**US Army Corps
of Engineers**
Waterways Experiment
Station

Installation Restoration Research Program

Transformation of RDX and HMX Under Controlled Eh/pH Conditions

by Cynthia B. Price, James M. Brannon, WES
Sally L. Yost, DynTel Corporation

WES

Transformation of RDX and HMX Under Controlled Eh/pH Conditions

by   Cynthia B. Price, James M. Brannon

U.S. Army Corps of Engineers
Waterways Experiment Station
3909 Halls Ferry Road
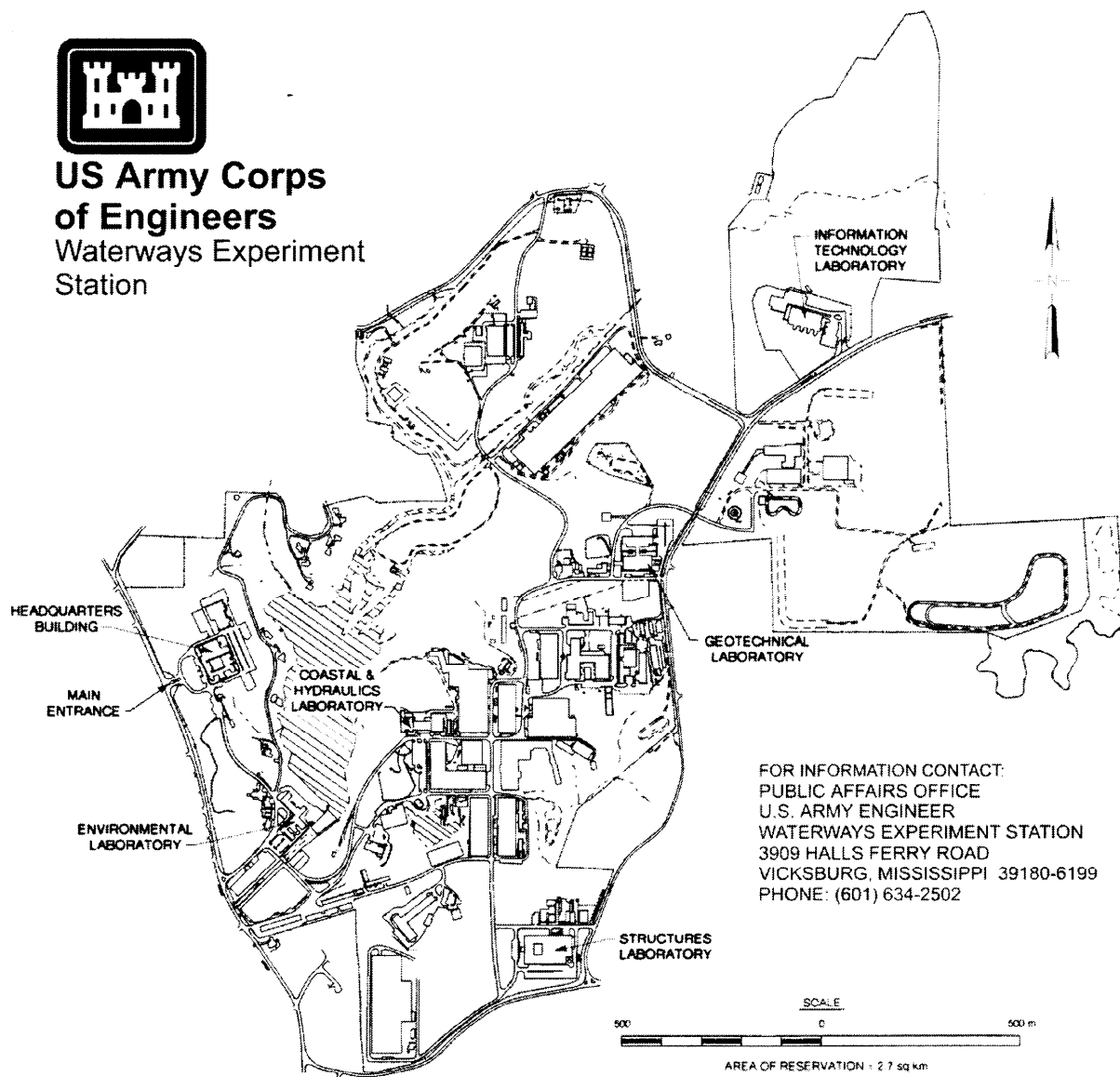Vicksburg, MS 39180-6199

Sally L. Yost

DynTel Corporation
3530 Manor Drive
Vicksburg, MS 39180-5693

Final report

**US Army Corps
of Engineers**
Waterways Experiment
Station

INFORMATION
TECHNOLOGY
LABORATORY

HEADQUARTERS
BUILDING

MAIN
ENTRANCE

COASTAL &
HYDRAULICS
LABORATORY

GEOTECHNICAL
LABORATORY

ENVIRONMENTAL
LABORATORY

FOR INFORMATION CONTACT:
PUBLIC AFFAIRS OFFICE
U.S. ARMY ENGINEER
WATERWAYS EXPERIMENT STATION
3909 HALLS FERRY ROAD
VICKSBURG, MISSISSIPPI 39180-6199
PHONE: (601) 634-2502

STRUCTURES
LABORATORY

SCALE

500   0   500 m

AREA OF RESERVATION : 2.7 sq km

Contents

List of Figures

List of Tables

Preface

The studies reported herein were conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), 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, WES, 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 (EPEB), Environmental Processes and Effects Division (EPED), and Ms. Sally Yost, DynTel Corporation. The authors wish to acknowledge Ms. Toni Neuman and Mr. Gregory Young for technical assistance. Technical reviews were provided by Drs. Judith C. Pennington and Chris J. McGrath, EPED.

The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED, and under the general supervision of Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Robin R. Cababa, EN.

This report should be cited as follows:

1   Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are widely used military high explosives. Past manufacturing, loading, assembling, and packing operations of these compounds have resulted in soil and groundwater contamination (Layton et al. 1987). For example, Spalding and Fulton (1988) found an extensive groundwater plume of RDX in association with past activities conducted at Cornhusker Army Ammunition Plant. Off-post groundwater concentrations greater then 35 μg/L have been reported (Hansen et al. 1984).

RDX is toxic to aquatic organisms including algae, some invertebrates, and fish (Etnier 1986; Burton and Turley 1995). Cataldo et al. (1990) found RDX to be more mobile and plant available than related munitions such as TNT. RDX is also toxic to rodents (Merck and Co. 1983) and is detrimental to reproduction in rats (Cholakis et al. 1980). Transformation of RDX to mononitroso, dinitroso, and trinitroso derivatives under anaerobic conditions has been reported (McCormick, Cornell, and Kaplan 1984a; Crawford 1995). Under anaerobic conditions, 80 percent of the radioactivity in $[C^{14}]$ RDX was mineralized to $^{14}CO_2$ (Sikka et al. 1980). Resistance to aerobic degradation has also been reported (McCormick, Cornell, and Kaplan 1984a, b; Spanggord et al. 1980; Hoffsommer et al. 1978). Little or no soil sorption of RDX occurs (Selim, Xue, and Iskandar 1995; Sikka et al. 1980; Leggett 1985; Pennington and Patrick 1990).

