



## Dissolution and transport of 2,4-DNT and 2,6-DNT from M1 propellant in soil

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### ARTICLE INFO

#### Article history:

Received 23 February 2009

Received in revised form 20 May 2009

Accepted 20 May 2009

Available online 2 September 2009

#### Keywords:

2,4-Dinitrotoluene

2,6-Dinitrotoluene

Column studies

HYDRUS-1D

Propellant

### ABSTRACT

Live-fire training exercises can result in particulate propellant contamination on military training ranges and can potentially contaminate ground water. This study was conducted to evaluate dissolution of the 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) from the propellant formulation, M1 (87.6% nitrocellulose, 7.3% 2,4-DNT, 0.57% 2,6-DNT, 1.06% diphenylamine, 3.48% dibutyl phthalate) and their subsequent transport in soil. Batch dissolution studies were followed by saturated column transport experiments. Neat, dissolved 2,4-DNT, and M1 in solid and dissolved forms were used as influent to columns filled with Plymouth loamy sand (mesic, coated Typic Quartzipsamments) from Camp Edwards, MA. Dissolution rates and other fate and transport parameters were determined using the HYDRUS-1D code. M1 dissolution was limited by DNT diffusion from the interior of the pellet, resulting in an exponential decrease in dissolution rate with time. The HYDRUS-1D model accurately described release and transport of 2,4- and 2,6-DNT from M1 propellant. Dissolution rates for M1 in the stirred reactor and column studies were similar, indicating that batch dissolution rates are potentially useful to represent field conditions.

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### 1. Introduction

Live-fire training can result in soils contaminated with propellants. One of the propellant components commonly detected in soil samples collected on military training ranges is 2,4-DNT (Jenkins et al., 2006), an energetic binder in single-based propellants and high explosives formulations (Mirecki et al., 2006). When produced for military applications, 2,4-DNT, a suspected carcinogen (Quigley, 1994), is accompanied by its isomers, particularly, 2,6-DNT. Both 2,4- and 2,6-DNT are listed as US EPA priority pollutants (40 CFR 423).

Brannon and Pennington (2002) reviewed available batch-determined fate and transport parameters for propellants used by the military, including 2,4-DNT. Adsorption coefficients are generally low ( $0.02$ – $0.67 \text{ cm}^3 \text{ g}^{-1}$ ) for low organic matter sediments (Pennington et al., 1999; Hernández et al., 2006), but can be higher

*Abbreviations:* 2,4-DNT, 2,4-dinitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; DPA, diphenylamine; DBPH, dibutyl phthalate; CEC, cation exchange capacity; DNT, dinitrotoluene; HPLC, high performance liquid chromatography;  $k_d$ , adsorption coefficient; MMR, Massachusetts Military Reservation; OC, organic carbon; OM, organic matter; RIA, Rock Island Arsenal.

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for clay soils ( $12.5 \text{ cm}^3 \text{ g}^{-1}$ ) (Pennington et al., 2001), and very high for the phyllosilicate clays ( $690$ – $7400 \text{ cm}^3 \text{ g}^{-1}$ ) (Haderlein et al., 1996). The 2,6-DNT has much lower adsorption coefficients in clays than 2,4-DNT ( $10$ – $125 \text{ cm}^3 \text{ g}^{-1}$ ), with the difference attributed to the steric hindrance of the  $\text{NO}_3$  group in the ortho position. Work on clays (Haderlein et al., 1996) indicated linear adsorption at low concentrations and a decrease in adsorption coefficients as concentrations increase and available adsorption sites are taken. Specific adsorption through electron donor–acceptor complexes with the siloxane surfaces, analogous to other nitroaromatic compounds, was suggested as the mechanism (Haderlein et al., 1996). Low calculated  $K_{OC}$  values ( $1.79$  for both 2,4- and 2,6-DNT) (Rosenblatt et al., 1991) indicate limited hydrophobic partitioning to organic carbon in soils. However, DNT degradation products can form covalent bonds with the natural organic matter in soils resulting in removal of DNTs from solution (Pennington et al., 2003; Thorn et al., 2008).

In addition, some work has been performed to examine behavior of 2,4-DNT and 2,4-DNT-contaminated soils under flow conditions (Yamamoto et al., 2004; Hewitt and Bigl, 2005). Dinitrotoluenes have relatively high aqueous solubilities:  $280 \text{ mg L}^{-1}$  at  $25 \text{ }^\circ\text{C}$  for 2,4-DNT (Kaye, 1980) and  $208 \text{ mg L}^{-1}$  at  $25 \text{ }^\circ\text{C}$  for 2,6-DNT (Rosenblatt et al., 1991). However, in propellant formulations, 2,4-DNT is impregnated into an insoluble nitrocellulose matrix. This

process will likely affect release of propellants into solution. For explosives, binders and waxes present in formulations have been shown to decrease dissolution rates of individual explosive compounds (Lynch et al., 2002; Phelan et al., 2002). A similar trend was observed for dissolution of several propellant formulations in batch studies (Mirecki et al., 2006). In columns, Hewitt and Bigl (2005) measured no 2,4-DNT release from a soil containing particulate M1 propellant residues. The effects of formulation on other fate and transport processes are unknown.

