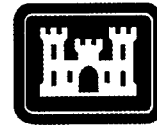


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Environmental Laboratory



US Army Corps
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Engineer Research and
Development Center

Installation Restoration Research Program

Adsorption and Transformation of RDX in Low-Carbon Aquifer Soils

Cynthia B. Price, James M. Brannon, Sally L. Yost, and
Charolett A. Hayes

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Adsorption and Transformation of RDX in Low-Carbon Aquifer Soils

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Final report

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Preface

The studies reported herein were conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS. The research was conducted as part of the Installation Restoration Research Program (IRRP) and the Environmental Quality Basic Research Program. Dr. M. John Cullinane, EL, was the Program Manager. Dr. Clem Meyer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers.

Personnel who cooperated in the execution of the study and preparation of this report included Ms. Cynthia B. Price and Dr. James M. Brannon, Ecosystem Processes and Effects Branch, Environmental Processes and Effects Division (EPED), EL; and Ms. Sally L. Yost and Ms. Charolett A. Hayes, DynTel Corporation, Vicksburg, MS. Technical reviews were provided by Dr. Judith C. Pennington, EPED, and Dr. Patrick Deliman, Water Quality and Contaminant Modeling Branch, EPED.

The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED, and under the general supervision of Dr. Edwin A. Theriot, Acting Director, EL.

At the time of publication of this report, Director of ERDC was Dr. James R. Houston. Commander and Executive Director was COL John W. Morris III, EN.

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1 Introduction

The explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5,-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) have been widely used in manufacturing, loading, assembling, and packaging munitions for many decades in the United States. Disposal processes from these operations resulted in contamination at many active and inactive munitions sites (Pugh 1982, Spaulding and Fulton 1988), leading to migration of these compounds into groundwater (Cattaneo et al. 2000). The rate of movement in an aquifer soil depends on the hydraulic properties of the aquifer and processes such as transformation and adsorption of the explosive. TNT is unstable under a wide range of environmental conditions, undergoing rapid transformation and binding by soil organic matter (Price, Brannon, and Hayes 1997). RDX and HMX may pose the more persistent groundwater problem because their mobility is not limited by sorption, degradation, and immobilization as is TNT and its degradation products (Pennington and Brannon, in press; Price et al. 2001). RDX plumes that are larger than the associated TNT plumes have been observed under sites heavily contaminated with both compounds (Spalding and Fulton 1988).

Results of microbial batch culture studies in wastewater and in media other than soils have shown that RDX is subject to transformation and mineralization under anaerobic conditions (Spanggord et al. 1980; McCormick, Cornell, and Kaplan 1984; Crawford 1995). Transformation of RDX to mono, di, and trinitroso derivatives under anaerobic conditions has been reported (Sikka et al. 1980; Spanggord et al. 1980; McCormick, Cornell, and Kaplan 1984; Crawford 1995). Resistance to aerobic degradation has also been reported (Spanggord et al. 1980; McCormick, Cornell, and Kaplan 1984). Studies conducted with soils have shown that transformation rather than sorption is a more important mechanism for removal of RDX, but the processes affecting transformation are not well understood (Myers et al. 1998). Surface soils have been shown to rapidly transform and sorb TNT and its transformation products under a wide range of redox potential (Eh) and pH conditions (Price, Brannon, and Hayes 1997; Price et al. 2001). Studies conducted with surface soils (typically comprised of 1 to 3 percent organic carbon) revealed that RDX was relatively stable in soil-water slurries under all but highly anaerobic conditions (Price et al. 2001). Results of adsorption tests in low-carbon aquifer soils indicate that sorption and transformation of explosives are significantly lower than in surface soils (Pennington and Patrick 1990; Pennington et al. 1999).

Surface soils have been shown to rapidly adsorb and transform TNT under a wide range of Eh and pH conditions (Price, Brannon, and Hayes 1997; Pennington and Brannon, In Press). Specific adsorption to clay minerals can also be a significant process for nitroaromatics in which the magnitude of sorption is affected by the specific cation sorbed (Haderlein and Schwarzenbach 1993; Haderlein, Weissmahr, and Schwarzenbach 1996; Weissmahr, Haderlein, and Schwarzenbach 1998; Weissmahr et al. 1999). Saturation of clay exchange sites with NH_4^+ , K^+ , Cs^+ , and Rb^+ increases the adsorption of nitroaromatics (Haderlein and Schwarzenbach 1993) and explosives (Haderlein, Weissmahr, and Schwarzenbach 1996), while saturation with Ca^{++} decreases adsorption (Haderlein, Weissmahr, and Schwarzenbach 1996). Although most of the work has been conducted with clay minerals, the potential for electrolyte injections in the field to control the mobility of 4-nitrotoluene has been demonstrated (Weissmahr et al. 1999).

Although nitroaromatics can undergo natural attenuation in aquifer soils, the processes governing the transformation of explosives in these soils are not well understood. Therefore, investigations are needed to understand the effects of physicochemical conditions on the sorption and transformation of RDX in soil/water slurry systems. Adsorption tests conducted with unmodified aquifer soils indicate that sorption and transformation of explosives are minimal in low carbon compared with surface soils (Pennington and Patrick 1990; Pennington et al. 1999). Understanding the effects of groundwater quality on the sorption of explosives is necessary to understand the mechanisms of natural attenuation in aquifer soils. The objective of the investigations described in this report was to determine the effects of Eh and pH on RDX sorption and transformation in a low-carbon aquifer soil. Studies addressing the various degrees of cation substitution on adsorption of TNT in aquifer soils and on two clay minerals are also reported.

2 Materials and Methods

Soil Preparation

An aquifer soil obtained from Louisiana Army Ammunition Plant (LAAP), Minden, LA, was used to investigate the effects of Eh and pH on the transformation of RDX. The aquifer soil was obtained by excavating approximately 3 cu m of soil 1.2 to 3 m (4 to 10 ft) below the ground surface. The soil was transported offsite, air-dried, sieved through a 3-mm mesh sieve, and homogenized in a cement mixer. Explosives analyses were performed using a modified (ultrasonic extraction) EPA SW-846 Method 8330 (U.S. Environmental Protection Agency (USEPA) 1994).

Eh/pH Incubations

Tests were conducted in 2,800-ml Fernbach flasks. Glucose was added as an energy source at a rate of 1 g every 4 days to maintain microbial removal of oxygen and other electron acceptors from the systems. Sufficient distilled deionized water was added to the flasks to produce a water-to-solids ratio of 18:1 (150 g oven dry weight soil in 2,600 ml water). The water-soil slurries were kept in suspension by magnetic stirring and were maintained at room temperature that averaged $24^{\circ}\text{C} \pm 2$.

The Eh and pH in the slurries were maintained using the methods developed by Patrick, Williams, and Moraghan (1973) with some modifications (Brannon 1983). The Eh was monitored by platinum and Ag-AgCl electrodes connected to a pH-millivolt meter (Beckman Instruments, Fullerton, CA). The desired Eh was set on a meter relay (Currier and Roser, New Orleans, LA), which by activating an aquarium pump to introduce air into the system when the set point was reached, prevented the Eh from falling below a preset value (Figure 1). To help maintain anaerobic conditions, nitrogen gas was flushed through the system at a rate of approximately 15 ml/min. System pH was monitored using a combination pH electrode connected to a separate pH-millivolt meter. A set slurry pH was maintained by injecting 1.0 N HCl or 1.0 N NaOH via a syringe through a serum cap. The soil suspensions were allowed to incubate and stabilize for approximately 3 weeks. The study consisted of triplicate tests at two Eh levels, +500 (oxidizing) and -150 mV (highly reduced), and three pH values, 6.0, 7.0, and 8.0.