Little is known of the transformation of HMX. Spanggord et al. (1980) reported formation of mononitroso, dinitroso, and trinitroso derivatives of HMX under anaerobic conditions. McCormick, Cornell, and Kaplan (1984a, b) found HMX to be persistent under aerobic conditions, but observed transformation under anaerobic conditions. Little evidence for aerobic degradation of HMX was reported from soil column studies (Green, Kaplan, and Kaplan 1985).

In order to fully evaluate problems with release into soils and the aquatic environment, an understanding of the mobility, persistence, and transformation of RDX and HMX is required. The objective of this study was to determine the effects of redox potential (Eh) and pH on RDX and HMX transformation in soil.

2   Materials and Methods

Soil Preparation

The study used a predominantly clay (49 percent) agricultural surface soil from the Mississippi River floodplain. The soil was classified as very fine, montmorillonite, nonacid, thermic Vertic Haplaquept (U.S. Soil Conservation Service classification) and designated Yokena Clay. The soil was air-dried, ground, and sieved through a 2-mm sieve before storing at room temperature.

Eh/pH Incubations

Tests were conducted in 2,800-ml Fernbach flasks. Organic matter (0.5 percent w/w) obtained from the Atchafalaya Basin, Louisiana, was added as an energy source to increase the rate of reduction in the soil by the native microbial community. 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 30.5 ± 1.02 °C.

Control of Eh and pH in the slurries was 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) (Figure 1). Eh was set on a meter relay (Currier and Roser, New Orleans, LA), which, by activating an aquarium air pump when the set point was reached, prevented the Eh from falling below the preset value. When the suspension was oxidized to the set Eh, the meter relay automatically switched off the air pump. 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 NaOH via a syringe through a serum cap. The soil suspensions were allowed to incubate and stabilize for 1 to 2 weeks before addition of RDX or HMX.
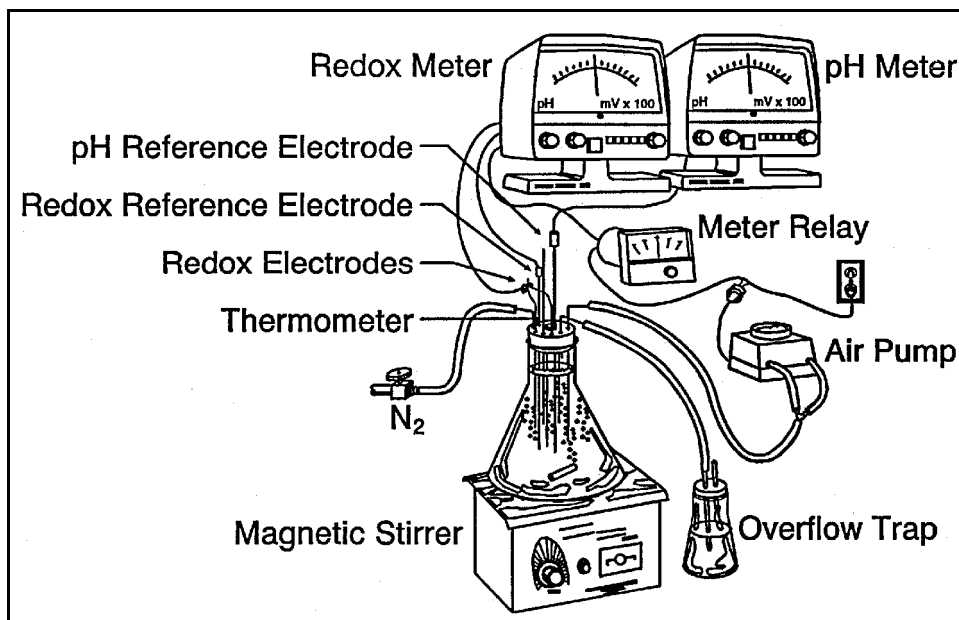
Figure 1.   System used to control Eh and pH over time

The study consisted of triplicate tests at three Eh levels, +500 (oxidizing), +250 (moderately reducing), and -150 mV (highly reduced), and four pH values, 5.0, 6.0, 7.0, and 8.0. After stabilization, one milliliter of acetone containing 2.6 mg RDX or HMX (equivalent to 10 mg/L) was added. All flasks were covered with aluminum foil prior to spiking to prevent photodecomposition of the added compounds. For RDX treatments, slurry samples were withdrawn at 15 min, 1, 3, 6, 10, and 15 days after addition of 26 mg RDX. For HMX treatments, samples were taken at 15 min, 2, 7, 12, 16, and 21 days after addition of 26 mg HMX. Samples were centrifuged at 1,000 RCF for 30 min. For RDX treatments, the aqueous phase was analyzed for RDX and its transformation products including the mononitroso, dinitroso, and trinitroso derivatives and for the coproduction product HMX. For HMX treatments, the aqueous phase was analyzed for HMX and its mononitro derivative (MN-HMX). Analyses were performed according to EPA SW-846 Method 8330 (U.S. Environmental Protection Agency (EPA) 1990). At the end of the experiment, both aqueous and soil phases were analyzed. Due to limited changes in aqueous phase concentrations of HMX in RDX treatments over time, the incubation time for HMX treatments was increased to 21 days. The soil phases were analyzed for the same parameters as the aqueous phases.

Mass Balance of [^{14}C] RDX

Mass balance of RDX was determined using uniformly ring-labeled [^{14}C]RDX (New England Nuclear Research Products, Boston, MA). Tests were run in triplicate at +500, +250, and -150 mV at pH 5, 7, and 8. A bubble trap containing 1 N KOH was attached to each flask to trap CO_2. The total

incubation period was 15 days. The KOH traps were sampled daily, and the water and soil were sampled on Day 15. Radio-activity in the aqueous phase and in 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.

3   Results and Discussion

Effects of Eh and pH on RDX

At all pH levels in the +500- and +250-mV Eh treatments, RDX mass was relatively stable over time, with the exception of the pH 8, +250-mV treatment, where a marked concentration decrease was noted on Day 15 (Figure 2). RDX concentrations decreased over time in all -150-mV treatments, but never completely disappeared from solution (Figure 2). Results of soil analyses were consistent with results for the aqueous phase, in that the ratios of concentrations in oxidized to reduced treatments were similar (Figure 3). However, approximately 8:1 of the RDX was recovered from the aqueous phase. Similar results have been reported for groundwater (Spaulding and Fulton 1988), river systems (Spanggord et al. 1980), and activated sludge (Hoffsommer et al. 1978). Under anaerobic conditions (-150 mV), RDX removal (aqueous plus soil) removal from the slurries (soil plus water) was observed over the entire pH range (5-8) (Figure 4). The highest apparent removal occurred at pH 7, in agreement with Crawford (1995), who found that pH 6.5 to 7.0 and redox potentials between -100 and -300 mV were optimum for RDX removal. To determine if Eh/pH conditions affected sorption of RDX, single-point distribution coefficients (*Kd*) for each Eh and pH were calculated from measured aqueous and soil RDX concentrations on Day 15, where

