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Dissolution, Sorption, and Kinetics Involved in Systems Containing Explosives, Water, and Soil

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Knowledge of explosives sorption and transformation processes is required to ensure that the proper fate and transport of such contaminants is understood at military ranges and ammunition production sites. Bioremediation of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and related nitroaromatic compounds has met with mixed success, which is potentially due to the uncertainty of how energetic compounds are bound to different soil types. This study investigated the dissolution and sorption properties of TNT and RDX explosives associated with six different soil types. Understanding the associations that explosives have with a different soil type assists with the development of conceptual models used for the sequestration process, risk analysis guidelines, and site assessment tools. In three-way systems of crystalline explosives, soil, and water, the maximum explosive solubility was not achieved due to the sorption of the explosive onto the soil particles and observed production of transformation byproducts. Significantly different sorption effects were also observed between sterile (γ -irradiated) and nonsterile (nonirradiated) soils with the introduction of crystalline TNT and RDX into soil–water systems.

Introduction

Soils at munitions plants and military ranges contain varying concentrations of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)-based explosives (1, 2). These soils can serve as long-term contamination sources for the surrounding areas, and at elevated temperatures the RDX solubility will increase (3). TNT and RDX solubility is statistically affected more by changes in temperature than by small changes in pH, ranging from 4.2 to 6.2 (4). An elevated pH (alkaline conditions) can rapidly initiate base-catalyzed hydrolysis and can rapidly transform the energetic material (5). A solubility equation for TNT was derived and can also be applied to RDX solubility, on the basis of the Clapeyron–

Clausius equation assuming that the solubility is a function of time and temperature rather than pH (6). When the pH was kept constant, the solubility concentrations of pure laboratory-grade and field TNT were demonstrated to be statistically equivalent (6). The similarity between pure versus field TNT is important since it reduces the potential variability of dissolution and sorption constants associated with the different grades of TNT used in experiments to determine such field parameters used in fate and transport models.

TNT sorption appears to have a direct relationship with the grain size of the soil (7). In addition, biological activity can also increase the disappearance of TNT (8). Previous RDX sorption experiments were carried out with three different soils; the observed tendency was for the higher-clay-content soil to have larger partition coefficients with adsorption best characterized by the Freundlich isotherm (3). There were no observed effects on RDX sorption based on temperature and minor pH fluctuations (3).

A study investigating the sorption–desorption behavior of RDX indicated that it was not extensively sorbed to the soil, $K_d \approx 0.83 \text{ L kg}^{-1}$, and the sorption was nearly reversible (9). It was determined that there was little difference in the RDX sorption behavior between sterile and nonsterile topsoil (9). The literature suggests that most explosives exhibit near-linear isotherm conditions (10, 11), while linear sorption capacity constants for TNT can range from 0.58 to 12 L kg^{-1} and for RDX have been reported to range from 0.21 to 0.37 L kg^{-1} (9, 11, 12). Sorption properties are dependent on many factors such as the soil particle size and organic carbon (OC) content (7). For instance, peat moss, with a high OC, was introduced to soil, and the peat moss soil retained TNT more readily in column studies than the control (13).

Competitive sorption does occur between TNT and transformation products, where near-linear desorption is observed for some of the transformation products (14). It was reported that soils with monovalent cation clays (K^+ , NH_4^+ , and Na^+) had adsorption constants ranging up to 21 500 L kg^{-1} , whereas clays that contained multivalent cations (Ca^{2+} , Mg^{2+} , and Al^{3+}) had much lower adsorption constants ranging up to 1.7 L kg^{-1} (14). Linear sorption models associated with TNT may not provide an accurate description of the natural environment (14, 15). Following batch soil sorption studies, it was determined that, depending on the soil, TNT sorption characteristics were best represented by the Freundlich or Langmuir isotherm and RDX sorption was best characterized by the Freundlich over linear isotherm (16). There is little to no atmospheric loss of TNT and RDX since they have relatively low Henry's Law constants (HLC), K_H , on the order of 1.10×10^{-8} and 1.96×10^{-11} , respectively; these HLCs fall in the region between semi- and negligible-volatile compounds (10).

