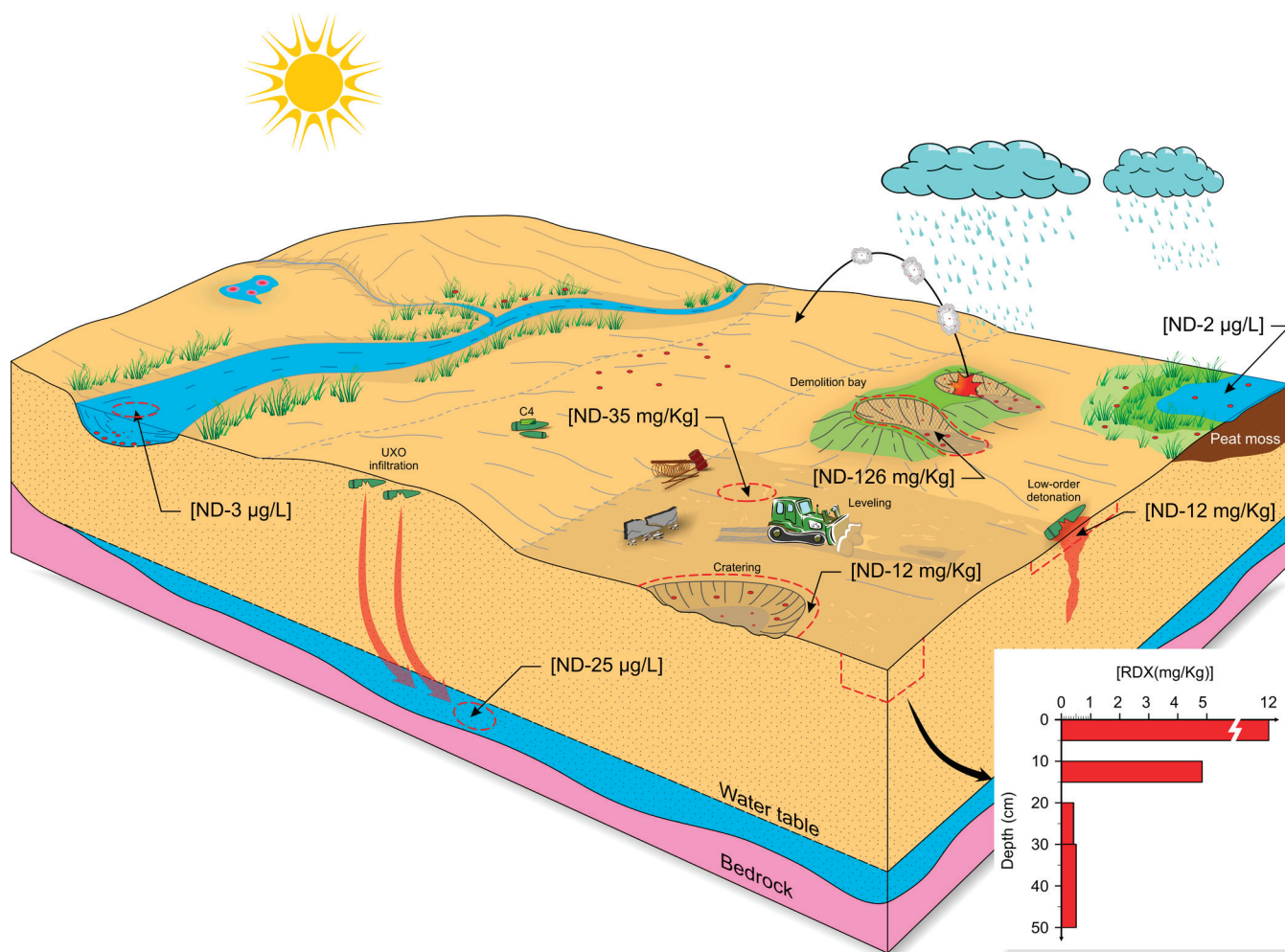
of open demolition sites, fragments of munitions, burn residues, and explosive particles can be found. The concentration of RDX within the soil ranges from not detectable to 35 mg kg<sup>-1</sup> soil. Seventy percent of the samples with concentrations ≥3 mg RDX kg<sup>-1</sup> soil were located beyond 2.5 m from the center of the craters, and 80% were within 5 m, where vegetation was absent and soils were rework from detonations. Findings suggest that craters had only traces of RDX at the center but had increasing RDX concentrations with distances up to a 5-m radius.