$$Kd = Q(t)/C(t) \tag{1}$$

where

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

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

Kds were lowest under highly anaerobic conditions, specifically at pH 5, 6, and 7, indicating decreased soil sorption under anaerobic conditions (Table 1). Effects of pH on sorption were noted in the +250-mV test where sorption at pH 8 exceeded that observed at lower pH values by a factor of 9.2. Under moderately reducing conditions, sorption was highest at pH 8. Under highly aerobic conditions, pH did not affect sorption.
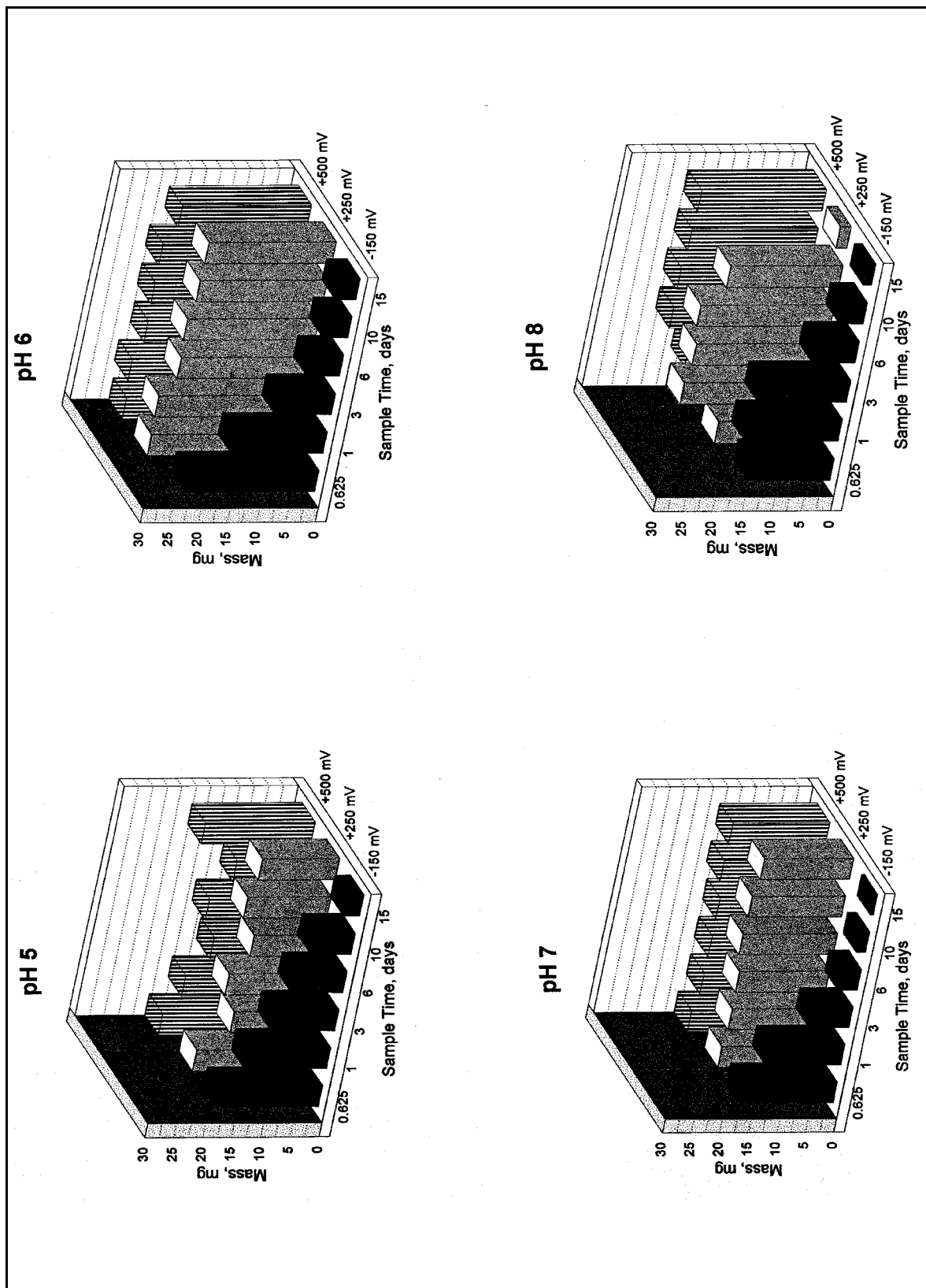
Figure 2.   RDX aqueous concentrations over time at each pH level
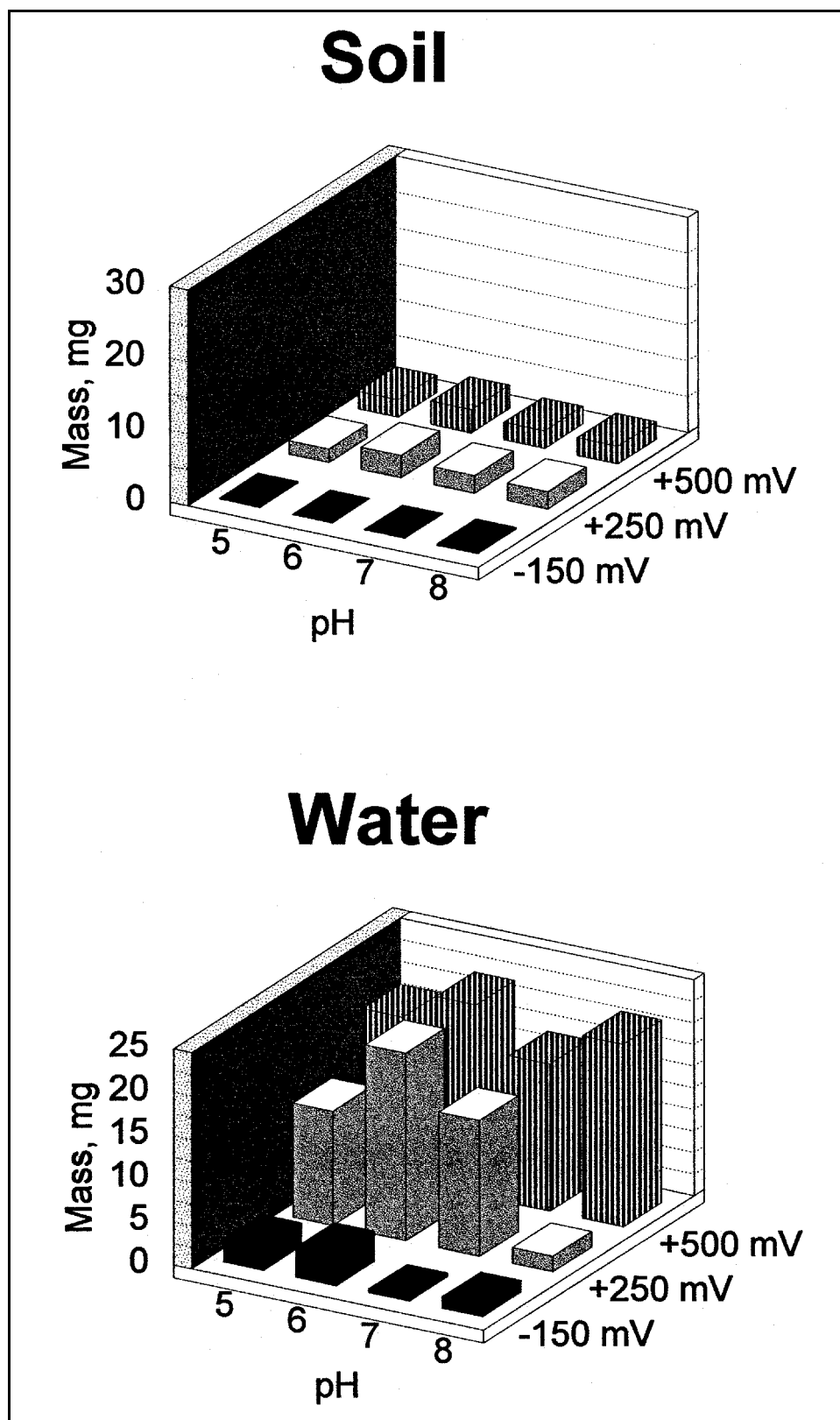
Figure 3.   Mass of RDX remaining (aqueous and soil phases) 15 days after
           addition of 26 mg RDX
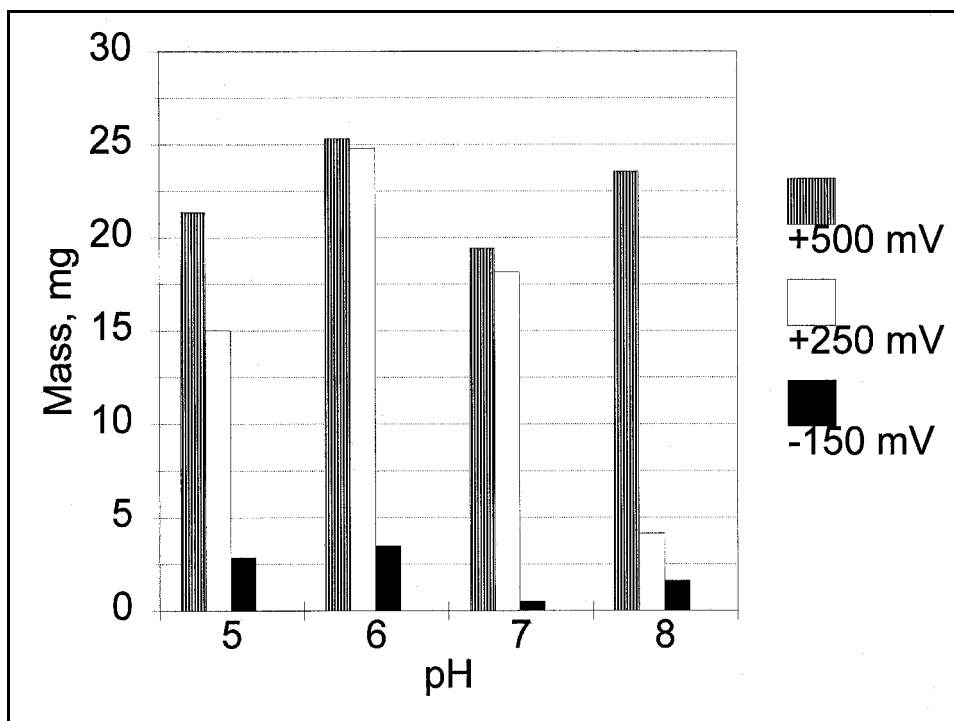
Figure 4.   Total mass of RDX remaining (aqueous plus soil) 15 days after
            addition of 26 mg RDX at various Eh and pH values