Models have been developed to look at the explosives' dissolution, sorption, and kinetics in various systems. A study investigated the fate and transport of RDX and TNT in sandy soils; near-linear sorption isotherms were observed on the basis of a five day study influenced by the amount of organic carbon in the soil (11). In a similar study using surface soil and peat moss amended surface soil, there was a 2 orders of magnitude increase in the sorption capacity of peat moss soil (17). The sorption capacity of soil provides key parameters for detailed model development and a better understanding of the fate and transport of explosives in the environment (18). A two-site sorption model with a decay function to characterize nonequilibrium adsorption–desorption reactions in flux-controlled columns was used to fit experimental data, while producing variable dissolution rates for com-

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TABLE 1. Soil Characteristics

soil characteristic	Vicksburg Loess	Alligator Clay	Ottawa Sand	Telleco Loam	Gessie Loam (Celina Loam)	Crot Sandy Loam
soil location	Vicksburg, MS	Itta Bena, MS	Ottawa, IL	McMullens, TN	Miami County, IN	Willcox, AZ
Unified Soil Classification System (UCS)	clay (CH), brown	clay (CL)	SP	sandy clay (CL), red	sandy clay (CL), gray	sandy clay (CH) grey
percent sand	0.5	2.8	97.6	30.9	36.4	49.1
percent fines ^a	99.5	97.2	2.4	69.1	63.6	50.9
surface area	22.68	28.87	<1.0	31.66	12.76	34.68
pH of 20% slurry	4.97	5.21	6.20	4.28	6.81	9.73
total Ca (mg kg ⁻¹)	1440	2560	<20	416	13300	59500
total Fe (mg kg ⁻¹)	21100	16400	103	51600	17900	13500
total Mg (mg kg ⁻¹)	2090	2850	<25	1050	7920	15000
total Mn (mg kg ⁻¹)	449	462	<0.5	3850	647	255
total K (mg kg ⁻¹)	1140	1560	<100	580	983	4,470
total Cl (mg kg ⁻¹)	33	<31	<30	<32	<31	249
CEC (meq 100 g ⁻¹)	10.8	16.7	0.4	10.5	15.3	13.6
TOC (mg kg ⁻¹)	5320	7,227	14	6033	14296	4746

^a Fines were defined in this study as silts and clays as per ASTM guidelines.

position B (60% RDX, 39% TNT, and 1% wax binder) (19). Dissolution rates were examined in a mixed system with the addition of heat; it was determined that dissolution rates will double with a 10 °C temperature increase (19).

This study investigated the dissolution and sorption of RDX and TNT in several different media configurations. The solubility, dissolution, and sorption properties of TNT and RDX in systems containing six different soils were investigated. Parameters were determined using separate mixtures of sterile (γ -irradiated) and nonsterile soils where the explosives were introduced as soluble and in crystalline form. Typically, γ -irradiation at 15 kGy will eliminate all fungi and actinomycetes, and doses up to 70 kGy will eliminate most algae and bacteria (20). Depending on the γ -irradiation dose, there is cell lysis and the potential release of nutrients (N, P, Mn, and K) into the soil matrix (20); a dose of 50 kGy was selected to effectively sterilize (γ -irradiate) the soils.

Experimental Section

Chemicals. Reagents used conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. High-pressure liquid chromatography (HPLC) grade acetonitrile (CH₃CN; catalog # JT9017-03) and methanol (CH₃OH; catalog # JT9093-33) were obtained from Mallinckrodt Baker, Inc., Phillipsburg, New Jersey. Organic-free reagent-grade water (18 m Ω Milli-Q) was used to prepare the solutions. The HPLC mobile phase [1:1 (v/v) methanol/reagent-grade water] was prepared by volumetrically measuring 500 mL of each and mixing them prior to filtration. The mobile phase was degassed using a vacuum filtration system with 0.22- μ m filters from Millipore. Military-grade RDX was obtained in crystalline form; it was then purified and recrystallized for use in the experiments. TNT crystals were obtained from Kodak, purified, and recrystallized similarly to the process used for RDX. The TNT and RDX particle size used in the experiments was between 20 mesh (1041 μ m) and 40 mesh (470 μ m). All experimental conditions were conducted at an ambient temperature of 21 \pm 1 °C that was maintained in the laboratory. TNT and RDX calibration standards (catalog # NAIM-833A and NAIM-833B) were

obtained from Ultra Scientific, North Kingston, Rhode Island. There are potential hazards associated with the handling of explosive materials so antistatic gloves, mats, and grounding devices were used; nonsparking equipment was used during the separation of the sieved material from the bulk material, and all quantities used in the experiments were less than or equal to 150 mg.