Factors such as wind speed and direction, precipitation, evaporation index, and humidity are known to affect dust transportation (Chu et al., 2011). Those factors may contribute to the spreading of EM such as RDX crystals when military detonations are initiated. The present management of Canadian demolition sites does not permit the control of hyperfine dust production after detonation. Consequently, EM particles can travel hundreds of meters far (Lapointe and Martel, 2014) and deposit onto adjacent sites and/or into a water system and be remobilized as particles seeping into the soil profile and/or as dissolved particles. Hence, this phenomenon may explain why concentrations of RDX have been found within the surface soil (Ampleman, personal communication, 2014), in the biomass (Thiboutot et al., 2004), and within water streams (Lapointe et al., 2012) close to demolition ranges.

In a more controlled environment, such as demolition bays, the concentration of RDX is higher with a maximum of 126 mg kg<sup>-1</sup> soil. The fact that demolition bays are surrounded by berms might have helped to confine the unconsumed RDX particles within the bay. The surface soil samples (0–5 cm deep) taken 50 m behind the demolition bays contain undetectable trace of RDX.

The vertical migration of RDX was evaluated from subsurface soil samples collected at an open demolition range. RDX was detected in five of the seven samples, down to a depth of 50 cm below the surface. RDX concentrations in the first 5 cm of soil were >12 mg kg<sup>-1</sup> soil. On average, 85% of the RDX was located within the first 5 cm. The concentrations lowered again between 10 and 15 cm, with 97% of the RDX being located within the 0- to 15-cm depth interval. At depths >20 cm, RDX concentrations did not exceed 1 mg kg<sup>-1</sup> soil, where it plateaued from a depth of 20 to 50 cm. It is therefore clear that RDX did migrate vertically within the soil profile from studied sites.

The grain size distribution of RDX was measured in surface and subsurface soils at one of the studied site. Seven fractions were obtained: <0.063, 0.063 to 0.125, 0.125 to 0.250, 0.250 to 0.500, 0.500 to 1.000, 1.000 to 2.000, and 2.000 to 4.000 mm. Most of the RDX was located within the larger fractions of the surface soil between 0.250 and 4.000 mm. It was noted that as the depth of the samples increases, the proportion of RDX decreases in the coarser fractions of the soil and increases in the finer fractions. This supports the hypothesis that RDX particles may move down the soil profile in a nondissolved form, rather than as dissolved RDX molecules leaching from an energetic formulation left at the soil surface. However, the decrease of RDX concentration in the coarser fraction of the collected soil profiles is not very pronounced, as opposed to the finer fraction, indicating that further investigation is needed to confirm this assumption. Nonetheless, demolition site's soil topography is substantially and consistently reworked by the detonations of a variety of ammunitions over the years, and the presence



**Fig. 2.** Range of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) concentrations observed in water and soil samples collected from studied Canadian military demolition sites.

of solid-form RDX in the soil profile up to a depth of 50 cm is also possible.

Confinement practices, such as the burial of the charges to be detonated and the filling of craters to allow passage by motorized vehicles, may contribute to the variation in concentration of RDX along the soil profile. Moreover, small variation in local soil conditions caused by filling of the craters with other types of soil can potentially have a strong influence on the movement of moisture and, by extension, the transportation of dissolved contaminants such as RDX (Lewis et al., 2013). The hydraulic property of the unsaturated soil can also be perturbed by the maneuvers of heavy-wheeled vehicles which, depending on the soil moisture content at the time of tracking, compact the soils, making them more prone to runoff and erosion (Reyers et al., 2005; Perkins et al., 2007). Burned areas caused by ammunition detonations are also particularly prone to runoff and erosion because of the fire-induced formation of a hydrophobic layer at shallow depths, which prevents or limits water infiltration (Doerr et al., 2000, 2006). Thus, RDX particles may remain buried in the soil for long periods of time from confinement practices and surface reworking.

### Presence of RDX in Surface and Groundwater

Surface and groundwater samples located near demolition sites present undetectable trace amounts of RDX up to  $25 \mu\text{g L}^{-1}$  and resulted in 26 out of 36 of the samples testing above the

USEPA environmental criteria (USEPA 2014). Concentrations found within groundwater samples are higher than those found in surface water samples, with a maximum concentration of  $25 \mu\text{g L}^{-1}$ . Surface water samples contained significantly less RDX, ranging from undetectable to  $3 \mu\text{g L}^{-1}$ . This indicates its presence might originate mainly from dust deposition, runoff, or groundwater discharged into the surface water system (Fig. 2).