Table 1 Mean *Kds* (L/kg) (standard error) for RDX on Day 15			
pH	+500 mV	+250 mV	-150 mV
5	2.25 (0.19)	2.35 (0.59)	1.14 (0.08)
6	2.52 (0.22)	2.46 (0.21)	0
7	2.46 (0.17)	2.73 (0.25)	0.76
8	2.01 (0.09)	23.1 (3.0)	2.51 (2.0)

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

$$dc/dt = -kc \qquad (2)$$

where

c = chemical concentration of reacting substance

k = pseudo first-order reaction constant

t = time

Alternatively, a pseudo first-order kinetic model may be expressed as

$$\ln (c_o /c) = kt \tag{3}$$

where c_o is the initial ($t = 0$) concentration of the reacting substance. Once a value of k is obtained, the half-life period of the reacting substance $t_{1/2}$ can be calculated using the equation (Fair, Geyer, and Okun 1968)

$$k = 0.693/t_{1/2} \tag{4}$$

To quantify the rates of disappearance, RDX concentrations were fit to the pseudo first-order kinetic equation. The RDX removal rate from solution was much faster at -150 mV than at +500 mV or +250 mV (Table 2). The rate coefficients (k) for the highly anaerobic systems were substantially higher, ranging from 0.12 at pH 5 and 6 to 0.24 at pH 7 as compared with 0 to 0.008 in the +500- and +250-mV tests (Table 2). Half lives ($t_{1/2}$) for RDX were less than 6 hr for the -150-mV tests compared with $\geq$ 77 hr for the +500- and +250-mV tests (Table 2).

Table 2			
Regression Coefficient (r^2), First-Order Rate Coefficient (k), and Half Life ($t_{1/2}$) for RDX at Each Eh/pH Treatment			
pH	r^2	k, hr^{-1}	$t_{1/2}$, hr
+500 mV			
5	0.002	NS[1]	NS
6	0.75	0.007	99
7	0.16	NS	NS
8	0.40	NS	NS
+250 mV			
5	0.09	NS	NS
6	0.66	0.008	77
7	0.0008	NS	NS
8	0.58	NS	NS
-150 mV			
5	0.96	0.12	6.0
6	0.85	0.12	5.7
7	0.99	0.24	2.9
8	0.97	0.17	4.1
[1] NS indicates rate constant was not significantly ($p < 0.05$) different from zero.			