Soils. Six soils from several geographic locations throughout the United States were selected for soil characterization and bench-scale experiments (Table 1): Vicksburg Loess, Alligator Clay, Telleco Clay, Gessie Loam, Ottawa Sand, and Crot Sandy-Loam. These soils ranged from clay to loam, with percent fines ranging from less than 3% to greater than 99%, and they contained a wide range of total organic carbon (TOC). Experiments were conducted using sterile (γ -irradiated) and nonsterile (nonirradiated) samples of the six soils (12 test soils in all). The soils were γ -irradiated with a minimum and maximum delivery dose of 50.1 kGy and 52.7 kGy by Isomedix, Spartanburg, South Carolina, a subsidiary of Steris Corporation. This dose would eliminate the majority of the biological activity present in the soil (20). The following samples were sent for γ -irradiation: 60 1-L jars with 100 g of soil, 60 125-mL bottles with 10 g of soil, 60 40-mL vials with 2.5 g of soil, 60 12-mL vials with 1 g of soil, and 1 16-oz jar of each soil type.

Dissolution Experiments. TNT (150 mg) or RDX (75 mg) crystals were placed in separate amber bottles (in triplicate) with 800 mL of reagent-grade water, where the crystals were allowed to dissolve under static conditions (no shaking or stirring). Aliquots of the resulting solutions were taken: five samples the first 24 h, then one sample every 24 h until day 5, and then one sample on day 7 and every 7 days until day 70. The samples were analyzed for TNT or RDX. The change in concentration over time was used to determine the dissolution constants, K_{dis} , for TNT and RDX.

The 48 h K_d Study. Aliquots (25 mL) of solutions at four concentrations (1, 5, 10, and 25 mg L⁻¹) of TNT or RDX were added to 2.5 g of one of the 12 test soils (sterile and nonsterile samples of the six selected soils; in triplicate). The resulting slurries were allowed to settle for 48 h, and aliquots (5 mL)

were removed. Concentration data of TNT or RDX were used to determine sorption isotherms.

Extended Sorption Study. Solutions (100 mL) that contained 25 mg L⁻¹ of TNT and 5 mg L⁻¹ of RDX were placed in amber bottles, each containing 10 g of one of the 12 test soils (in triplicate). Aliquots of the resulting slurries were periodically removed and analyzed for TNT or RDX following a similar sampling schedule described for the dissolution experiments. The change in explosives concentration was used to determine the sorption constants, K_{sorb} , associated with the six soils and TNT or RDX.

Dissolution and Sorption Experiments. Crystals of TNT (150 mg) and RDX (75 mg) were placed in 800 mL of reagent-grade water that contained 100 g of one of the 12 test soils (in triplicate) to determine the dissolution and sorption rates associated with each system. Aliquots (5 mL) were periodically removed according to the sampling schedule previously described. The change in explosives concentration was used to determine the TNT or RDX dissolution-sorption constant, $K_{\text{dis/sorb}}$, associated with the six soils. In addition, the concentrations of two of the transformation byproducts of TNT, 4-amino-2,6-dinitrotoluene (4A-DNT) and 2-amino-2,6-dinitrotoluene (2A-DNT), were determined.

Explosives Analysis. Slurry samples were filtered using 0.45- μm Millipore Millex FH PTFE filters (catalog # SLFH-025-NK), placed into scintillation vials, covered, and preserved at 4 °C until the analysis was conducted. The samples were analyzed using HPLC following U.S. EPA Method 8330. HPLC columns (25 cm \times 4.6 mm; 5- μm i.d.) were ordered from Sigma-Aldrich, St. Louis, Missouri, with the primary column being a Supelco LC-18 (catalog # 5-8298) reverse-phase HPLC column, and the secondary (confirmatory) column was a Supelco LC-CN (catalog # 5-8231) reverse-phase HPLC column. An eight-level calibration curve for TNT and RDX was obtained by diluting calibration standards. Midlevel calibration verification standards were analyzed at the beginning and end of each HPLC analysis. The samples were also analyzed for the TNT degradation byproducts 4A-DNT and 2A-DNT. Check standards were analyzed after each set of 10 samples. A passing standard calibration curve had a correlation coefficient, r^2 , of >0.999 for each compound. All continuing calibration standards were considered to be passing if they were $\pm 10\%$ where ranges between 90 and 100% were acceptable. Quality assurance and control that was performed had to be within 20% where ranges between 80 and 120% were acceptable. Selected sample concentrations were statistically compared using SigmaStat 3.5 for Windows.