### RDX's Behavior in the Environment

RDX's volatility is relatively low (vapor pressure of 133.3 Pa at  $20^\circ\text{C}$ ) so that, when released into the environment, it does not migrate to the atmosphere, except as dust. Thus, the fate of RDX is driven by its dissolution, solubility, and sorption and its degradation pathways. Table 1 emphasizes the degradation processes of RDX that occur at Canadian demolition sites.

### Sorption Processes and Bioavailability

#### Dissolution

Dissolution is the first step in RDX transportation toward the vadose zone. The values for maximum concentration (solubility:  $18\text{--}85 \text{ mg L}^{-1}$ ) and the dissolution rate ( $0.002\text{--}0.100 \mu\text{g cm}^{-2} \text{ s}^{-1}$ ) of RDX vary within the literature (Supplemental Table S2). Studies indicate that whether RDX is contained in C4, Composition B, or an Octol matrix, the dissolution of the

**Table 1. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) fate and behavior processes and their importance in transport models.**

Transport processes	Fate and behavior importance		
	Low	Medium	High
Dissolution			X
Adsorption†	X		
Alkaline hydrolysis‡		X	
Photolysis		X	
Iron or clay minerals reduction	X		
Thermal decomposition	X		
Anaerobic degradation§	X		
Aerobic degradation	X		

† Organic matter content dependent.

‡ pH dependent.

§ Degradation process more important than aerobic degradation.

embedded RDX crystals depends on the solubility of its matrix components. The solubility of the components drives the accessibility of the RDX within the compound (Taylor et al., 2009; Lapointe, 2010). The degree of dissolution depends not only on the solubility of the compound, but also on the antecedent concentrations in water and the pressure and the temperature of the locality. Douglas et al. (2011, 2012) also mentioned that dissolution of explosive residues, and dissolution of undetonated explosive compounds in soils, is largely dependent on soil mineralogical and biogeochemical conditions.

#### Adsorption

Leggett (1985), Ainsworth et al. (1993), Xue et al. (1995), Haderlein et al. (1996), Myers et al. (1998), Sheremata et al. (2001), Tucker et al. (2002), and Yamamoto et al. (2004) describe RDX's adsorption to soil particles as linear isotherms. RDX adsorption coefficients, also termed partitioning coefficient ( $K_d$ ), are generally low between 0.0 and 8.4 L kg<sup>-1</sup> (Brannon and Pennington, 2002), which means that its mobility is nearly influenced when transiting into the soil profile (Selim et al., 1995; Townsend and Myers, 1996). Haderlein et al. (1996) noted that RDX has no particular tendency to adsorb onto clay minerals, although other studies demonstrate that RDX sequestration into soil is controlled by the organic matter and possibly the nature (Xue et al., 1995) and its clay content (Leggett, 1985), where clay is known to be capable of ion exchange. Brannon et al. (1999) evaluated the RDX  $K_d$  from the cationic exchange capacity (CEC) and reported a correlation that is expressed by Eq. [1] below ( $r^2 = 0.734$ ), although the inclusion of organic carbon content ( $f_{oc}$ ), as well as the percentage of clay, does not result in a better correlation (Brannon et al., 1999). Szecsody et al. (2004) observed no dependence of RDX adsorption on organic carbon, iron, or clay content in studied sediments. On the other hand, according to Card and Autenrieth (1998), RDX sorption and desorption are largely dependent on organic carbon content ( $f_{oc}$ ) of the soil. They reported that ~2% of RDX is adsorbed onto soil particles for each 1% of its organic carbon content. Overall, no matter if a correlation between RDX  $K_d$  and the percentage of soil organic or clay content exists, the sorption has a minimal retardation effect on the transportation of RDX within the soil profile:

$$K_{d(RDX)} = 0.056CEC + 0.15 \quad [1]$$

Experimental results from Douglas et al. (2009) suggest that adsorption and/or transformation leads to the lower RDX aqueous concentrations in the presence of fractured soil particles. They state that fractured minerals surfaces could contain reactive sites due to lattice defects, which could reinforce RDX adsorption affinity onto these surfaces. Also, Douglas et al. (2011) mentioned 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. They say that this is likely due to the heterogeneous interactions between explosive residues and soil particle surfaces.