The RDX transformation product, MNX, appeared in all treatments. Aqueous concentrations generally increased over time in the +500- and +250-mV tests (Figure 5). By Day 15, solution concentrations in the +500-mV test ranged from 0.07 mg/L at pH 8 to 0.14 mg/L at pH 7. The moderately reducing (+250-mV) test results showed an increase in MNX concentrations over time in the pH 6, 7, and 8 treatments to approximately 0.1 mg/L and a disappearance of MNX in solution by Day 15 in the pH 5 tests. The disappearance of MNX in the +250-mV tests was accompanied by the appearance of 0.058 mg/L DNX and
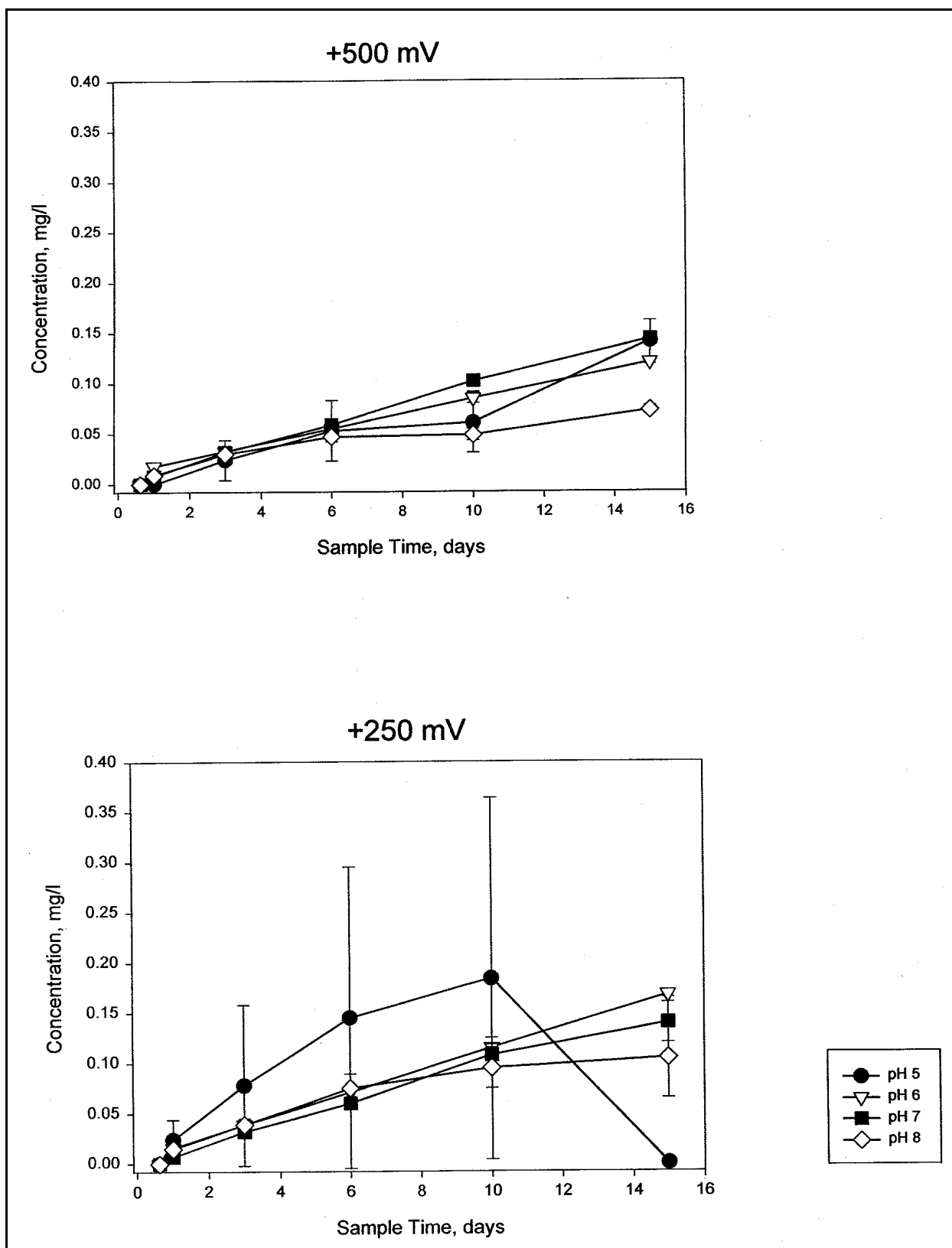
Figure 5.   MNX aqueous concentrations over time at each pH/Eh condition

0.018 mg/L TNX in the pH 8 tests. This marked the only detection of DNX and TNX in the +500-mV and +250-mV treatments.

As reported by McCormick, Cornell, and Kaplan (1984a), the disappearance of RDX in the -150-mV test was accompanied by the appearance of MNX, DNX, and TNX derivatives of RDX formed by sequential reductions of the nitro groups to nitroso groups (Figure 6). MNX appeared in solution within 24 hr following addition of RDX with a corresponding decrease in RDX concentrations. Similarly, DNX and TNX solution concentrations increased as MNX concentrations began to decrease (Figure 6). Peak DNX and TNX aqueous concentrations occurred in the pH 7, -150-mV tests (0.24 and 0.18 mg/L, respectively).

HMX, a homologue and coproduction product of RDX, was also present in solution during the entire incubation period. Production grade RDX generally contains significant amounts of HMX, from 8 to 13 percent (Rosenblatt 1981). The RDX used for the Eh/pH incubations contained 12 percent HMX. HMX concentrations in solution remained relatively stable over time in the +500- and +250-mV tests, but decreased over time in the -150-mV tests (Figure 7). Disappearance of HMX was slower than disappearance of RDX, which agrees with results reported by McCormick, Cornell, and Kaplan (1984a) for anaerobic sewage sludge. The rate coefficients (k) for HMX in the anaerobic systems were lower (0.03 and 0.06) than for the anaerobic systems for RDX (0.12 to 0.24) (Table 3). The half lives for HMX ranged from 11 and 22 hr while half lives for RDX ranged from 4.1 to 6 hr.

Redox potential had a marked effect on RDX recovery. RDX was relatively stable at +500 mV for all pH levels (Figure 8). At +250 mV, RDX was less stable, particularly at pH 8, where only 16 percent of the unlabeled RDX was recovered from the water and soil phases. RDX was least stable at -150 mV, where only 1.7 percent of the added RDX remained in the pH 7 treatment following 15 days of incubation (Figure 8). These results indicate that RDX is relatively stable in the systems under oxidizing and moderately reducing conditions at pH 7 or lower and unstable in highly reduced systems. McCormick, Cornell, and Kaplan (1984a) observed similar results in nutrient broth culture studies and found that the biotransformation of RDX occurred only under anaerobic conditions with no activity observed under aerobic conditions.