Results and Discussion

Dissolution Experiments. By plotting TNT experimental data reported in the literature (6), the empirical constants $A = 15.68$ and $B = 3283.1$, $r^2 = 0.9792$, were determined (see the Supporting Information) for eq 1, which is based on the phase-transition Clapeyron-Clausius equation. Using eq 1 and assuming that TNT solubility is affected by a dominant temperature dependence at neutral to low pH, the solubility limit, C_{sol} , for TNT at 21 °C was calculated $C_{\text{sol(TNT)}} = 91.75 \text{ mg L}^{-1}$ ($\approx 0.0004 \text{ M}$). Using RDX solubility concentration results reported in the literature (21), the empirical constants $A = 21.26$ and $B = 5140.1$, $r^2 = 0.9996$, were determined (see the Supporting Information) and used to calculate the solubility limit of RDX at 21 °C where $C_{\text{sol(RDX)}} = 44.42 \text{ mg L}^{-1}$ ($\approx 0.0002 \text{ M}$). Most explosives have an aqueous solubility less than 0.002 M (8). Using eq 1, the calculated aqueous solubilities at an ambient temperature of 21 °C is within the reported explosives' solubility range.

$$\ln(C_{\text{sol}}) = A - B/T \quad (1)$$

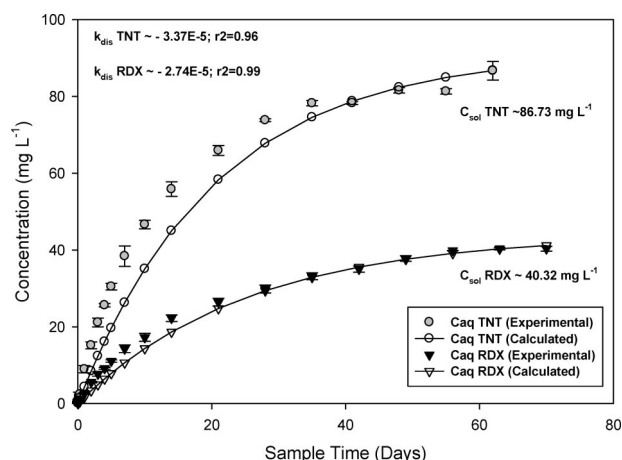


FIGURE 1. Dissolution of crystalline TNT and RDX in water [solid symbol (■) = average ($n = 3$) TNT or RDX experimental values, open symbol with line (—□— = TNT or RDX values calculated using eq 3].

C_{sol} is the solubility concentration (mg L^{-1}), A and B (K) are the empirical constants derived above, and T is the temperature (K).

Dissolution is affected more by the temperature than by small changes in pH (4) except at elevated pH values where alkaline hydrolysis can quickly transform explosives into lower-molecular-weight byproducts (5). As discussed in the literature (4), Fick's Law can be used to determine the concentration of explosives in water; eq 2 is used to describe such dissolution:

$$\frac{dC}{dt} = K_{\text{dis}}(C_{\text{sol}} - C_{\text{aq}}) \quad (2)$$

Here, dC/dt is the change in concentration per unit time, C_{sol} is the solubility concentration (mg L^{-1}), C_{aq} is the aqueous concentration (mg L^{-1}), and K_{dis} is the dissolution constant (min^{-1}).

Similar to the literature (4), eq 2 can be integrated to obtain eq 3, where the TNT and RDX concentrations at a specified time can be determined.

$$C_{\text{aq}} = C_{\text{sol}}(1 - e^{K_{\text{dis}}t}) \quad (3)$$

Dissolution rates are dependent on several factors such as the explosive particle size, the mixing of the solution (19), and the capacity of the solvent to dissolve and retain the explosives in solution (6, 21). In this experiment, the dissolution rates associated with the explosives crystals were determined under static conditions in reagent-grade water. Using the results from the dissolution experiments, the dissolution constants, k_{dis} , for TNT and RDX were determined as $(-3.37 \times 10^{-5} \text{ min}^{-1})$ and $(-2.74 \times 10^{-5} \text{ min}^{-1})$, respectively. Samples were taken over a specified time period and analyzed for their respective explosives concentrations (Figure 1). As seen in Figure 1, using K_{dis} and C_{sol} in eq 3 provides a better fit for the RDX dissolution than for the TNT dissolution. The maximum calculated solubility concentration (C_{sol}) is approached by both methods after 60 days of dissolution, where $C_{\text{sol(TNT)}} = 86.73 \text{ mg L}^{-1}$ and $C_{\text{sol(RDX)}} = 40.32 \text{ mg L}^{-1}$. Knowing the initial and changing explosives particulate surface area could also aid in providing a better fit for the experimental data presented in Figure 1 (19).