This study focused on M1, one of the single-base, 2,4-DNT containing propellants used by the military. In addition to insoluble nitrocellulose and DNTs, M1 contains diphenylamine (DPA) and dibutyl phthalate (DBPH). Diphenylamine is used as a stabilizer, while DBPH is a plasticizer. These compounds were not evaluated in this study.

The objective of this study was to determine release rates and transport parameters for 2,4- and 2,6-DNT from solid phase M1 propellant under saturated flow conditions. The parameters for solid M1 propellant were compared with those for neat 2,4-DNT; 2,4- and 2,6-DNT in dissolved M1; and with adsorption coefficients reported in the literature.

## 2. Materials and methods

### 2.1. Soils

Plymouth loamy sand (mesic, coated Typic Quartzipsamments) was used for this experiment. Samples were collected at Camp Edwards, MA (Massachusetts Military Reservation [MMR]) to a depth of 20 cm. Soil was air-dried, ground, passed through a 2-mm sieve, and analyzed for cation exchange capacity (CEC) using the NaAc method (US Environmental Protection Agency, 1986) and organic matter using the Walkley-Black method. Particle size was determined by the hydrometer method (Gee and Or, 2002). The soil pH in 1:1 soil/water slurry, exchangeable cations, and base saturation were also measured. The soil had relatively low organic matter ( $8.5 \text{ g kg}^{-1}$ ) and CEC ( $4.4 \text{ cmolc kg}^{-1}$ ), base saturation of 9.7%, and pH of 5.2. Collected samples contained 93.3% sand, 5.8% silt, and 0.8% clay.

### 2.2. Propellants

M1 propellants are produced as dark green, single- or multi-perforated cylinders. Single-perforated cylinders are smaller with one perforation in the middle, while multi-perforated are larger and have seven perforations per cylinder. According to specifications, all M1 formulations contain  $85 \pm 2\%$  nitrocellulose,  $10 \pm 2\%$  DNT,  $5 \pm 1\%$  DBPH, and  $1.0 \pm 0.10$  DPA. They can also contain  $\text{PbCO}_3$  ( $1.0 \pm 0.3\%$ ),  $\text{K}_2\text{SO}_4$  ( $1.0 \pm 0.3\%$ ) and retain some residual solvent (max 0.9%) and moisture ( $0.6 \pm 0.2\%$ ) (Defense Ammunition Center, 2003). Propellant compositions used in this study contained  $\text{K}_2\text{SO}_4$  as a flash reducer.

Two different M1 formulations were obtained from Rock Island Arsenal (RIA): multi-perforated M1 propellant (8 mm in length and 3 mm in diameter) and single perforated M1 propellant (5 mm in length and 1 mm in diameter). Propellants were manufactured by Radford Army Ammunition Plant, Radford, VA, in 2005 and 2006, respectively.

Both formulations of M1 propellant were analyzed for total composition. Propellant cylinders were extracted in acetonitrile. Extracts were analyzed for 2,4- and 2,6-DNT by High Performance Liquid Chromatography (HPLC) (Waters HPLC, GenTech Scientific, Inc., Arcade, NY), Method 8330 (US Environmental Protection Agency, 1994) and for DPA and DBPH by GC/MS, Method 8270C (US Environmental Protection Agency, 1996).

### 2.3. Dissolution in stirred reactors

In stirred reactor batch dissolution studies, 10 g samples of propellant were added to 3.5 L of de-ionized water and stirred for 6 days. The solution was sampled before adding the propellant and at 2, 6, 12, 24, 48, 72, 96, 120, and 144 h of stirring. After 6 days, the 144 h samples were analyzed for 2,4-DNT by HPLC Method 8330 (US Environmental Protection Agency, 1994). Stirring of the small single-perforated propellant resulted in higher concentrations ( $4.69 \pm 0.13 \text{ mg L}^{-1}$ , average of two replications) than stirring of the larger multi-perforated formulation ( $3.01 \pm 0.03 \text{ mg L}^{-1}$ ). Consequently, dissolution kinetics were determined for the single-perforated formulation by analysis for 2,4-DNT, and 2,6-DNT in samples collected over time. Samples collected at 144 h were also analyzed for DPA and DBPH. Solutions obtained from the single-perforated M1 propellant tests were used in column experiments.

### 2.4. Saturated flow experiments

Methods for saturated flow column experiments are described in detail in Dontsova et al. (2006). Briefly, flux-controlled stainless steel flow-through columns (10.16-cm internal diameter by 17.00-cm height) were supplied with solution by a Fisherbrand Ultralow-Flow Peristaltic Pump (Fisher Scientific Houston, TX). Outflow samples were collected continuously into 40-mL vials using an automated Universal fraction collector with 50-vial capacity (Eldex Laboratories, Inc. Napa, California). Soils were packed into columns to an average bulk density of  $1.67 \pm 0.09 \text{ g cm}^{-3}$ .