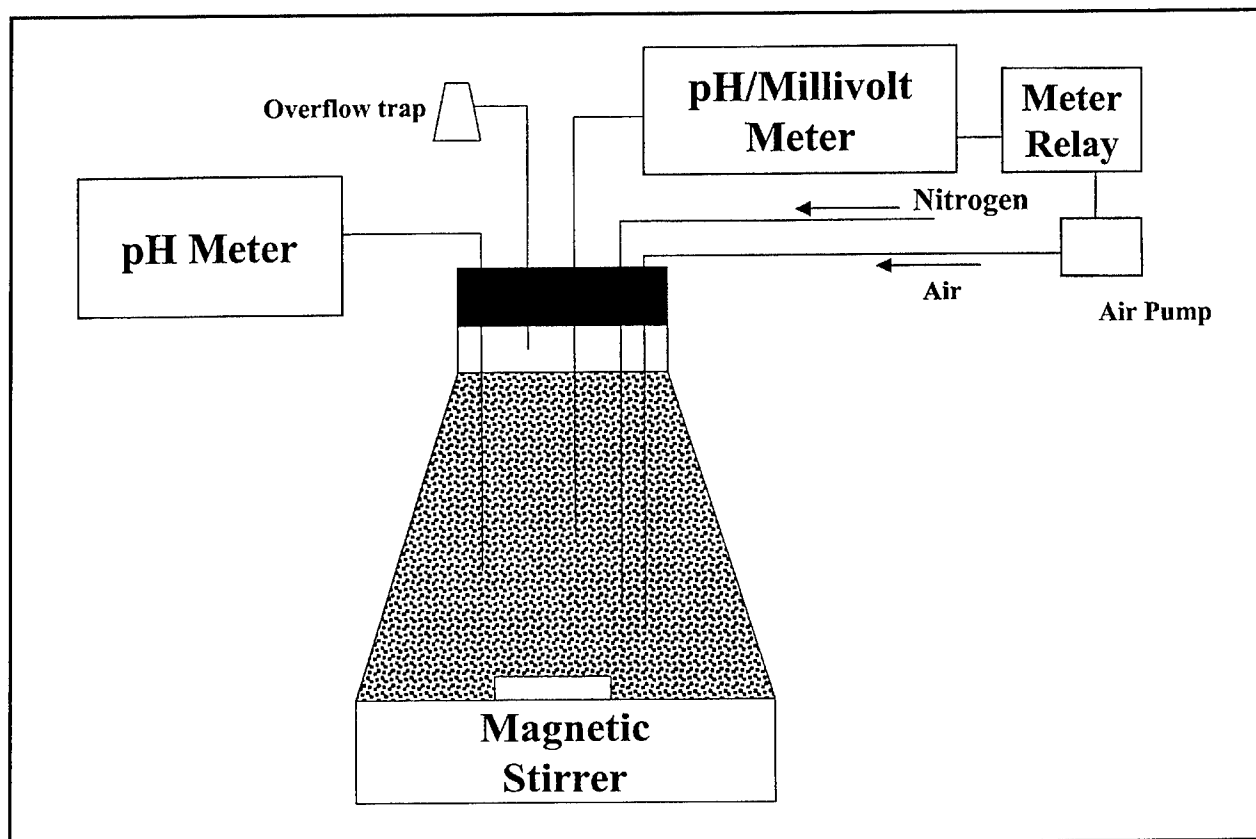


Figure 1. System used to control Eh and pH over time

Following stabilization of the Eh and pH in each reactor, 1 ml of acetone containing 26 mg RDX (equivalent to 10 mg/L) was added to each flask. All flasks were covered with aluminum foil prior to spiking to prevent photo-decomposition of the added compound. Slurry samples were withdrawn 24 hr and 4, 12, and 21 days after addition of RDX, then centrifuged at 1000 relative centrifugal force (RCF) for 30 min to separate the aqueous phase. Aqueous phase was analyzed for RDX and its mono, di, and trinitroso transformation product derivative according to EPA SW-846 Method 8330 (USEPA 1994). Following 15 days incubation, the soils and waters were separated via centrifugation, and soils were analyzed for the same parameters as the waters (USEPA 1994).

Mass Balance of [^{14}C] RDX

Mass balance of RDX was determined using uniformly ring-labeled [^{14}C] RDX with a specific activity of 4.3 mCi/mmol and radiochemical purity of 98.4 percent (New England Nuclear Research Products, Boston, MA). Tests were run in triplicate at +500 and -150 mV at pH 7. A bubble trap containing 1 N KOH was attached to each flask to trap CO_2 . The total incubation period was 21 days. The water and KOH traps were sampled periodically throughout the incubation period. The soils were sampled on day 21. Radioactivity in the aqueous phase and in the CO_2 traps was determined by counting 1 ml of water or KOH in 15 ml Ultima Gold Liquid Scintillation Cocktail (Packard Instruments, Meridan, CT) on

a Packard Tricarb 2500 TR Liquid Scintillation (LS) Counter (Packard Instruments, Meridan, CT). The soil was analyzed for radioactivity by complete combustion in a Model 307 Packard Sample Oxidizer (Packard Instruments, Meridan, CT). Radiolabeled CO_2 was trapped in Carbo-Sorb and Permafluor Liquid Scintillation Cocktail (Packard Instruments, Meridan, CT) and assayed by LS.

A second test using [^{14}C] RDX was conducted to determine the effects of the addition of a surface soil to the aquifer soil on microbial activity in the reactors. The experiment was conducted in duplicate using an identical experimental design to that of the mass balance test described previously. Reactors were maintained at an Eh of -150 mV and a pH of 7. Glucose was added as an energy source, and an additional 1 g of Yokena Clay (a surface soil used in previous experiments (Price et al. 2001)) was added. The tests were allowed to incubate for 4 weeks to stabilize the Eh and pH of the systems and to allow the added microbial community in the surface soil to stabilize. Sampling of the aqueous phase and KOH was conducted as previously described over a 3-week period, and the soils were sampled at the completion of the test.

Cation Substitution

Characteristics of the three aquifer soils from LAAP and two clays have been previously reported (Price et al. 2000). Methods of saturating the ion exchange complex with K^+ and Ca^{++} and determining partitioning coefficients with TNT, RDX, and HMX have also been reported (Price et al. 2000). Therefore, only the methodologies involved in determining the effects of varying degrees of cation saturation on sorption of TNT are presented.