The 48 h K_d Study. After analysis and comparison of the linear, Freundlich, and Langmuir isotherms, the Freundlich isotherm (eq 4) provided the best fit for the TNT and RDX experimental sorption data (Table 2) based on the r^2 for the soils studied (see the Supporting Information). As expected, the soils had a higher sorption capacity for TNT than for

TABLE 2. Freundlich Parameters for TNT and RDX with Sterile and Nonsterile Soils

soil	TNT - Freundlich					
	sterile soils			nonsterile soils		
	K_f	n	r^2	K_f	n	r^2
V. Loess	1.051	0.7394	0.9783	1.266	0.8234	0.9029
Alligator	5.197	0.6818	0.9993	5.825	0.6850	0.9442
Telleco	1.910	0.6924	0.9457	2.232	0.7354	0.9542
Gessie	1.583	0.7440	0.9952	3.110	0.7955	0.9159
Crot	2.602	0.7122	0.9990	2.378	0.7735	0.9829
Ottawa Sand	0.014	0.4082	0.9172	0.187	0.9899	0.8726

soil	RDX - Freundlich					
	sterile soils			nonsterile soils		
	K_f	n	r^2	K_f	n	r^2
V. Loess	0.337	0.9560	0.8672	0.700	0.8171	0.9929
Alligator	0.626	0.9061	0.9951	1.978	0.7637	0.9933
Telleco	0.352	0.9015	0.9168	1.330	0.6571	0.9828
Gessie	0.438	0.8727	0.9996	1.282	0.8454	0.9820
Crot	1.010	0.7151	0.9707	1.289	0.7511	0.9900
Ottawa Sand	0.281	0.2984	0.5104	0.701	0.0311	0.0065

RDX for both the sterile and nonsterile soils. Studies have observed slight to no significant change in surface area for soils that had been γ -irradiated (20).

$$q = K_f C_e^n \quad (4)$$

q is the soil concentration (mg kg^{-1}), K_f and n are the Freundlich parameters, C_e is the equilibrium concentration (mg L^{-1}).

Extended Sorption Study. The approach for this study was to use a nonspecific soil type model that could generally be applied to the six different soils. Equation 5, a pseudo first-order sorption equation, was used to determine the soils sorption term, K_{sorb} , from the experimental data.

$$C_{\text{aq}} = C_0 \times e^{-K_{\text{sorb}} t} \quad (5)$$

C_{aq} is the aqueous concentration (mg L^{-1}), C_0 is the initial concentration (mg L^{-1}), K_{sorb} is the sorption capacity constant (min^{-1} ; K_{sorb} for the nonsterile soils), and t is the time (min).

The sorption coefficient values for TNT are typically large, and TNT tends to sorb to soils, as was observed in the 48 h K_d study. TNT exhibits C_{2V} symmetry and has a dipole moment of 1.37 D (10). Equation 5 provides an aqueous concentration representation over time for the TNT-amended sterile and nonsterile soils as well as the RDX-amended nonsterile soils. For the allotted time of the experiments, TNT sorption occurred in most of the irradiated soils except for the Ottawa Sand (Figure 2b). In the case of longer duration experiments, which were not conducted in this study, the sorption-desorption effects and the eventual transformation/degradation byproducts would also have to be determined.

The nonsterile soils had more of a tendency to sorb the TNT from the aqueous phase as seen in Figure 2b for three of the six soils (Alligator Clay, Gessie Loam, and Crot). For example, it took 40 days for the aqueous concentration of TNT to decrease below 5 mg L^{-1} with the sterile Gessie Loam soil, as seen in Figure 2a (bottom line and data set in figure). However, it only required 25 days for the aqueous TNT concentration to decrease to below 5 mg L^{-1} in the nonsterile Gessie Loam soil as seen in Figure 2b (third line and data set from the bottom). The nonsterile soil demonstrated an increased rate of sorption, increased potential transport effect on available soluble explosives, and the potential for TNT degradation due to the nonsterile environment (20). In addition the nonsterile soil sorption experimental data were

better represented by eq 5 (calculated values) than the sterile soil experimental sorption data.