Columns were saturated from the bottom using 0.005 M  $\text{CaBr}_2$  background solution. Pore volume ( $0.462 \pm 0.046 \text{ L}$ ) and volumetric water content ( $\theta$ ), were determined during saturation from the volume of solution necessary to fill the packed column. Columns were then connected to the pump and operated in downflow mode. The average flow rate was  $1.12 \pm 0.17 \text{ mL min}^{-1}$ , or solution flux of  $0.83 \pm 0.13 \text{ cm h}^{-1}$ . In 2,4-DNT or dissolved M1 experiments, studied solutes in 0.005 M  $\text{CaBr}_2$  background were applied to the column. In solid M1 experiments, M1 cylinders were placed on the soil surface between two layers of glass wool and a 0.005 M  $\text{CaBr}_2$  background solution was applied.

Target concentration of analytical grade 2,4-DNT for the neat 2,4-DNT experiments was  $10 \text{ mg L}^{-1}$ ; measured concentration was  $9.91 \pm 0.68 \text{ mg L}^{-1}$ . In experiments with dissolved M1 propellant, the input concentration of 2,4-DNT was  $4.87 \pm 0.15 \text{ mg L}^{-1}$ , while the 2,6-DNT concentration was  $0.194 \pm 0.005 \text{ mg L}^{-1}$ . M1 solutions also contained  $358 \pm 23 \text{ } \mu\text{g L}^{-1}$  of DPA and  $33 \pm 13 \text{ } \mu\text{g L}^{-1}$  of DBPH.

Uniformly ring-labeled  $^{14}\text{C}$ -2,4-DNT was added as a tracer to the bulk solutions (specific activity  $16.67 \text{ mCi mmol}^{-1}$ ) at 0.037% of total 2,4-DNT in solution. The radiotracer allowed monitoring of 2,4-DNT concentrations in outflow as the experiment progressed. Comparison of breakthrough curves of labeled and unlabeled 2,4-DNT allowed us to distinguish between transformation and mineralization of 2,4-DNT. Tritiated water ( $^3\text{H}_2\text{O}$ ) (specific activity of  $2.18 \text{ mCi mmol}^{-1}$  with  $1.239 \times 10^{-6}\%$  of  $^3\text{H}_2\text{O}$  in solution) was applied with the solutes to determine the longitudinal dispersivity ( $\lambda$ ) for each soil and monitor for signs of preferential flow.

After six pore volumes of propellant solution the flow was switched back to the background solution (or the solid M1 was removed), which was applied for another 14–18 pore volumes. Flow interruption was used to observe kinetic processes (Murali and Aylmore, 1980; Šimunek et al., 2002). For every soil/propellant treatment two experiments were conducted. In one, flow was continuous, while in the other, both inflow and outflow from the

**Table 1**

Total content of 2,6-DNT, 2,4-DNT, DBPH, and DPA in several M1 propellant formulations.

	2,6-DNT (%)	2,4-DNT (%)	DBPH (%)	DPA (%)
RIA <sup>a</sup> multi-perforated	0.48 ± 0.002	8.61 ± 0.045	3.40 ± 0.16	1.25 ± 0.28
RIA single-perforated	0.57 ± 0.028	7.34 ± 0.43	3.48 ± 0.28	1.06 ± 0.06

<sup>a</sup> RIA Rock Island Arsenal.

column were stopped for 24 h to allow propellant constituents to equilibrate with the soil.

Every second outflow sample (approximately every 0.075 L) was analyzed by scintillation counting (Tri-Carb 2500TX Liquid Scintillation Analyzer, PerkinElmer Life and Analytical Sciences, Inc., Boston, MA). Based on <sup>14</sup>C tracer results about 16–18 samples per breakthrough curve were selected for HPLC analysis using standard EPA Method 8330 (US Environmental Protection Agency, 1994). Detection limit was 20 µg L<sup>-1</sup> for both 2,4-DNT and 2,6-DNT.

### 2.5. Numerical analysis

Experiments were analyzed using the HYDRUS-1D code for simulating the one-dimensional movement of water, heat and multiple solutes in variably saturated porous media (Šimunek et al., 2005). The following models were used in analysis: convection–dispersion equation for <sup>3</sup>H<sub>2</sub>O tracer and the two-site sorption model (with decay) (chemical non-equilibrium model) for propellants using approach similar to one applied to dissolution of explosives (Dontsova et al., 2006). The <sup>3</sup>H<sub>2</sub>O breakthrough curves were used to estimate the longitudinal dispersivity, λ (cm). Then, λ was fixed at a value determined for tracer and the following parameters were estimated for propellants: a fraction of sites with instantaneous adsorption, *f*, adsorption coefficient, *k<sub>d</sub>* (cm<sup>3</sup> g<sup>-1</sup>), a first-order rate coefficient for dissolved phase (degradation rate), *μ<sub>w</sub>* (h<sup>-1</sup>), and a first-order rate coefficient for two-site non-equilibrium adsorption, *ω* (h<sup>-1</sup>). In <sup>14</sup>C radiotracer experiments the rate coefficient (*μ<sub>w</sub>*) corresponded to irreversible attenuation and mineralization, while in HPLC experiments it corresponded to the sum of attenuation, mineralization, and transformation.

For experiments with solid M1 propellant formulation, 2,4-DNT and 2,6-DNT dissolution rate, *γ* (µg g<sup>-1</sup> h<sup>-1</sup>) was defined as follows:

$$\gamma = \xi e^{-\chi t} \quad (1)$$

where *ξ* is the initial dissolution rate (µg g<sup>-1</sup> h<sup>-1</sup>), *χ* is decay constant (h<sup>-1</sup>) and *t* is time (T).