The effects of varying cation composition and degree of saturation on TNT sorption in LAAP C aquifer soil was evaluated in two ways. First, 4 g of aquifer soil was shaken for 24 hr with 16 ml of solution containing from 26.2 to 542 mg/L K^+ in 25-ml glass centrifuge tubes. The mixture was centrifuged and the liquid decanted. A solution at the same K^+ concentration was spiked with 100 μL of radiolabeled TNT and added to the soil. Tubes were shaken for an additional 24 hr. The mixture was centrifuged, decanted, and counted as previously described. This experiment was repeated with a mixed $\text{K}^+/\text{Ca}^{++}$ solution containing from 19.7 to 393 mg/L K^+ and from 6.5 to 130.7 mg/L Ca^{++} . The mixed solution maintained a constant $\text{K}^+/\text{Ca}^{++}$ ratio of 3/1. Second, LAAP C aquifer soils at various levels of homo-ionic K^+ and Ca^{++} saturation were obtained by mixing appropriate amounts of homo-ionic aquifer soil with unamended aquifer soil. Bi-ionic $\text{Ca}^{++}/\text{K}^+$ aquifer soil was obtained by mixing appropriate amounts of homo-ionic aquifer soils. Sufficient distilled deionized water was added to produce a 4:1 water:soil ratio, and the mixture was spiked with appropriate levels of radiolabeled TNT, shaken for 24 hr, centrifuged, and counted as previously described. Measured partition coefficients for K^+ (6.5 L/kg) and Ca^{++} (20.2 L/kg) in aquifer soil were sufficiently high so that desorbed K^+ and Ca^{++} would rapidly redistribute over the soil mass and not result in substantial alterations of the soil fraction occupied by either K^+ or Ca^{++} .

3 Results and Discussion

Eh/pH Incubations

Effects of Eh and pH on RDX stability

RDX was relatively stable at all pH levels under aerobic conditions (Figure 2a). Anaerobic conditions (-150 mV) resulted in decreased aqueous concentrations over time, yet RDX never completely disappeared from solution (Figure 2b). Results of soil analysis revealed lower concentrations of RDX remaining in the soil in the -150-mV tests as compared with the +500-mV tests; however, RDX never completely disappeared from the soil or solution phase 21 days after addition of 26 mg RDX (Figure 3a). Soil analysis results were consistent with results for the aqueous phase, in that the ratios of concentrations in oxidized-to-reduced treatments were similar. Approximately 10:1 of the RDX was recovered from the aqueous phase. These results are similar to those seen in experiments conducted with a surface soil where approximately 8:1 of the RDX was recovered in the aqueous phase in both oxidized and reduced treatments (Price et al. 2001). RDX was more stable under anaerobic conditions in the aquifer soil than in the surface soil. RDX decreased to low levels in the surface soil with complete removal at pH 7 at 15 days after addition of 26 mg RDX. The lack of RDX removal was probably due to either microbial community or nutrient limitations in the aquifer soil. The addition of a 1 g surface soil inoculum to the aquifer soil prior to RDX addition gave results similar to those observed for uninoculated aquifer soil (Figure 4). These results indicate that the surface soil microbial community was not able to function in the aquifer soil even in the presence of a glucose energy source.

RDX removal (aqueous plus soil) from the slurries was observed at all pH levels under anaerobic conditions, with the highest removal at pH 6 (Figure 5). To determine if varying Eh/pH conditions affected RDX sorption, single-point distribution coefficients (K_d) for each Eh and pH were calculated from aqueous and soil RDX concentrations on day 21:

$$K_d = \frac{Q(t)}{C(t)} \quad (1)$$

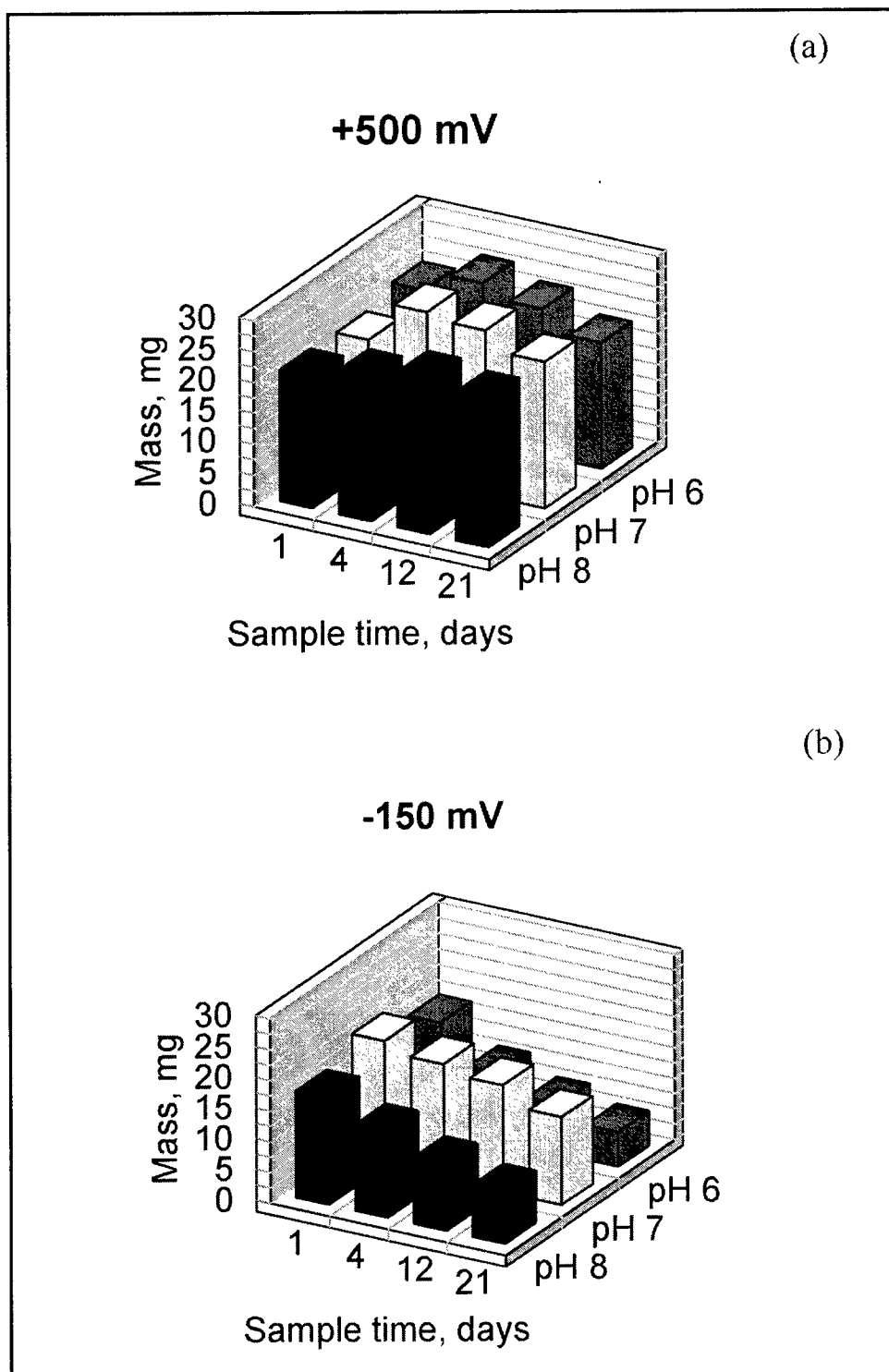


Figure 2. RDX aqueous concentrations over time at each Eh and pH

where

Q = soil concentration (mg/kg) at sample time (t)

C = aqueous concentration (mg/L) at sample time (t)