There was a statistically significant difference observed in the aqueous concentration of TNT that remained in the sterile soil system versus the nonsterile soil system except for the Telleco soil (Table 3). There was a statistically significant difference in the concentration of 4A-DNT in four of the soils, with the Telleco and Ottawa Sand showing no significant difference. The Gessie Loam soil was the only soil system that generated a significant difference for the production of 2A-DNT in the nonsterile versus sterile soils.

Similar statistical results were observed for RDX where all of the soil systems expressed statistically significant differences between the final RDX concentrations except for Telleco soil (see the Supporting Information). Since RDX is a nearly symmetrical molecule having a small dipole moment (≈ 0) (10), there is substantially less RDX sorption on the sterile soils (Figure 2c) as was observed during the 48 h K_d studies. There appears to be an initial sorption effect on some of the soils, but over time the observed concentration remains relatively unchanged for the sterile soils and demonstrates a potential cyclical sorption-desorption profile for RDX (Figure 2c).

RDX had less affinity for the sterile soils than did TNT, but the nonsterile soils removed more of the RDX and TNT from the solution than the sterile soils (Figure 2). After about 30 days, there were detectable concentrations of TNT transformation products (4A-DNT and 2A-DNT) in solution for both the sterile and nonsterile soils (Table 3). In general, there was more 4A-DNT present in the solution from the nonsterile soil system than the sterile soil system, while there was no statistically significant difference in the production of 2A-DNT with both soil types. This suggests degradation is also influencing the reduction in the dissolved concentration of TNT in addition to the sorption process.

Dissolution and Sorption Experiments. Using a modified version of eq 3 where the terms were defined to reflect the dissolution-sorption terms, predicted aqueous concentration values were obtained (see the Supporting Information). The experimental data was collected for 33 days, and in this situation, eq 3 does not provide a good representation of the experimental data. This is due to not having an accurate solubility limit since the system did