#### Natural Attenuation Pathways

Various abiotic (hydrolytic, photolytic, and reductive) and biotic (anaerobic and aerobic) reactions can be responsible for the attenuation of RDX once it has been released into the environment. Knowledge of the RDX degradation products provides insight into RDX stage of degradation, its causes, and the potential adverse effects of its byproducts in the environment.

#### Abiotic Degradation Pathways

##### Alkaline Hydrolysis

The military often blows up concrete during explosives training. Therefore, the soil on a demolition range can be alkaline (pH 10–13), as concrete generally contains calcium hydroxide as corrosion protection for the reinforcing steel rods. RDX has been reported to degrade under high pH conditions through the process of alkaline hydrolysis (Jones, 1954; Hoffsommer et al., 1977; Croce and Okamoto, 1979; Heilmann et al., 1996; Halasz et al., 2002; Hawari et al., 2002; Balakrishnan et al., 2003; Hwang et al., 2006; Monteil-Rivera et al., 2008). The alkaline hydrolysis of RDX is reported at very high pH conditions (usually pH > 10) and high temperatures (25–80°C), with a documented half-life varying between minutes and days, depending on the control settings. These settings are not representative of the conditions in surface and groundwater found in Canada, where groundwater temperatures are in the order of 5 to 10°C, and pH rarely exceeds 8. The experiment from Bordeleau et al. (2012) on the alkaline hydrolysis of RDX is one of the few conducted at pH and temperatures coinciding with conditions found in Canada.

Supplemental Table S3 details the reported activation energy and Arrhenius parameter calculated from a modified Arrhenius (1889) equation (Eq. [2]) that allows for prediction of the RDX reaction rate at different temperatures. The values detailed were either taken as reported or calculated from published values when the units had to be adjusted for compatibility:

$$\ln(k_2) = (E_a/R)(1000/T) + \ln(A) \quad [2]$$

For Eq. [2],  $k_2$  is the second-order rate constant (L mol<sup>-1</sup> min<sup>-1</sup>),  $E_a$  is the activation energy (kJ mol<sup>-1</sup>),  $R$  is the universal gas constant (8.3135 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the temperature (K), and  $\ln(A)$  is the Arrhenius parameter, or pre-exponential factor, in the same units as  $k_2$ .

Referenced values in Supplemental Table S3 were used to determine RDX half-life ( $t_{1/2}$ ) (Rutherford, 1900), which was



calculated from Eq. [3], where  $t_{1/2}$  has been isolated from a first-order kinetics reaction and  $k$  is the rate constant:

$$t_{1/2} = \ln(2)/k \quad [3]$$

RDX hydrolysis under Canadian conditions is expected to be slow, with a half-life much longer than what is found by the cited authors (Supplemental Table S3). However, when considering the time scale of groundwater movement, hydrolysis could potentially contribute to the overall decrease in RDX in water, especially if concrete is present or if lime or carbonates are added to the soil as a remediation strategy.

#### Photolysis

Important quantities of RDX particles remain on the surface of the soil or are dissolved in surface water and are subject to photodegradation. RDX photolysis has been reported by several studies (Spanggord et al., 1980, 1983; Bedford et al., 1996; Pennington et al., 2007). RDX particles once dissolved can absorb radiation at wavelengths up to ~330 nm and are therefore degraded by ultraviolet B (280–315 nm) and A (315–400 nm) rays present in sunlight. The few reaction rates documented for outdoor photolysis of dissolved or solid RDX were obtained at relatively southern locations (32–37° N) where annual sunlight intensity favors photolysis. In Canada, most demolition ranges are located between 40 and 55° N. As photolysis depends on sunlight spectral intensity, reaction rates vary with latitude, altitude, time of day, day of year, and cloud cover. Temperature does not affect the photodegradation rate. Bordeleau et al. (2012) conducted outdoor experiments at a latitude of 46.9° N (Quebec City, Canada) and determined that RDX degradation lasts between a few hours to a few days ( $t_{1/2} = 0.7$ –2.7 d) when the compound is in solution and for much longer ( $t_{1/2} = 55$ –138 d) when solid RDX particles are in moist or dry sand. Considering that RDX particles can remain at the surface of the soil for several months or years, the calculated half-lives clearly demonstrate that photolysis is a process that must be taken into account in fate and transportation studies. Burying RDX particles with soil may not be a good management strategy, since it cannot be degraded via photolysis.