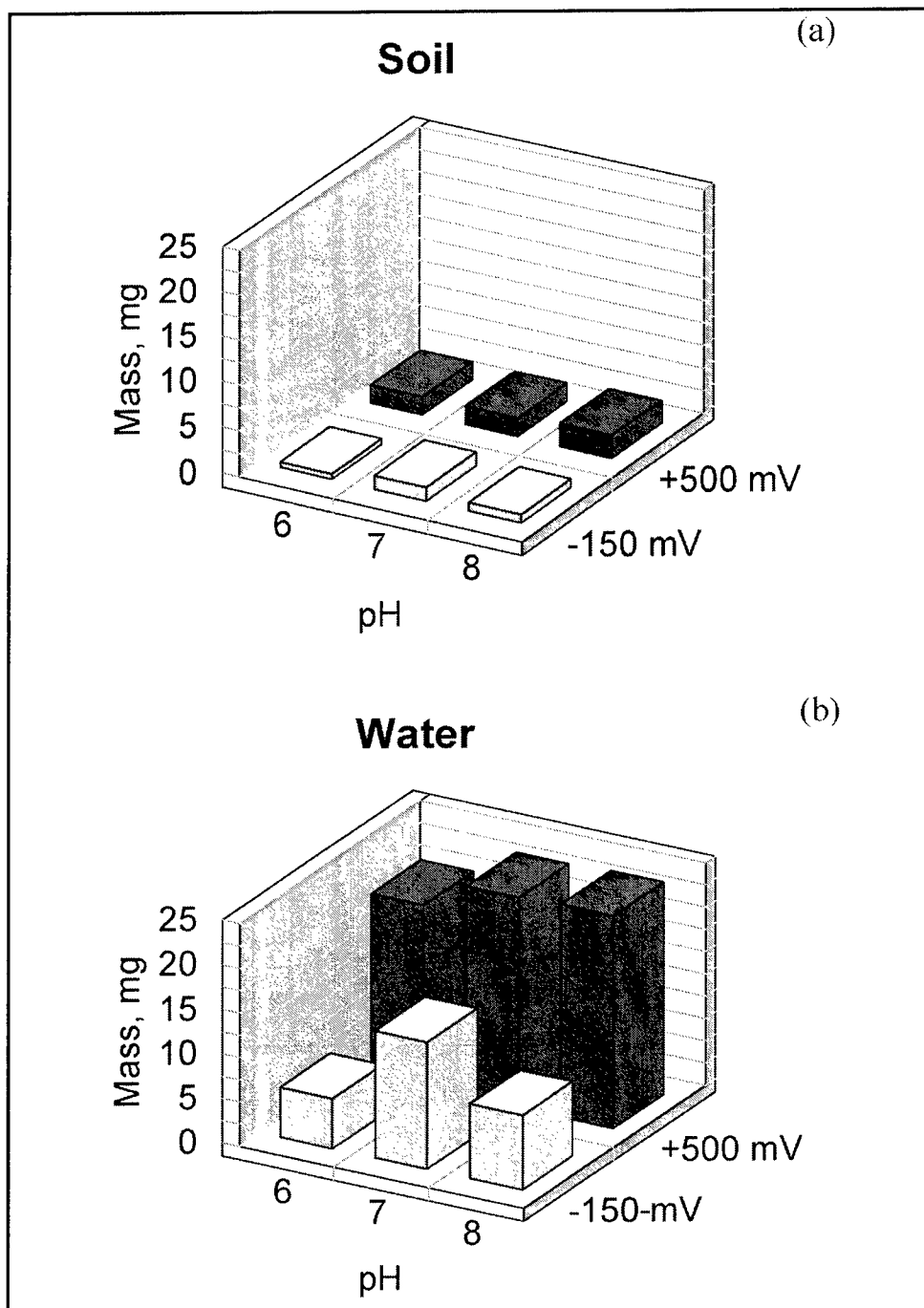


Figure 3. RDX soil and aqueous concentrations 21 days after addition of 26 mg RDX

No consistent trend was noted for soil sorption under aerobic and anaerobic conditions (Table 1). Increased effects of pH on sorption were noted in the -150-mV tests where pH 7 conditions promoted sorption. These results differ from those seen in studies conducted with a surface soil in which decreased soil sorption was noted for all pH conditions under anaerobic conditions (Price, Brannon, and Yost 1998).

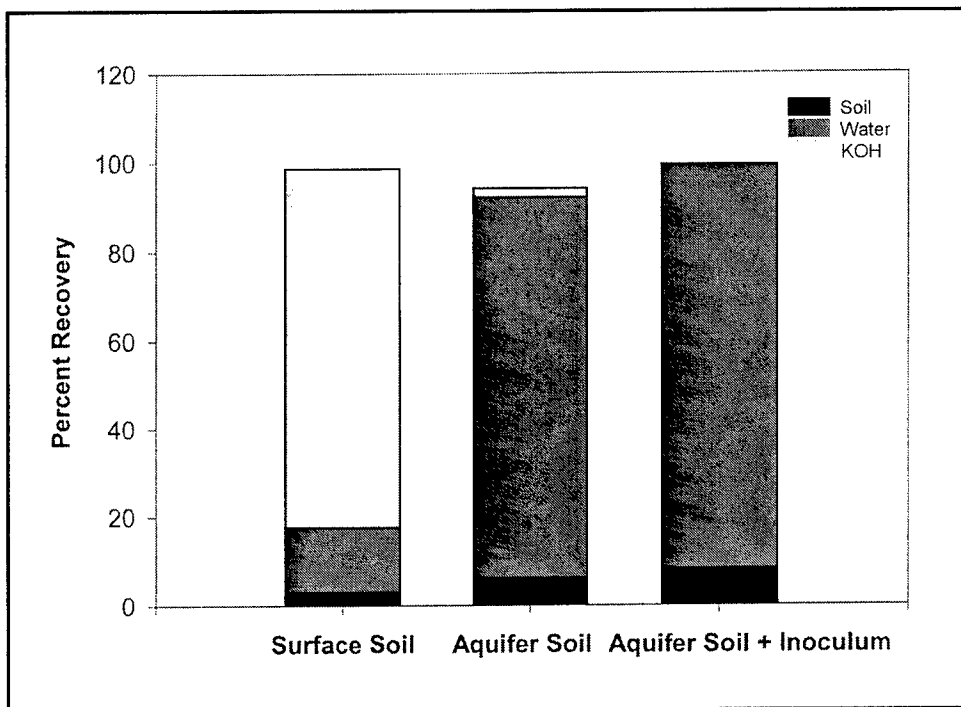


Figure 4. Percent recoveries of radioactivity in tests conducted with an uninoculated and inoculated aquifer soil and a surface soil