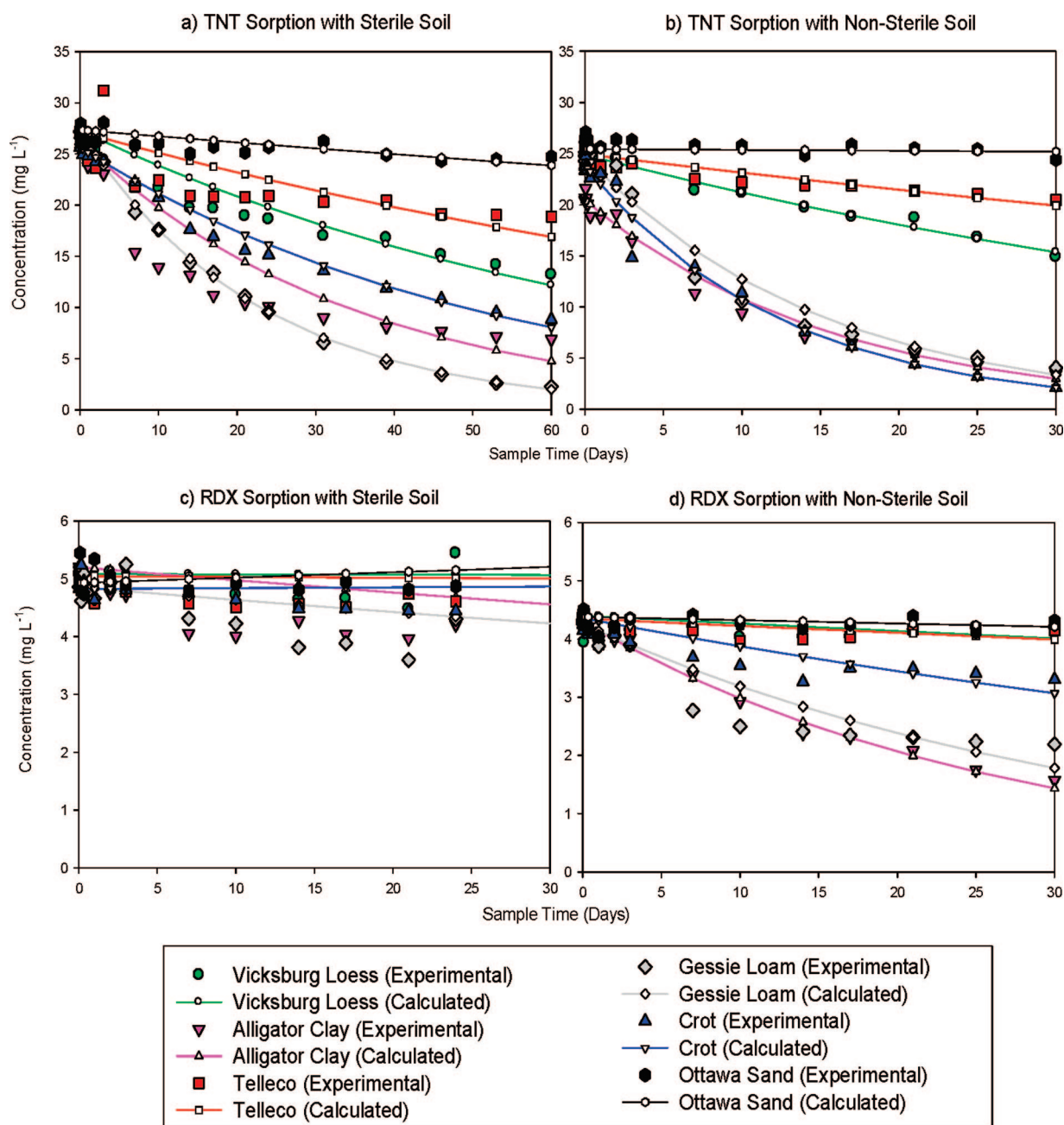


FIGURE 2. Sorption of aqueous TNT and RDX using sterile and nonsterile soils [solid symbol (■) = average concentration ($n = 3$) shown as "experimental", open symbol with line (—□—) = predicted values calculated using eq 5 and shown as "calculated"].

TABLE 3. Average ($n = 3$) Concentration of TNT, 4A-DNT, and 2A-DNT in Solution by Day 30/31 during Sorption Experiments for the Sterile and Nonsterile Soils, Respectively, and the Statistically Significant Difference between the Concentrations

soil	avg. conc. (mg/L)			avg. conc. (mg/L)			avg. conc. (mg/L)		
	TNT sterile soil	TNT nonsterile soil	stat. sig. difference ^a	4ADNT sterile soil	4ADNT Non-sterile soil	stat. sig. difference ^a	2ADNT sterile soil	2ADNT Non-sterile soil	stat. sig. difference ^a
V. Loess	16.98	14.88	yes	0.37	0.51	yes	0.24	0.26	no
Alligator	9.00	3.43	yes	0.85	2.36	yes	0.55	0.57	no
Tellico	20.32	20.44	no	0.20	n.d. ^b	no	0.13	n.d.	no
Gessie	6.57	4.06	yes	0.94	1.67	yes	0.70	0.38	yes
Crot	13.58	2.12	yes	0.49	0.90	yes	0.41	0.46	no
Ottawa	26.23	24.41	yes	0.11	n.d.	no	0.08	n.d.	no

^a Statistically significance difference determined using SigmaStat 3.5. ^b n.d. = non detect.

not approach equilibrium within the time limits of the experiments.

As expected, the solubility of TNT was greatly reduced due to the addition of a soil into the system. Depending on

TABLE 4. Average ($n = 3$) Concentration of TNT, 4A-DNT, and 2A-DNT in Solution by Day 47/48 during the Combined Dissolution and Sorption Experiments for the Nonsterile and Sterile Soils, Respectively, and the Statistically Significant Difference between the Concentrations

soil	avg. conc. (mg/L)		stat. sig. difference ^a	avg. conc. (mg/L)		stat. sig. difference ^a	avg. conc. (mg/L)		stat. sig. difference ^a
	TNT sterile soil	TNT nonsterile soil		4ADNT sterile soil	4ADNT nonsterile soil		2ADNT sterile soil	2ADNT nonsterile soil	
V. Loess	42.91	44.60	no	0.71	n.d. ^b	no	0.60	0.34	yes
Alligator	42.46	28.81	no	0.75	5.97	yes	0.57	5.24	yes
Telleco	71.95	77.47	yes	0.06	n.d.	no	n.d.	n.d.	no
Gessie	26.06	21.73	no	1.13	1.37	no	0.93	0.92	no
Crot	37.41	26.75	yes	0.88	2.48	yes	0.69	0.80	no
Ottawa	81.01	77.83	no	n.d.	n.d.	no	n.d.	n.d.	no