**Table 2**

Solute transport parameters obtained by HYDRUS-1D for column saturated flow experiments involving <sup>3</sup>H<sub>2</sub>O, <sup>14</sup>C-2,4-DNT, 2,4-DNT, and dissolved and solid M1 propellant in Plymouth soil (λ was estimated from <sup>3</sup>H<sub>2</sub>O, while *f*, *k<sub>d</sub>*, *μ<sub>w</sub>*, *ω*, *ξ*, and *χ* from propellants).

	<i>f</i>	<i>k<sub>d</sub></i> (cm <sup>3</sup> g <sup>-1</sup> )	<i>μ<sub>w</sub></i> (h <sup>-1</sup> )	<i>ω</i> (h <sup>-1</sup> )	<i>χ</i> (h <sup>-1</sup> )	<i>ξ</i> (µg g <sup>-1</sup> h <sup>-1</sup> )	<i>R</i> <sup>2</sup>
2,4-DNT solution, λ <sup>a</sup> = 0.52 ± 0.27 <sup>b</sup> cm							0.989
<sup>14</sup> C-2,4-DNT	0.48 ± 0.06	0.37 ± 0.02	0.0020 ± 0.0028	0.07 ± 0.03			0.992
2,4-DNT	0.56 ± 0.06	0.28 ± 0.03	0.0031 ± 0.0043	0.10 ± 0.06			0.988
Dissolved M1, λ = 0.75 ± 0.26 cm							0.996
<sup>14</sup> C-2,4-DNT	0.52 ± 0.05	1.11 ± 0.08	0.0129 ± 0.0021	0.06 ± 0.01			0.986
2,4-DNT	0.53 ± 0.03	1.08 ± 0.19	0.0238 ± 0.0067	0.09 ± 0.01			0.971
2,6-DNT	0.74 ± 0.28	0.97 ± 0.18	0.0085 ± 0.0020	0.12 ± 0.01			0.934
Solid M1, λ = 0.70 ± 0.29 cm							0.998
2,4-DNT	0.16 ± 0.05	2.01 ± 0.47	0.0238 <sup>c</sup>	0.06 ± 0.03	0.057 ± 0.023	69.00 ± 4.13	0.984
2,6-DNT	0.31 ± 0.04	0.84 ± 0.02	0.0085 <sup>c</sup>	0.11 ± 0.02	0.043 ± 0.009	1.27 ± 0.00	0.976

<sup>a</sup> λ = longitudinal dispersivity (determined from tracer experiments); *f* = fraction of sites with instantaneous adsorption; *k<sub>d</sub>* = adsorption coefficient; *μ<sub>w</sub>* = first-order rate coefficient for dissolved phase, degradation rate (for <sup>14</sup>C radiotracer experiments indicates irreversible attenuation and mineralization); *ω* = first-order rate coefficient for two-site non-equilibrium adsorption; *ξ* = initial dissolution rate for 2,4-DNT and 2,6-DNT from solid M1; *χ* = dissolution rate decay constant.

<sup>b</sup> (Means ± standard deviation).

<sup>c</sup> Degradation rate determined from dissolved M1 experiments was used.

**Table 3**

Fraction of solutes recovered in outflow in the column transport experiments involving <sup>3</sup>H<sub>2</sub>O, <sup>14</sup>C-2,4-DNT, 2,4-DNT, dissolved and solid M1 propellant in Plymouth soil.

Treatment	<sup>3</sup> H <sub>2</sub> O	<sup>14</sup> C-2,4-DNT	2,4-DNT	2,6-DNT
2,4-DNT	1.11	1.02	1.07	NA <sup>b</sup>
2,4-DNT IF <sup>a</sup>	1.06	0.95	0.92	NA
M1 solution	0.98	0.76	0.69	0.88
M1 solution IF	1.02	0.67	0.43	0.60
M1 solid	0.98	NA	NA	NA
M1 solid IF	1.01	NA	NA	NA
Average	1.03			
Standard deviation	0.05			

<sup>a</sup> IF = interrupted flow.

<sup>b</sup> NA = non-applicable.

Each breakthrough curve was integrated to calculate recovery of the <sup>14</sup>C-2,4-DNT and HPLC-measured 2,4-DNT and 2,6-DNT (Table 3). Recovery of conservative tracer was used to evaluate the accuracy of mass balance estimates of reactive solutes. The goodness of fit between measured and modeled breakthrough concentrations was evaluated using the *R*<sup>2</sup> values and confidence intervals for fitted parameters (Šimunek and Hopmans, 2002). Parameter estimates were considered significant if their confidence intervals did not intersect with zero.

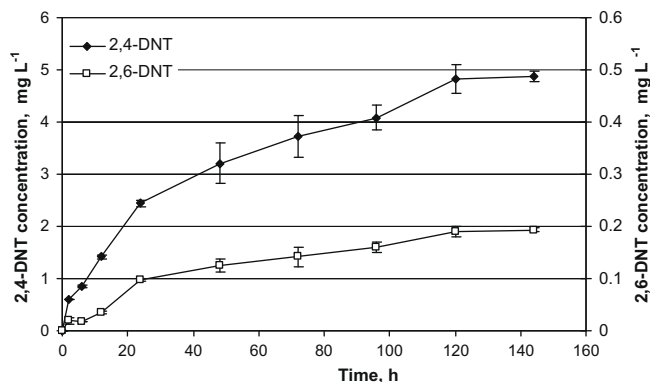
Interrupted and continuous flow experiments were treated as replicates for the purposes of statistical analysis of transport parameters. For comparison between treatments, differences between treatment means were considered significant when greater than the sum of their 95% confidence intervals.