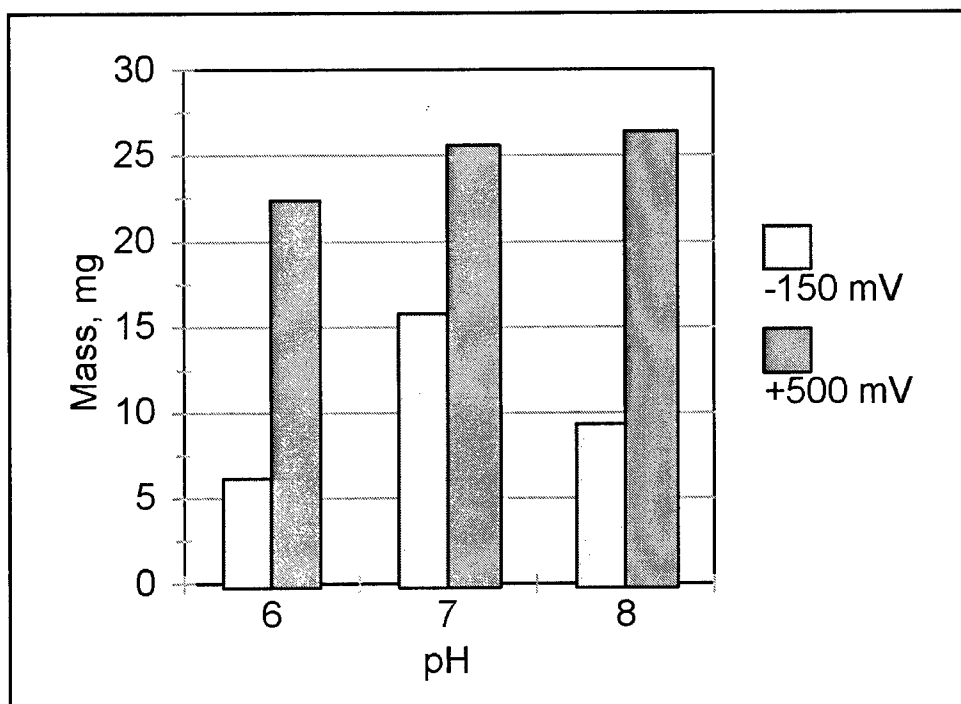


Figure 5. Total mass of RDX remaining after incubation at each Eh and pH

pH	+500 mV	-150 mV
6	5.81 (0.65)	1.94 (0.95)
7	6.27 (0.50)	15.8 (3.6)
8	4.89 (0.47)	4.12 (0.45)

Processes that remove RDX from solution can be expressed with pseudo first-order kinetics which take the form

$$\frac{dc}{dt} = -kc \quad (2)$$

where

c = chemical concentration of reacting substance

k = pseudo first-order reaction constant

First-order kinetics then reduce to the equation

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (3)$$

where c_0 is the concentration of the reacting substance at time 0. Once a value of k is obtained, the half-life period of the reacting substance, $t_{1/2}$, can be calculated using the equation

$$t_{1/2} = \frac{0.693}{k} \quad (4)$$

To quantify the rates of disappearance, RDX concentrations were fit to the pseudo first-order kinetic equation. RDX removal from solution was more rapid at -150 mV than at +500 mV, with the fastest removal occurring at pH 6 and the slowest at pH 7 (Table 2). The half lives for RDX in these studies differed

pH	r^2	k , hr ⁻¹	$t_{1/2}$, hr
-150 mV			
6	0.92	0.0021	328
7	0.98	0.0007	996
8	0.96	0.0014	485
+500 mV			
6	0.47	NS	NS
7	0.02	NS	NS
8	0.44	NS	NS

Note: NS indicates rate constant was not significantly ($p < 0.05$) different from zero.

significantly from those in identical studies conducted with a surface soil where half lives for RDX were less than 6 hr in the -150-mV tests as compared with a half life between 328 and 996 hr in these investigations (Price et al. 2001).

RDX transformation product formation was rapid and related to the Eh of the system, with lower Eh conditions resulting in a greater number and concentration of products (Figure 6). The RDX transformation product, MNX, appeared in all treatments within 24 hr following RDX addition. Aqueous concentrations generally increased over time in the +500-mV tests (Figure 7). By day 21, solution concentrations of MNX in the +500-mV tests ranged from 0.018 mg/L at pH 8 to 0.086 mg/L at pH 7. In the -150-mV tests, solution concentrations increased to day 11 of sampling in the pH 6 treatments followed by a decrease in solution concentration to 0.84 mg/L. In the pH 7 and 8 tests, MNX aqueous concentrations increased to day 4 and remained relatively stable for the duration of the test. These results are similar to those seen in tests conducted with a surface soil, where MNX appeared in solution 24 hr after additions of RDX (Price et al. 2001).

The disappearance of RDX in the -150-mV tests was also paralleled by the appearance of the aqueous RDX transformation products DNX and TNX (Figure 8). DNX appeared in the pH 6 and 8 treatments with the peak concentration of 0.18 mg/L appearing in the pH 6 reactors 24 hr after addition of RDX. TNX appeared in the pH 6 and 7 tests. The peak solution concentration of 0.045 mg/L was seen in the pH 7 test 21 days after addition of RDX. DNX and TNX were not detected in solution in the aerobic tests.

Redox potential had a marked effect on RDX recovery. RDX was stable at +500 mV and least stable at pH 6 in the -150-mV tests (Table 3). These results are similar to those seen in investigations conducted with a surface soil, but much lower recoveries were seen in the anaerobic tests conducted with the surface soil. Only 1.7 percent of the RDX was recovered in these investigations in the pH 7, -150-mV tests (Table 4) (Price et al. 2001). These results indicate that RDX is stable under oxidizing conditions and is moderately unstable under anaerobic conditions in the low carbon aquifer soil.

Mass balance of [¹⁴C] RDX

Most of the radioactivity remained in the aqueous phase of the soil:water slurries (Table 4). Higher mineralization was seen in the anaerobic tests, where 26 percent of radio-labeled carbon was mineralized as CO₂. These results differ from those seen in investigations conducted with a surface soil under the same Eh conditions at a pH of 7, where 80 percent of the radioactivity was mineralized as CO₂ (Table 4).

Cation Substitution

Of the untreated soils and clays, only untreated montmorillonite possessed a K_d comparable to that observed with the homo-ionic K⁺ and NH₄⁺ material (Price