Mass Balance of [^{14}C] RDX

Most of the radioactivity remained in the aqueous phase of the soil:water slurries except in the -150 mV, pH 7 tests, where 80 percent was mineralized as CO_2 (Table 4). Sikka et al. (1980) reported similar findings in sediment-amended wastewater reactors where the evolution of $^{14}CO_2$ accounted for 80 percent of the radiolabeled carbon in the tests.
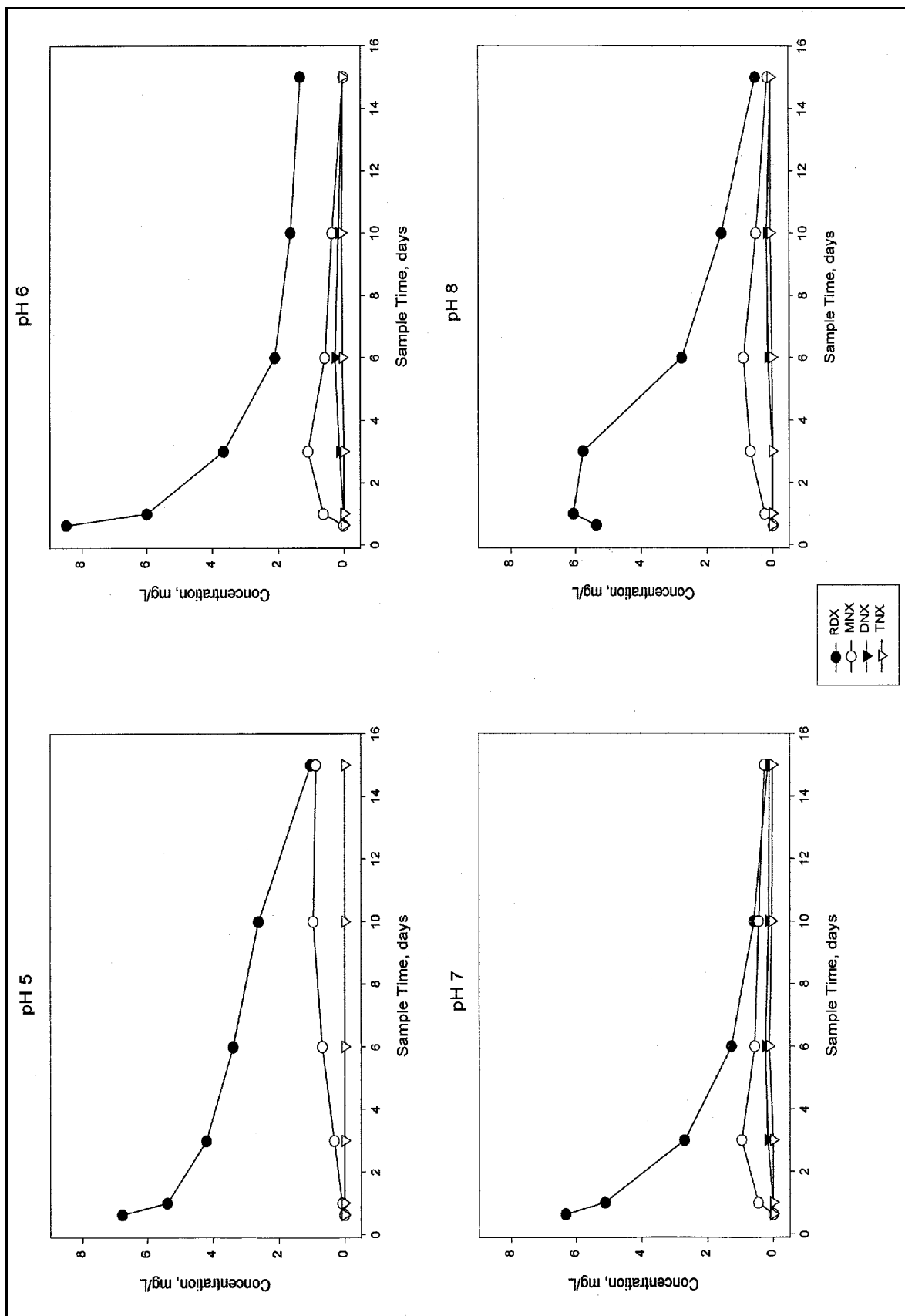
Figure 6. RDX and its transformation products in solution at each pH over time at -150 mV
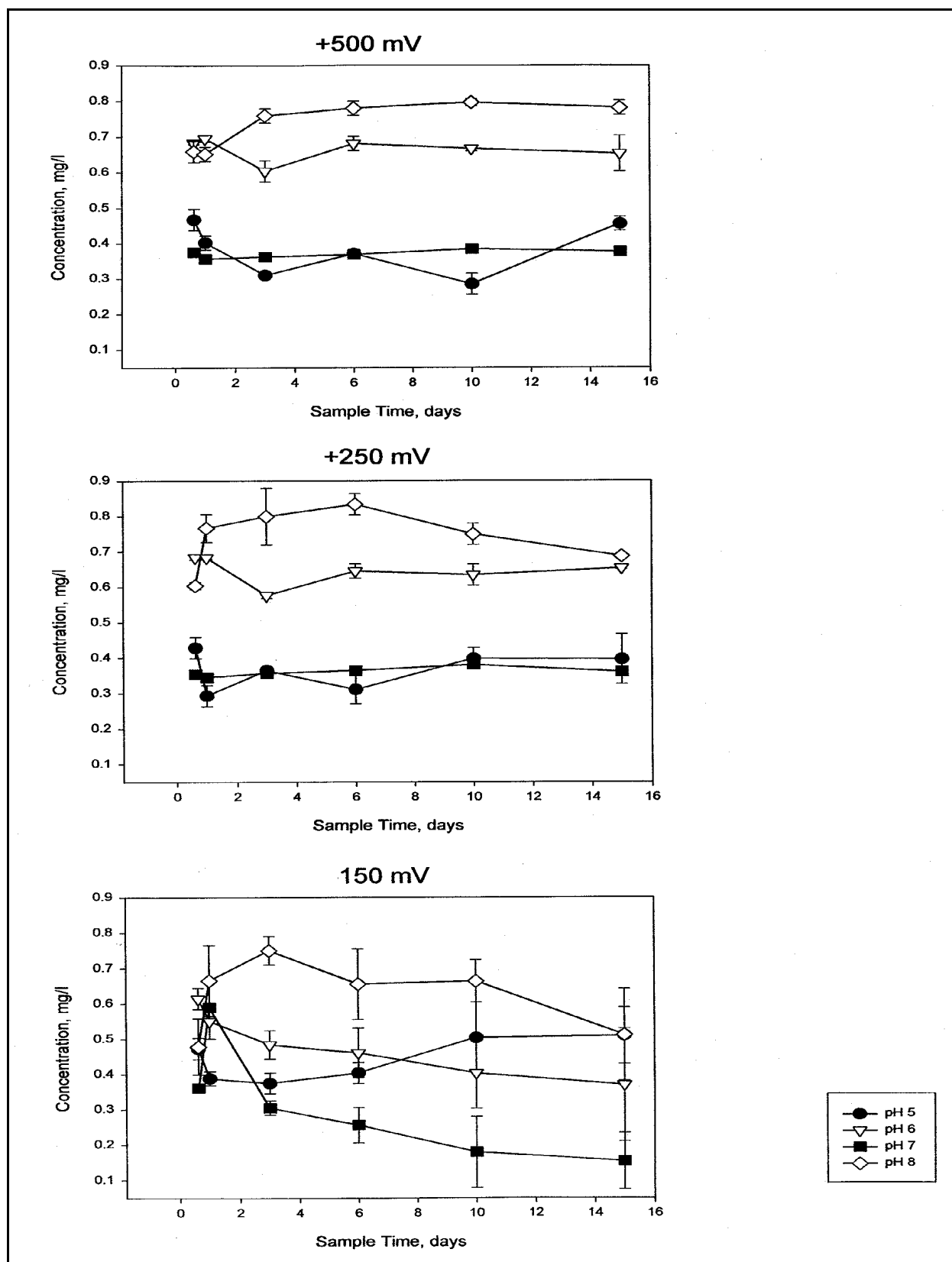
Figure 7. HMX aqueous concentrations over time at each pH/Eh condition in RDX test