## 3. Results and discussion

### 3.1. Dissolution in stirred reactors

Results of propellant analysis (Table 1) were in close agreement with the specified composition. Dissolution of RIA multi-perforated propellant resulted in lower concentrations of 2,4-DNT after 144 hours of stirring (3.01 ± 0.03 mg L<sup>-1</sup>) than dissolution of RIA single-perforated M1 propellant (4.69 ± 0.13 mg L<sup>-1</sup>). The same trend was observed for 2,6-DNT. Differences were attributed to the smaller size and, therefore, larger surface area per gram of single-perforated particles.

Measured concentrations were well below the solubility of both 2,4-DNT and 2,6-DNT (Fig. 1). Solubility limit at 25 °C is 280 mg L<sup>-1</sup> for 2,4-DNT (Kaye, 1980) and 208 mg L<sup>-1</sup> for 2,6-DNT (Rosenblatt et al., 1991). Mirecki et al. (2006) previously observed that



**Fig. 1.** Dissolution of 2,4-DNT and 2,6-DNT from solid M1 propellant in stirred reactors. Points are average of two replications; error bars equal standard error of the measurement.

propellant constituents from solid propellants (M9, M10, and M30) did not reach their solubility limits in stirred reactors. They concluded that aqueous solubility alone does not control the release of propellant compounds from the nitrocellulose matrix with leaching of soluble components becoming increasingly diffusion-limited as leaching progresses toward completion.

An exponential equation, where initial dissolution rate is equal to  $61.99 \pm 35.57 \mu\text{g g}^{-1} \text{h}^{-1}$ , and the exponential coefficient is  $0.029 \pm 0.017 \text{h}^{-1}$ , can be used to describe the observed decrease in dissolution rate of 2,4-DNT with time ( $R^2 = 0.655 \pm 0.004$ ). Apparently, as constituents were depleted in the propellant exterior, further release required diffusion from the interior of the pellets. The rapid decrease in dissolution rate indicates that for 2,4-DNT the diffusion rate was low relative to dissolution rate.

Total mass transferred from the solid into the liquid phase in 6 days ( $17.05 \pm 0.36 \text{mg}$  2,4-DNT and  $0.677 \pm 0.012 \text{mg}$  2,6-DNT) was small relative to the total mass of these nitroaromatic compounds in the formulations. According to our propellant analysis, 10 g of M1 propellant contained 734 mg 2,4-DNT, 57 mg 2,6-DNT, 106 mg DPA, and 348 mg DBPH.

### 3.2. Conservative tracer

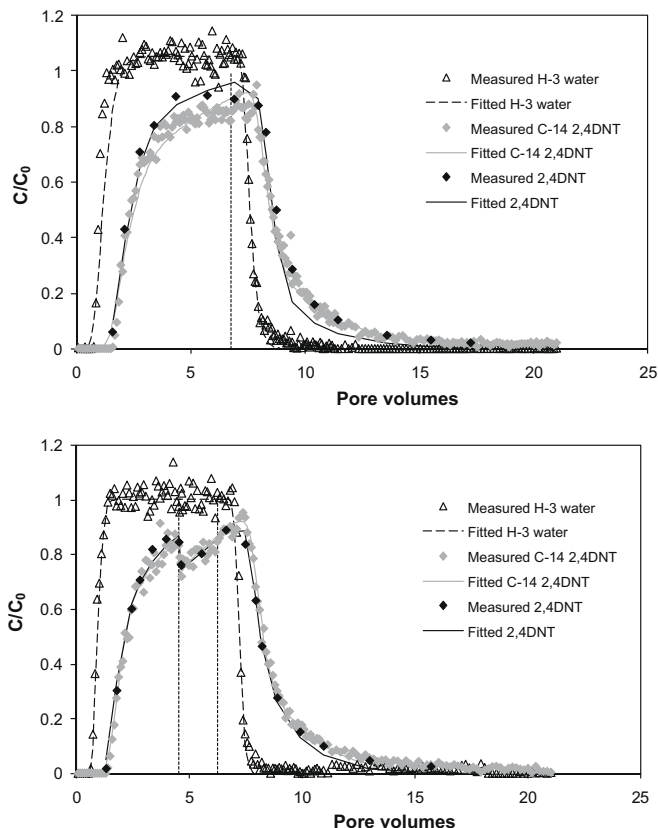
Measured concentrations of the conservative tracer,  $^3\text{H}_2\text{O}$ , are shown on the Figs. 2–4 by hollow triangles and labeled as “measured H-3 water.” Modeled breakthrough curves are shown as dashed lines. Values for longitudinal dispersivity determined from tracer breakthrough curves were between 0.33 and 1.46 cm (Table 2), similar to previously measured values for the same soil (Dontsova et al., 2006).