#### Iron Reduction

It has been reported that RDX can be reduced or degraded by iron or clay minerals (Hundal et al., 1997; Singh et al., 1998; Oh et al., 2002; Gregory et al., 2004; Naja et al., 2008). When RDX reacts with Fe(0), published byproducts include, but are not limited to, nitrite, ammonium, formaldehyde, methylenedinitramine (MEDINA), hexahydro-3,5-dinitro-1-nitroso-1,3,5-triazine (MNX), hexahydro-5-nitro-1,3-dinitroso-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) (Hundal et al., 1997; Singh et al., 1998; Oh et al., 2001, 2002; Naja et al., 2008). Naja et al. (2008) reported that 82  $\mu\text{mol L}^{-1}$  of RDX was completely degraded in 5 min with 3 g  $\text{L}^{-1}$  of Fe(0) nanoparticles. Hundal et al. (1997) reported that 144  $\mu\text{mol L}^{-1}$  of RDX was completely degraded in 96 h with 10 g  $\text{L}^{-1}$  of micro Fe(0). Micro- or nanoparticles of Fe(0) are rarely found in the natural environment, however, suggesting that RDX degradation by Fe(0) would be uncommon unless the site is undergoing remediation strategies. Gregory et al. (2004) observed no RDX

transformation in the presence of magnetite alone at pH 6.0, 6.5, 7.0, 7.5, and 8.0 after a week of exposure. In the absence of magnetite and at pH 6.0 to 7.5, they have noted negligible removal of RDX in the presence of 1.5 mM dissolved Fe(II), whereas at pH 8, 72  $\mu\text{M}$  of RDX was degraded over 10 d. However, works from Cho et al. (2012) have shown RDX degradation in the presence of lepidocrocite (0.1811  $\text{h}^{-1}$ ), magnetite (0.1700  $\text{h}^{-1}$ ), green rust (0.0757  $\text{h}^{-1}$ ), hematite (0.0495  $\text{h}^{-1}$ ), and goethite (0.0394  $\text{h}^{-1}$ ). Despite the fact that RDX degradation from iron or clay minerals processes are known to be dependent on pH and redox potential of the area, its reduction by those media naturally present in the environment is unlikely to happen or be of significance.

#### Thermal Decomposition

Pure RDX melts at 205°C (Hussain and Rees, 1995). The thermal decomposition of RDX particles left on demolition site grounds may therefore be possible, as additional detonations could yield enough exothermic energy to reach 205°C temperatures. Results obtained from different studies suggest that the combustion mechanisms depend on RDX phase and its heating rate (Botcher et Wight, 1994). A pyrolysis study using a  $\text{CO}_2$  laser, which created conditions resembling explosions, resulted in a nitro (N-N) bond being detached from RDX, causing a ring cleavage. Afterward, the other two nitro groups were converted to NO and  $\text{N}_2\text{O}$  before being detached from the ring (Botcher et Wight, 1994; Oxley et al., 1994). Wight and Botcher (1992) also reported that RDX combustion degradation occurs through the scission of its N-N bond.

### Biotic Degradation Pathways

#### Anaerobic Degradation

RDX anaerobic biodegradation has long been considered more efficient than aerobic degradation (Seth-Smith, 2002), and many microorganisms are considered capable of degrading it (Sunahara et al., 2009). Reported RDX degradation rates with *Klebsiella pneumoniae* strain SCZ-1, and *Clostridium* sp. varies between 0.41 and 24  $\mu\text{mol h}^{-1} \text{g}^{-1}$  (dry weight) of cells (Zhao et al., 2002, 2003). RDX transformation into mono-, di-, and tri-nitroso, which implies a nitro reduction causing RDX ring cleavage, happens almost exclusively in anaerobic conditions (McCormick et al., 1981; Coleman et al., 1998; Brannon et Pennington, 2002). This degradation pathway has been also supported by Kitts et al. (1994), where they also identified the nitroso byproducts of RDX with *Providencia rettgeri*, *Citrobacter freundii*, and *Morganella morganii*. The direct ring cleavage of RDX has been updated by Hawari et al. (2000). They identified a ring cleavage product name MEDINA. Both RDX degradation studies from Zhao et al. (2002, 2003) also produced MEDINA, as well as formaldehyde, methanol, nitrous oxide, and carbon dioxide. As MEDINA has been quantified in groundwater samples taken from various US military sites (Paquet et al., 2011), RDX anaerobic biodegradation may therefore be possible on demolition sites, as RDX percolates through the soil profile.