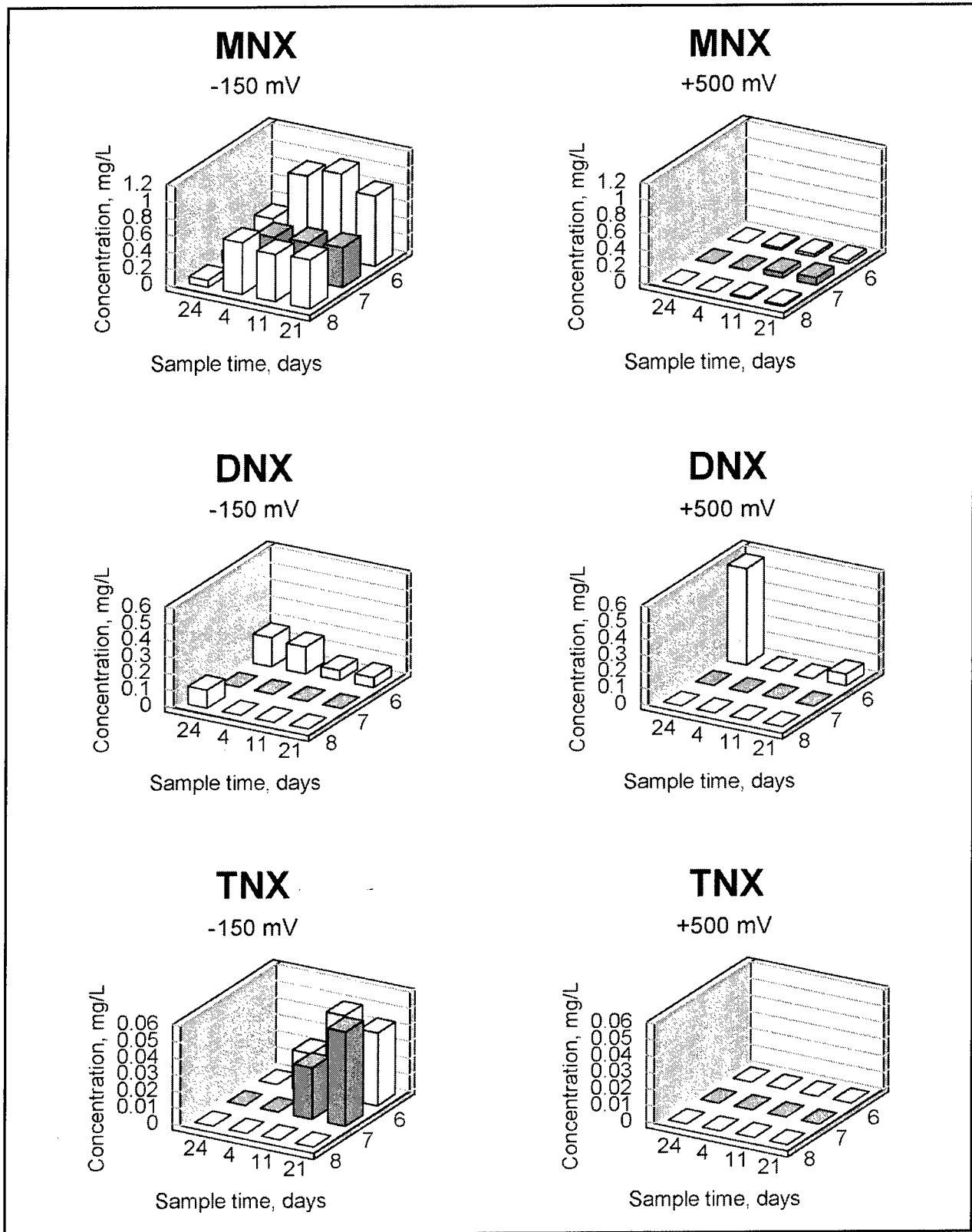


Figure 6. RDX transformation products in solution over time at each Eh and pH

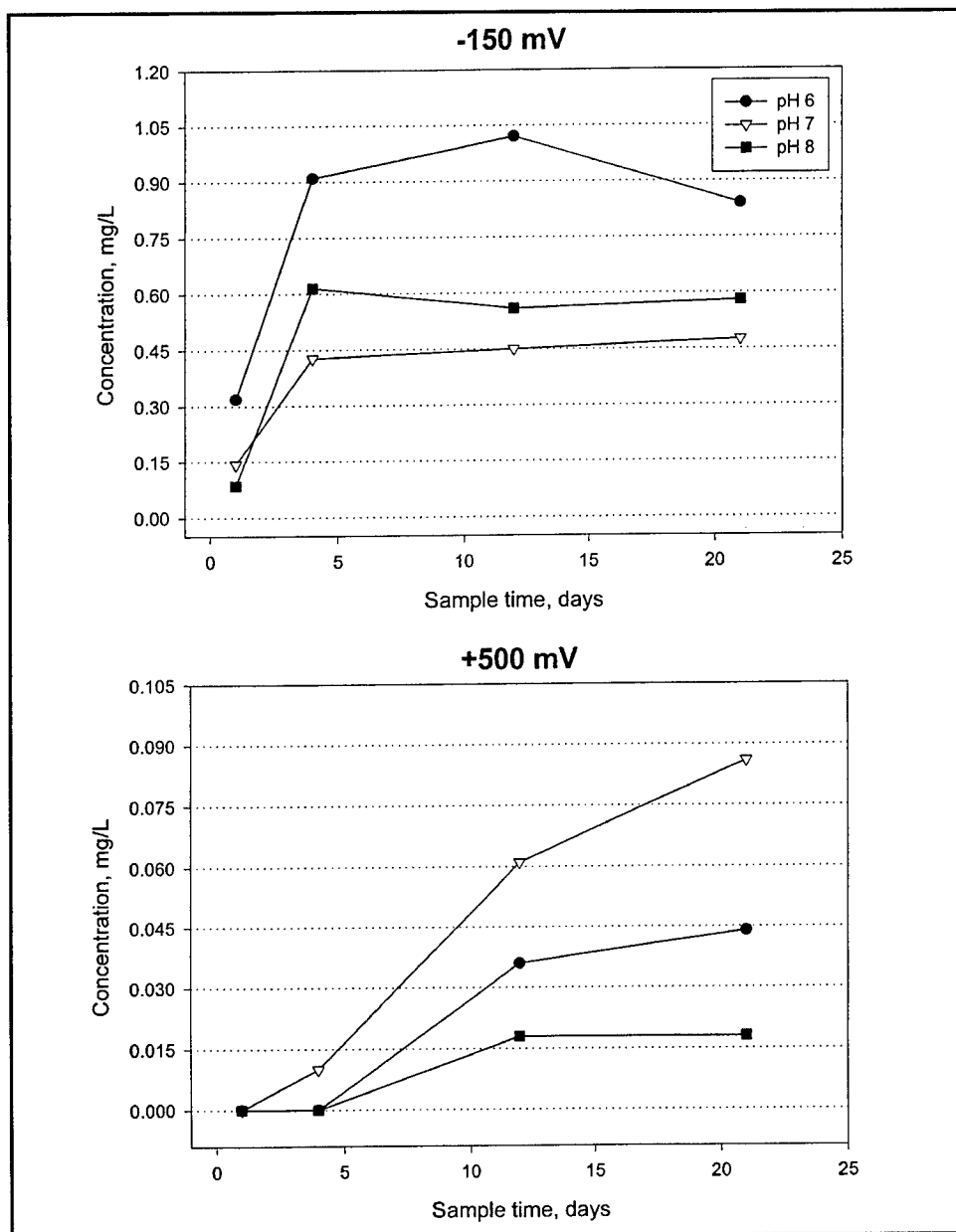


Figure 7. MNX aqueous concentrations over time at each Eh and pH

et al. 2000). Saturation with K^+ and NH_4^+ did not significantly increase TNT K_d above that of untreated montmorillonite. However, Ca^{++} saturation resulted in a K_d well below those resulting from K^+ and NH_4^+ saturation or the untreated montmorillonite. Exchangeable K^+ , NH_4^+ , Na^+ , and Ca^{++} constituted 97.6 percent of the total cation exchange capacity (CEC) of the montmorillonite, with 9 percent of the exchange sites containing K^+ and NH_4^+ and the remainder Ca^{++} (87.7 percent) and Na^+ (3.5 percent). Sorption of TNT on montmorillonite containing 90-percent Ca^{++} and 10-percent K^+ produced a K_d of 172 L/kg, well below the unamended K_d of 413 L/kg. These results indicate that the interactions of cations with clay mineral surfaces may be more complex than interactions with aquifer soils.