Breakthrough of the conservative tracer at one pore volume ( $462 \pm 46 \text{mL}$ ) indicated the absence of preferential pathways for flow. Physical equilibrium in the soil columns was also supported by the fact that  $^3\text{H}_2\text{O}$  outflow concentrations resumed at similar values after the flow interruption. All  $^3\text{H}_2\text{O}$  water was recovered ( $103 \pm 5\%$ ) (Table 3) as was expected for the conservative tracer.

### 3.3. 2,4-DNT

Fig. 2 presents measured values and HYDRUS generated fit for the transport of neat 2,4-DNT in Plymouth soil columns with and without interrupted flow. Grey diamonds represent measured values for the  $^{14}\text{C}$ -2,4-DNT radiotracer (Fig. 2), while black diamonds represent HPLC-measured 2,4-DNT concentrations.

For both radiolabeled and unlabeled 2,4-DNT breakthrough was observed later than for the conservative tracer, indicating adsorption to the solid phase. Calculated  $k_{ds}$  were  $0.37 \pm 0.02 \text{cm}^3 \text{g}^{-1}$  and  $0.28 \pm 0.03 \text{cm}^3 \text{g}^{-1}$ , respectively (Table 2). These values are



**Fig. 2.** Breakthrough curves for  $^{14}\text{C}$ -2,4-DNT, 2,4-DNT, and  $^3\text{H}_2\text{O}$  in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments. Dashed vertical lines indicate when flow was interrupted or inflow solution switched to 0.005 M  $\text{CaBr}_2$ .

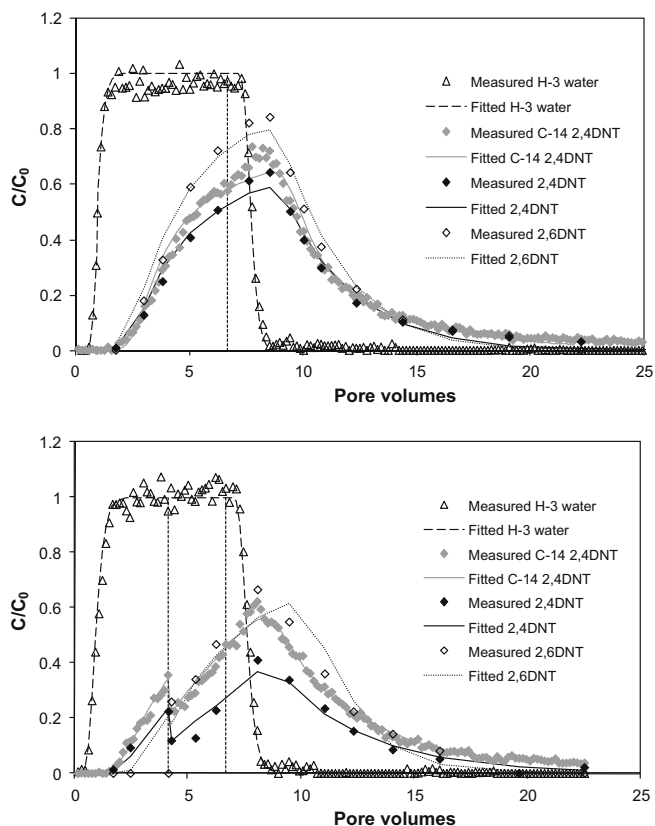
similar to the  $k_{ds}$  for the MMR soil obtained in column experiments ( $0.47 \pm 0.11 \text{cm}^3 \text{g}^{-1}$ ), and lower than measured in batch experiments for the same soil ( $3.3 \pm 0.2 \text{cm}^3 \text{g}^{-1}$ ) (Yamamoto et al., 2004). Batch experiments have previously been shown to over-predict  $k_{ds}$  for compounds that experience irreversible adsorption (Dontsova et al., 2006). The breakthrough curve was asymmetric, a feature that can indicate either kinetic or non-linear adsorption. HYDRUS-1D modeling supported kinetic sorption. About 50% of adsorption sites in Plymouth soil exhibited kinetic adsorption, with the first-order rate coefficient of 0.07 to  $0.10 \text{h}^{-1}$ . Chemical non-equilibrium was also supported by the decrease in concentration following flow interruption, which was observed for both 2,4-DNT and 2,6-DNT.

Degradation rate calculated for the 2,4-DNT was not statistically different from zero (Table 2). This agreed with the mass balance calculations for these experiments (Table 3). Recovery of  $^{14}\text{C}$ -2,4-DNT was  $99 \pm 5\%$ , while recovery of HPLC-measured 2,4-DNT was  $100 \pm 11\%$ . Lower recoveries were observed for the interrupted flow experiments, where more time was available for degradation in agreement with previous studies of explosives (Dontsova et al., 2006).

Low values for degradation rate in the  $^{14}\text{C}$ -2,4-DNT experiments indicate that no irreversible attenuation or mineralization to  $\text{CO}_2$  was occurring, while overlap between breakthrough curves for the  $^{14}\text{C}$ -2,4-DNT and HPLC-measured 2,4-DNT indicated negligible transformation of 2,4-DNT to its products.