Table 3
Regression Coefficient (r^2), First-Order Rate Coefficient (k), and Half Life ($t_{1/2}$) for HMX in RDX Test at Each Eh/pH Treatment

pH	r^2	k, hr^{-1}	$t_{1/2}$, hr
+500 mV			
5	0.004	NS[1]	NS
6	0.04	NS	NS
7	0.46	NS	NS
8	0.59	NS	NS
+250 mv			
5	0.10	NS	NS
6	0.03	NS	NS
7	0.39	NS	NS
8	0.0006	NS	NS
-150 mV			
5	0.44	NS	NS
6	0.91	0.03	22
7	0.98	0.06	11
8	0.04	NS	NS

[1] NS indicates that the rate constant was not significantly ($p < 0.05$) different from zero.

Table 4
Percent Recoveries of Radioactivity in Each Phase of the [^{14}C] RDX Mass Balance Studies

	+500 mV				-150 mV			
pH	Soil	Water	KOH	Total	Soil	Water	KOH	Total
5	25.7	64.8	2.87	93.4	15.0	50.6	18.1	83.7
7	7.03	87.8	5.35	100.2	3.19	14.3	80.1	97.6
8	19.9	68.4	2.74	91.0	19.9	46.4	17.6	83.9

Mineralization was higher in the pH 5 and 8 reactors under anaerobic conditions (~18 percent) compared with mineralization in the oxidized reactors under the same pH conditions (~ 3 percent). Mineralization rates were higher under anaerobic conditions compared with aerobic conditions, regardless of pH (Figure 9). The rate of anaerobic mineralization was highest at pH 7 (19.6 μg/day).
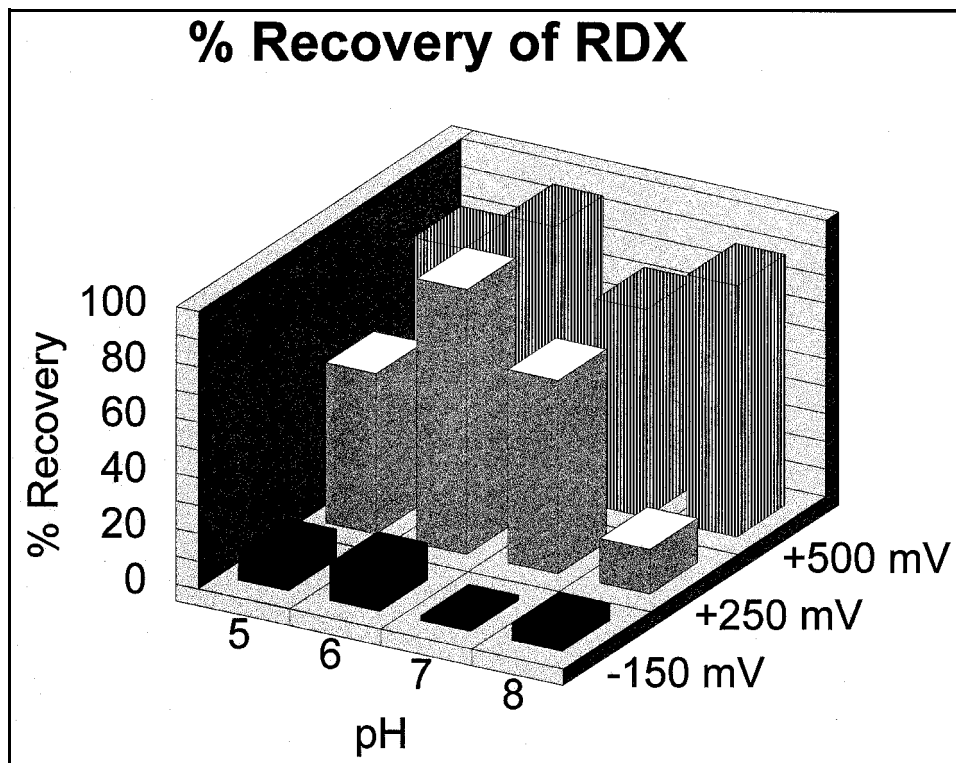
% Recovery of RDX

Figure 8. Percent recovery of RDX (aqueous plus soil) 15 days after addition of
RDX

Effects of Eh and pH on HMX

   HMX aqueous concentrations were relatively stable over time with the
exception of the pH 6 and 7, -150-mV tests in which HMX concentrations
decreased over time (Figure 10). These results reveal trends similar to those for
HMX that co-occurred with RDX treatments. A first-order kinetic equation was
used to describe the rate of HMX disappearance. HMX removal from pH 6 and
7 solutions was more rapid in the -150-mV than in the +500-mV test (Table 5).
The HMX removal rate in the +250-mV, pH 7 treatment approximated that in
the -150-mV tests (Table 5).