^a Statistically Significance Difference determined using SigmaStat 3.5. ^b n.d. = non detection.

the sorption capacity of the soil, the predicted maximum solubility concentration of the TNT ($C_{\text{sol(TNT)}} = 91.75 \text{ mg L}^{-1}$) was not always approached. For the RDX systems, since RDX has less of a tendency to sorb onto the sterile soils, the majority of these systems approached the solubility limit ($C_{\text{sol(RDX)}} = 44.42 \text{ mg L}^{-1}$).

TNT breakdown products were evaluated for the TNT dissolution-sorption systems and at days 47–48 (Table 4) noticeable levels of 4A-DNT and 2A-DNT were detected in the systems containing the Vicksburg Loess, Gessie Loam, and Crot Sandy Loam soils. Detectable levels of 4A-DNT and 2A-DNT were first observed in the sterile and nonsterile Alligator Clay system at day 10 of sampling (see the Supporting Information). The Telleco Clay (except for 4A-DNT in the sterile soil system) and Ottawa Sand did not have detectable levels of the TNT byproducts in solution. The degradation of TNT is another variable in these systems that can help explain why the calculated solubility limit of TNT at 21 °C of 91.75 mg L^{-1} is not achieved.

For the RDX sorption and dissolution experiments, there was no statistical difference in the aqueous RDX concentration between the sterile and nonsterile soils (see the Supporting Information). For each soil type, the different soils expressed statistically similar RDX concentrations measured at days 33–35 for the nonsterile and sterile soil samples.

Relationship between Soil Properties and Explosives.

There is a general correlation with concentration of TNT and RDX that is removed from solution on the basis of the soil TOC, surface area, and the percent fines (Table 1). A general ranking of the six soils studied by their ability to remove RDX and TNT from solution starting with the least to greatest ability to remove explosives on the basis of observed concentrations of explosives in solution is as follows: Ottawa Sand < Telleco Loam < Vicksburg Loess < Crot Sandy Loam < Alligator Clay < Gessie Loam. Of the six soil types studied, Ottawa Sand sorbed the least amount of RDX and TNT with the smallest values for TOC, surface area, and percent fines. Gessie Loam had a tendency to sorb the most RDX and TNT from solution while having the highest TOC and midrange surface area and percent fines. The four other soils fell into the middle with varying ranges of TOC, surface area, and percent fines.

Monovalent and multivalent cations can affect the sorption of TNT and RDX to the soils (14). For the six soils, a general trend was observed when the concentrations of multi- and monovalent cations increase in the soil, the aqueous explosives concentration decreased. The increased sorption related to the cations present in the soil was not observed at the lower concentrations of RDX, for example, $<5 \text{ mg L}^{-1}$. It has been demonstrated in anoxic environments that the presence of Fe(II) can transform RDX (22), but there was not any observed evidence that by themselves the concentrations

of iron and manganese in the soil affected the sorption capacity of the soil in this study.

Due to many interactions in the soil and water systems, the predicted solubility constants of TNT and RDX were not achieved due to the competing sorption reactions as the crystals dissolved. As expected, the degradation byproducts of TNT during the sorption study with nonsterile and sterile soil systems are statistically different, and in general there are more byproducts produced in the nonsterile soil systems. In contrast, when the crystalline TNT was placed in the water and soil systems, there was generally not a significant difference in TNT and TNT byproducts in solution. Among other soil characteristics, the TOC, surface area, and percent fines predominantly affect the sorption of TNT and RDX.

TNT has a larger equilibrium solubility concentration than RDX, and at the same time, TNT had a greater affinity for sorption to the soils used in these experiments. Our results indicate that RDX-contaminated soil will not retain the RDX within the soil, and this could potentially provide a long-term release of more RDX than TNT from the soils. Understanding the soil types that have an affinity for the different explosives and the solubility of the explosives within these systems can be used to better estimate the potential explosives migration from contaminated soils.

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Supporting Information Available

Sorption parameters, literature review data, TNT byproduct data, and statistical comparisons. This material is provided free of charge via the Internet at <http://pubs.acs.org>.

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