### 3.4. Solution phase M1

Greater adsorption and degradation was observed when dissolved M1 was applied to the columns, compared to neat



**Fig. 3.** Breakthrough curves for  $^{14}\text{C}$ -2,4-DNT, 2,4-DNT, 2,6-DNT, and  $^3\text{H}_2\text{O}$  in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments. Dashed vertical lines indicate when flow was interrupted or inflow solution switched to 0.005 M  $\text{CaBr}_2$ .

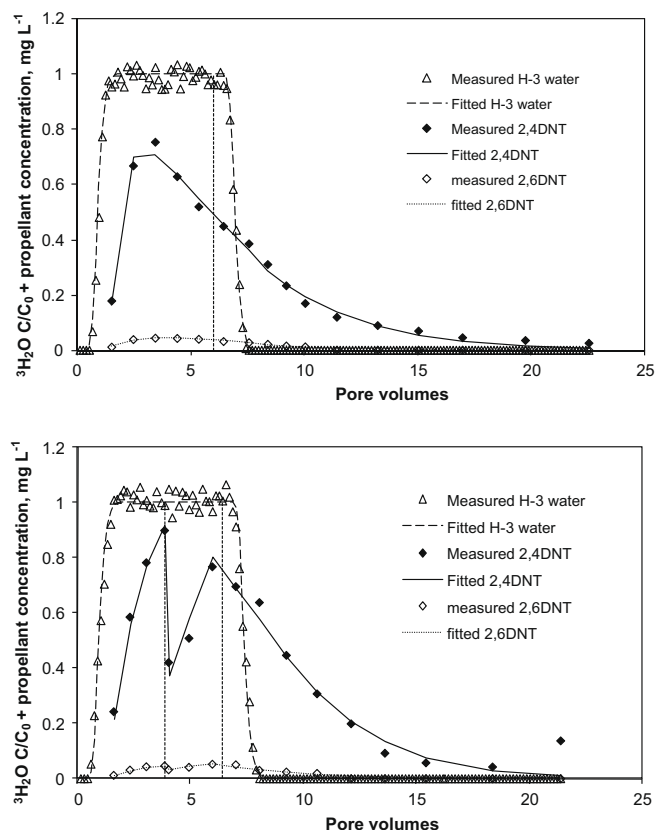
2,4-DNT (Table 2, Fig. 3). Non-linear sorption can explain this phenomenon. During non-linear adsorption, lower inflow concentrations, as in M1 experiments, will result in greater adsorption coefficients. Haderlein et al. (1996) demonstrated non-linear sorption behavior of nitroaromatic compounds. However, non-linear adsorption was not significant when modeled using HYDRUS-1D (parameter B in Freundlich equation was not significantly different from 1).

Incomplete recovery of  $^{14}\text{C}$ -2,4-DNT indicated irreversible attenuation or mineralization to  $\text{CO}_2$ . Both mineralization (Nishino et al., 1999) and reduction to aminonitrotoluenes with subsequent covalent bonding of the products to the soil organic matter (Pennington et al., 2003; Thorn et al., 2008) have been demonstrated. Higher recovery of the tracer than of the HPLC-determined 2,4-DNT (Table 3), indicated transformation of 2,4-DNT to intermediate daughter products. Higher recoveries 2,6-DNT compared to 2,4-DNT agreed with the lower degradation rate (Table 2) that was observed in the solution experiments.

When flow was interrupted, concentrations of DNTs in outflow decreased due to continued degradation and kinetic adsorption, but later recovered to levels similar to ones measured before flow interruption.

### 3.5. Solid M1

Breakthrough curves for DNTs in experiments with solid M1 had a different pattern compared to the dissolved propellant compound breakthroughs (Fig. 4). An initial peak in concentration that decreased with time was observed. This behavior indicated non-constant dissolution rate of DNTs from M1 propellant. A con-



**Fig. 4.** Breakthrough curves for 2,4-DNT, 2,6-DNT from M1 and  $^3\text{H}_2\text{O}$  in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments. Dashed vertical lines indicate when flow was interrupted or M1 removed from the column.

stant dissolution rate model previously used for explosives (Dontsova et al., 2006) did not adequately describe the shape of the breakthrough curves. Therefore, a model that predicted an exponential decrease in dissolution rate of the propellant with time was applied to the data. The difference in dissolution behavior of explosives and M1 propellant can be explained by the presence of the insoluble nitrocellulose matrix that prevents 2,4-DNT from entering solution. Unlike patterns observed for explosives, breakthroughs were similar between the replicates due to the regular size of the particles. A similar trend was observed for other propellants (Dontsova et al., 2008).

Using an exponential decrease in dissolution rate resulted in a very good fit of the breakthrough curves ( $R^2$  between 0.976 and 0.984) (Table 2, Fig. 4). Estimated dissolution rates and transport parameters were also in good agreement for the two replicates. Degradation rate for these experiments could not be estimated, because it would require a defined source term. As we needed to estimate source term, degradation rate values for DNTs in solution for the same soil and run conditions ( $0.0238\text{ h}^{-1}$  for 2,4-DNT and  $0.0085\text{ h}^{-1}$  for 2,6-DNT) were used.