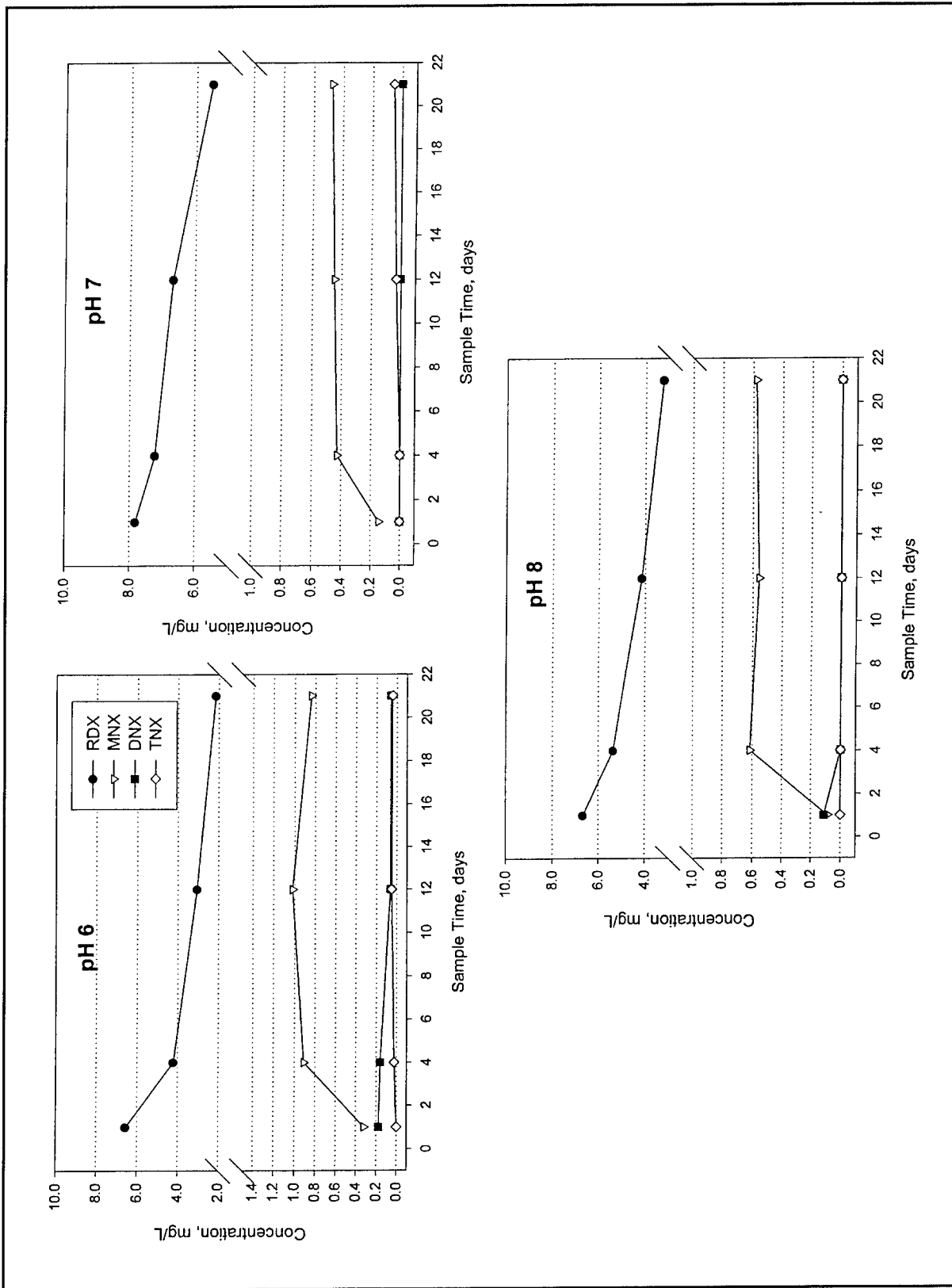


Figure 8. RDX and its transformation products in solution over time at each pH under highly reduced conditions

Table 3 Percent Recovery of RDX (Aqueous Plus Soil Phase) 21 days After Addition of 26 mg RDX			
Treatment	pH		
	6	7	8
Aquifer Soil			
-150 mV	27	61	40
+500 mV	86	98	100
Surface Soil			
-150 mV	13	1.7	6
+500 mV	97	75	91

Table 4 Percent Recovery of Radioactivity in Tests Conducted With an Aquifer Soil and a Surface Soil			
Treatment	Phase		
	Water	Soil	CO ₂
Aquifer Soil			
-150 mV	85	6	26
+500 mV	100	15.2	5.6
Surface Soil			
-150 mV	14.3	3.2	80.1
+500 mV	87.8	7.03	5.4

Specific adsorption of TNT in homo-ionic K⁺ and NH₄⁺ aquifer soils and clay minerals was highly correlated with CEC, showing values of $r^2 = 0.976$ and $r^2 = 0.993$, respectively. The strong relationship between TNT adsorption and CEC is not surprising in view of the relationship between CEC and TNT adsorption observed for a wide range of surface and aquifer soils (Brannon et al. 1999). Adsorption of nitroaromatic compounds such as TNT primarily occurs at easily accessible external surfaces of clay minerals (Haderlein, Weissmahr, and Schwarzenbach 1996), which CEC is apparently measuring.

Increasing the concentration of K⁺ in solution decreased concentrations of TNT, indicating increased TNT sorption (Figure 9). Increasing concentrations of a 3:1 K⁺:Ca⁺⁺ mixture resulted in lower sorption and increased solution concentrations of TNT compared to K⁺ alone after K⁺ concentrations exceeded 150 mg/L (Figure 9). This result is consistent with Weissmahr et al. (1999) who showed that 4-nitrotoluene K_d 's in montmorillonite increased in bi-ionic mixtures of K⁺ and Ca⁺⁺ as the equivalent fraction of exchangeable K⁺ increased. However, the curves diverge at a threshold due to increased coverage of the exchange complex by Ca⁺⁺ at higher solution concentrations. The aquifer soils K_d for Ca⁺⁺ was approximately three times that of K⁺. Therefore, as the concentration of Ca⁺⁺ increased, increased surface coverage by Ca⁺⁺ relative to K⁺ apparently occurred.

This premise was tested by determining K_d values of TNT for the same aquifer soil at various equivalent fractions of K⁺ and Ca⁺⁺. The K_d values for bi-ionic K⁺:Ca⁺⁺ soils were intermediate to homo-ionic K⁺ and Ca⁺⁺ soils (Figure 10). However, the curves exhibited similar shapes. This is consistent with

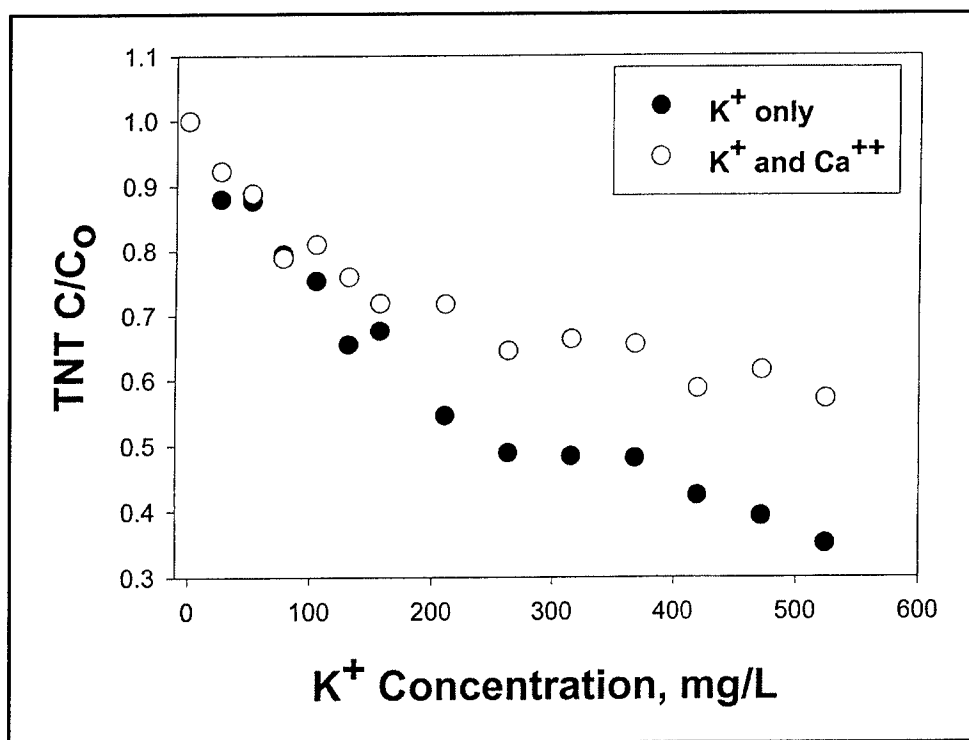


Figure 9. Change in relative TNT concentrations as a function of K⁺ and Ca⁺⁺ solution concentrations