#### Aerobic Degradation

Many studies on RDX biodegradation concluded that its aerobic degradation is rare (McCormick et al., 1981; Townsend et Myers, 1996; Brannon et Myers, 1997) or happens at a very low rate (Ringelberg et al., 2003), although some microorganisms

have been found to be effective (Osmon and Klausmeier, 1972; Binks et al., 1995; Jones et al., 1995; Coleman et al., 1998; Ringelberg et al., 2003; Fournier et al., 2002; Seth-Smith, 2002; Thompson et al., 2005). It is reported that RDX aerobic degradation by *Rhodococcus* sp. strain DN22 proceeds exclusively through denitration (Coleman et al., 1998; Fournier et al., 2002; Seth-Smith, 2002), producing nitrogen dioxide, nitrous oxide, ammonium, formaldehyde, and 4-nitro-2,4-diazabutanal (NDAB). That being said, the relevance of RDX aerobic biodegradation under non-nitrogen-limiting conditions remains controversial (Hawari, 2000; Indest et al., 2013). It is known that RDX aerobic degradation resulted only from controlled laboratory conditions, as opposed to field conditions where other microorganisms and contaminants (heavy metals) can be present (see references in Sunahara et al., 2009). As oxygen concentration normally decreases with soil depth due to soil compaction and the presence of water, chances that this RDX degradation process occurs on demolition sites, where conditions have been proven to be favorable, are considered small.

Overall, dissolved RDX can be progressively degraded through natural attenuation processes as it moves downward in the unsaturated zone. Alkaline hydrolysis and photolysis are the dominant processes that contribute to RDX degradation in a relatively short period of time, as opposed to biodegradation processes, which are slower and require accurate soil physico-chemical parameters to be efficient. Therefore, these two processes should be considered in fate and transport modeling of RDX but need to be measured under site-specific conditions.

## Proposed Technologies for the Remediation of RDX-Contaminated Sites

As the presence of RDX in soil at demolition sites is of concern, better site management and technologies must be developed to reduce long-term environmental impacts generated by military demolition practices. An option is to evaluate an onsite remediation method of the source zone containing solid ammunition residues. The developed technology must be safe, fast, and easy to implement to reduce the disturbance to military training activities.

Removing soil from contaminated sites for incineration, landfilling, or composting is extremely expensive and disrupts the ecology of the site. Amending the soil with microbes able to transform the contaminant into less harmful compounds would be expensive, and the added microorganisms may compete poorly with native bacteria, requiring additional amendments to the soil (van Dillewijn et al., 2007). As for bioaugmentation, phytoremediation may require long periods of time to be effective (Anderson, 2010). Besides, both technologies seem unsuitable in the context of demolition sites, as contamination is too widespread and the local soil conditions are continuously changing from detonations.

Modifying in situ groundwater conditions to favor anaerobic biodegradation of RDX (such as adding an edible vegetable oil to produce a reductive zone in the aquifer below the source zone; Hatzinger and Fuller, 2014) can be an option. Alternatively, an adjustment to range design could be made by burying an engineered reactive barrier in the unsaturated zone or on the groundwater flow path. However, this option does not remediate the soil at the surface, which is the source zone of the contamination.

The introduction of reactive compounds into the soil to chemically transform energetic material through oxidative processes is a suitable approach. Hence, research should be performed on the ability of chemical oxidants to degrade solid RDX present in soil.

## Conclusion

This study was conducted to illustrate impacts of Canadian and North American military demolition exercises on local soil and water, and to promote environmental awareness by indicating the characteristics of the RDX particle formation, fate, and behavior via conceptual models. Understanding the characteristics of RDX deposition and concentration levels at military demolition sites is critical to provide to training range managers, environmental chemists, and remediation professionals as to better design technology and identify potential risk substrates. The environmental fate of RDX is attributed to its molecular structure, water solubility, dissolution rate, affinity for stationary components of the soil matrix, and the production of metabolites through biotic and abiotic routes. The natural attenuation processes of RDX are slow, and thus management of those sites is needed to control potential contamination with RDX or to prevent its offsite migration. Monitoring programs for this type of site are recommended every 2 yr for offsite migration and the load of RDX evaluations. Sampling should be focused in and up to 10 m around demolition craters. Surface and groundwater should also be sampled up to 1 km away from demolition sites. It is also recommended to detonate munitions containing RDX only at a few selected point areas on this type of site to support more active monitoring or remediation strategies. Technologies based on RDX chemical oxidation could here be considered to undergo site remediation.

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