Adsorption coefficients for 2,6-DNT determined from solid M1 were similar to the values obtained for dissolved M1. Simulated  $k_{d,s}$  for 2,4-DNT were higher than for 2,6-DNT. However, due to the fact that estimated fractions of adsorption sites at equilibrium with the solution were lower for 2,4-DNT than for 2,6-DNT, this did not result in significantly higher retardation of 2,4-DNT in the columns.

The total amount of propellant recovered in outflow during column experiments ( $2.957 \pm 0.565\text{ mg}$  of 2,4-DNT and  $0.156 \pm 0.018\text{ mg}$  of 2,6-DNT) was considerably lower than the total available in the pellets ( $734\text{ mg}$  2,4-DNT and  $57\text{ mg}$  2,6-DNT).

Integration of dissolution over time using the HYDRUS-1D simulated equation showed that a smaller amount of 2,4-DNT and 2,6-DNT was dissolved during column experiments ( $11.20 \pm 2.90$  mg of 2,4-DNT and  $0.237 \pm 0.024$  mg of 2,6-DNT) than in stirred reactors ( $17.05 \pm 0.36$  mg of 2,4-DNT and  $0.677 \pm 0.012$  mg of 2,6-DNT). When we took into account duration of dissolution (144 h in batch studies and 44 h in column studies) and extrapolated column dissolution to 144 h, the calculated amount dissolved was still lower ( $12.69 \pm 4.48$  mg of 2,4-DNT and  $0.276 \pm 0.041$  mg of 2,6-DNT), but not significantly different from batch dissolution. Extending time of dissolution did not impact total values to a great extent due to an exponential decrease in dissolution rates with time. Total volume of solution in contact with solid M1 propellant was similar between batch and column experiments.

Simulated dissolution rates were consistent between the replicates with low error and high  $R^2$  (Table 2). The values obtained for 2,4-DNT in columns ( $69.00 \pm 4.13 \mu\text{g g}^{-1} \text{h}^{-1}$  and exponential coefficient of  $0.057 \pm 0.023 \text{h}^{-1}$ ) were not significantly different from the ones obtained in batch studies ( $61.99 \pm 35.57 \mu\text{g g}^{-1} \text{h}^{-1}$  and exponential coefficient of  $0.029 \pm 0.017 \text{h}^{-1}$ ). The values for 2,6-DNT were also similar ( $1.27 \pm 0.00 \mu\text{g g}^{-1} \text{h}^{-1}$  and exponential coefficient of  $0.043 \pm 0.009 \text{h}^{-1}$  in column studies and  $1.07 \pm 0.82 \mu\text{g g}^{-1} \text{h}^{-1}$  and exponential coefficient of  $0.015 \pm 0.014 \text{h}^{-1}$  in batch studies). This supported the accuracy of HYDRUS estimates of dissolution rates of M1 and indicated that batch studies may closely approximate dissolution of propellants in the field.

Dissolution rate was higher for 2,4-DNT than for 2,6-DNT. Previous studies of explosives formulations showed that dissolution rate was affected by the concentration of a component in the formulation (Dontsova et al., 2006). However, in this study, release of 2,4-DNT was preferred to the 2,6-DNT as the ratio between the concentration of 2,4- and 2,6-DNT was 13 in solid propellant, 25 in solution after batch dissolution and 47 in column dissolution. This indicates that 2,6-DNT has slower dissolution kinetics even after we account for its lower concentration in the M1 propellant.

Flow interruption resulted in a similar pattern for neat 2,4-DNT and dissolved M1. A decrease in outflow concentration was followed by an increase to the levels observed before flow interruption indicating continued release of DNTs from propellant particles.

It was speculated that diffusion of 2,4-DNT from propellant matrix limits dissolution of solid propellants. Limitations on dissolution due to matrix effects may explain why 2,4-DNT is detected in soils on military installations, but not in ground water (Clausen et al., 2004).

#### 4. Conclusions

A batch dissolution study evaluated dissolution of DNTs from solid M1 propellant. In addition, a saturated column transport study was conducted to assess dissolution of M1 propellant and transport of its soluble components: 2,4-DNT and 2,6-DNT in soil. Dissolution rates, sorption and transformation coefficients were estimated and contribution of non-equilibrium sorption was established. Dinitrotoluenes showed adsorption and transformation in soil. 2,4-DNT had higher dissolution rate than 2,6-DNT even after its greater content in the propellant was taken into consideration. Dissolution rates of DNTs were similar in batch and column studies, and were consistent between the samples indicating applicability of batch dissolution results to flow and by extension, field, conditions. Both studies showed that dissolution rates of DNTs were decreasing with time. Observed non-constant dissolution rate was consistent with diffusion limitation on the dissolution.

It was concluded that solution phase concentrations of 2,4-DNT were diffusion-limited rather than solubility limited.

#### Acknowledgements

The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the US Army Environmental Quality Technology Basic Research Program by the US Army Engineer Research and Development Center. Permission was granted by the Chief of Engineers to publish this information. Work of Šimunek was supported by the Terrestrial Sciences Program of the Army Research Office (Terrestrial Processes and Landscape Dynamics and Terrestrial System Modeling and Model Integration). The views expressed in this article are those of the authors' and do not reflect the official policy or position of the Department of the Army, Department of Defense, or the US Government. The use of trade, product, or firm names in this paper is for descriptive purposes only and does not imply endorsement by the US Government.

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