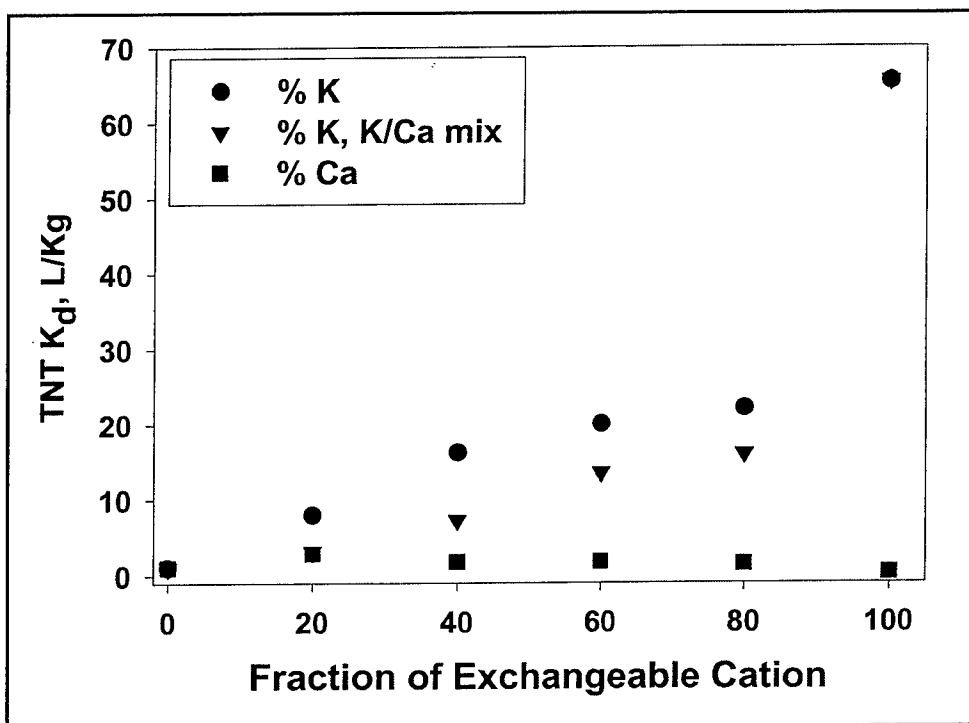


Figure 10. Adsorption of TNT to bi-ionic K⁺:Ca⁺⁺, and homo-ionic K⁺ and Ca⁺⁺ aquifer soil

most of the exchange complex being occupied by Ca^{++} (Jackson 1958). The increase in K_d with increasing fraction K^+ was not linear, increasing most steeply up to the point where K^+ occupied 40 percent of the exchange complex. The increase in K_d between 40- and 80-percent coverage of the exchange complex by K^+ was relatively minor compared to the pronounced increase once homo-ionic K^+ coverage of the exchange complex was attained. These results indicate that the greatest impact of K^+ on increasing sorption of TNT occurs when 100-percent coverage is attained, but that sorption increases substantially up to 40-percent coverage of the exchange complex. Coverage of the exchange complex with between 40 and 80 percent K^+ yields only small increments of improved sorption.

4 Conclusions

Results of investigations conducted under controlled redox potential and pH conditions indicated that RDX was relatively stable in solution under aerobic conditions. Highly reducing conditions promoted removal of RDX from solution, particularly at pH 6. RDX persistence was highest under oxidizing conditions and under anaerobic conditions at pH 7. Anaerobic conditions promoted increased transformation of RDX to MNX, DNX, and TNX. The pH affected the disappearance of RDX in the anaerobic systems, with increased removal of RDX from solution observed at pH 6 and 8 compared with pH 7.

Radioactivity recovered in the [^{14}C] RDX mass balance tests was found primarily in the aqueous phase following 21 days incubation under both oxidized and reduced conditions. This distribution was similar to that observed in other investigations conducted with a surface soil, with the exception that in the surface soil tests, most of the radio-label was mineralized under anaerobic, pH 7 conditions.

These results indicate that RDX in an aquifer soil (in the presence of an added energy source) moving into an area of intense reduction will not persist long, even at the lowest rate observed at pH 7. RDX moving into an oxidizing environment will be relatively stable from pH 6 to 8. Typical aquifer pH values in the United States range from 6 to 8.5 (Driscoll 1987).

Results of batch shake tests showed that groundwater cation composition strongly affected the sorption of TNT in aquifer soils. TNT adsorption by bi-ionic $\text{K}^+:\text{Ca}^{++}$ aquifer soil increased until 40-percent coverage of the exchange complex was attained. Past this point, pronounced increases in adsorption were not observed until 100-percent saturation with K^+ was reached. This indicates that increases in TNT sorption by aquifer soils as a consequence of cation saturation is most pronounced at 100-percent saturation with K^+ , but that useful increases in sorption can be attained at saturation levels below 40 percent.

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14. ABSTRACT
Disposal operations from the manufacturing process of the explosives 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) have resulted in the contamination of soil and groundwater at many active and inactive munitions sites. Natural attenuation of these compounds is one option for addressing site cleanup. The potential for this option to be successful in low-carbon aquifer soils is dependant upon the ability of these soils to adsorb and transform explosives. Therefore, an understanding of the processes that control the mobility and transformation of explosives in these types of soils is needed to evaluate the processes of natural attenuation in aquifers.
The objective of these studies was to investigate environmental conditions such as redox potential, pH, and groundwater quality on sorption and transformation of explosives in low-carbon aquifer soils.
Laboratory investigations addressing the effects of redox potential and pH on RDX transformation in an aquifer soil were conducted by testing at two different redox potentials and three pH levels. An 18:1 (water:soil) suspension spiked with 15 mg RDX was used. Results indicate that RDX added to a low-carbon soil was relatively stable under aerobic conditions. Highly reducing conditions promoted removal of RDX from solution, and increased transformation was seen.

(Continued)

15. SUBJECT TERMS Aquifer soil Cation substitution	Groundwater pH RDX sorption	Redox potential TNT adsorption
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Studies addressing various degrees of cation substitution on adsorption of TNT in an aquifer soil and two clay minerals were conducted. Results of batch shake tests showed that groundwater cation composition strongly affected TNT sorption by aquifer soils. TNT sorption was most pronounced at 100-percent saturation with K^+ , but results showed that increases in sorption could be attained at saturation levels below 40 percent.

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