   Eh and pH affected HMX sorption characteristics (Figure 11). At pH 8 in the
+500-mV tests, less HMX was in solution than at pH 5, 6, and 7. HMX soil
concentrations in the pH 8 test (10.2 mg) were also higher than the concentra-
tions in the pH 5, 6, and 7 treatments (Figure 11). Single-point distribution coeffi-
cients (Kd) for each Eh and pH were calculated from measured aqueous and soil
HMX concentrations on Day 21. Kds were lowest under highly anaerobic condi-
tions at all pH levels indicating decreased soil sorption under anaerobic conditions
(Table 6). Effects of pH on sorption were noted only in the +500-mV treatment,
where sorption at pH 8 exceeded that observed at lower pH by a factor of approxi-
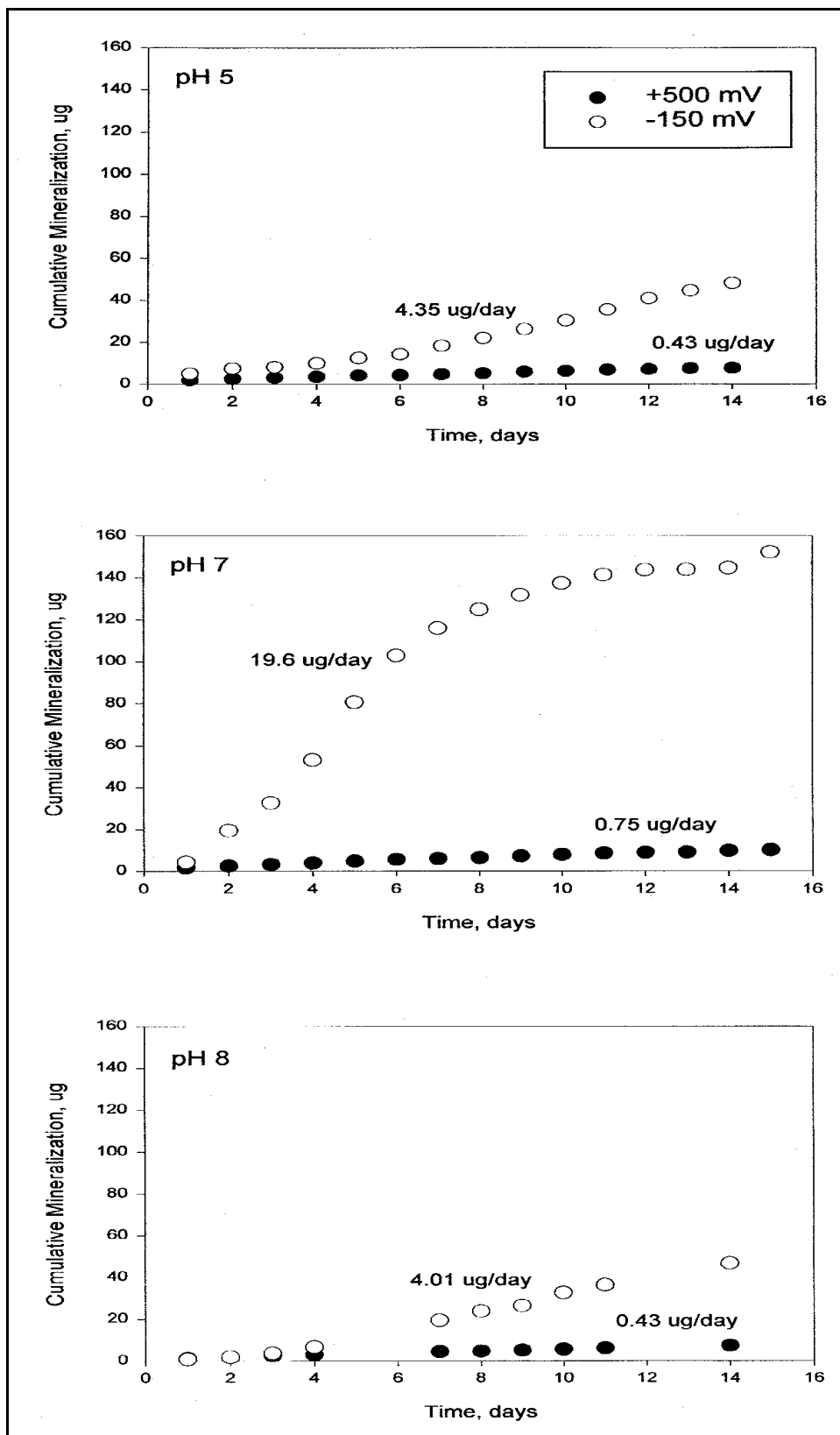mately 8. These results indicate that HMX sorption will be lowest under highly

Figure 9.   Cumulative mineralization rate for RDX in mass balance reactors
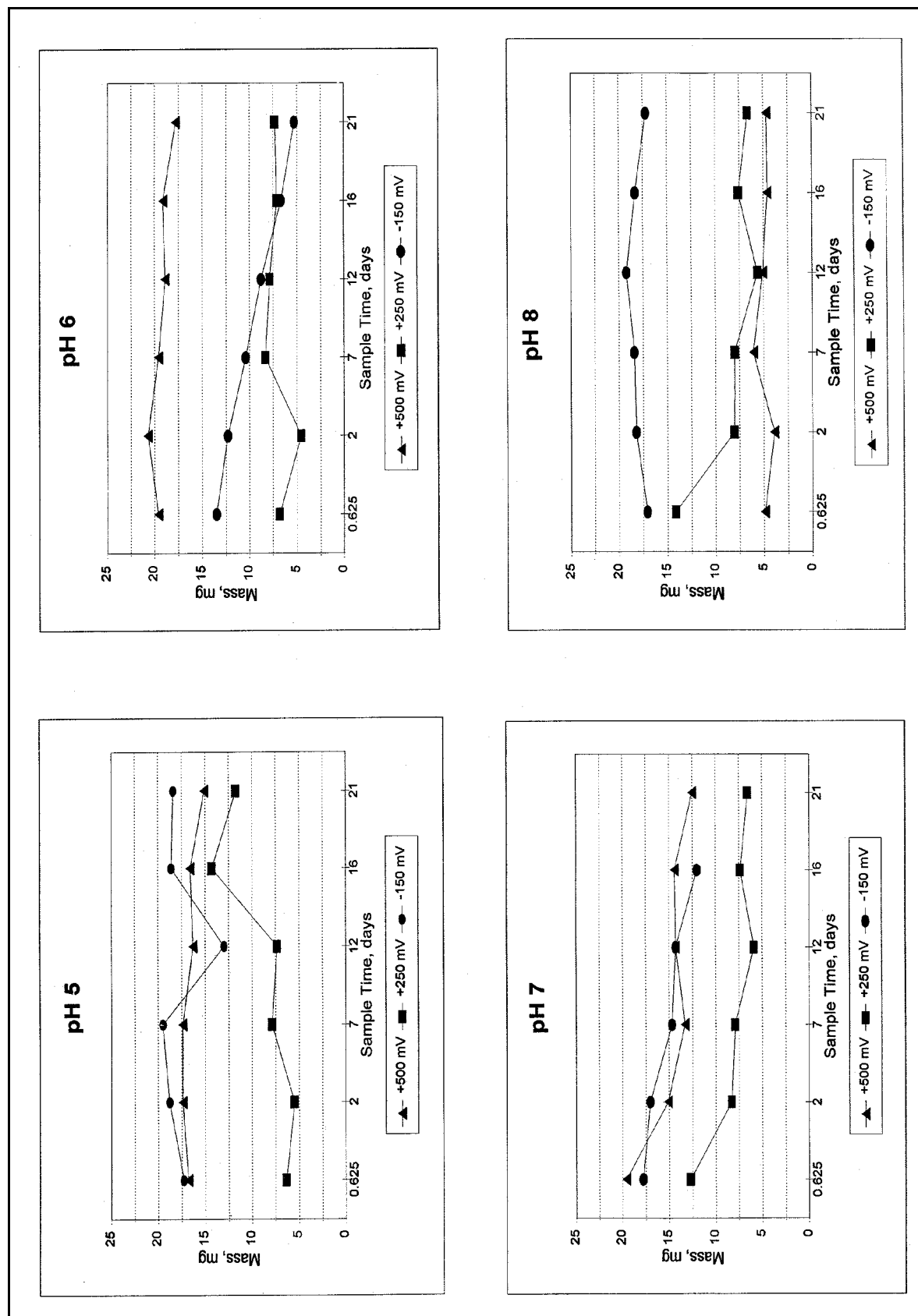
Figure 10. HMX aqueous concentrations over time at each pH level

Table 5
Regression Coefficient (r^2), First-Order Rate Coefficient (k), and Half Life ($t_{1/2}$) for HMX at Each Eh/pH Treatment

pH	r^2	k, hr^{-1}	$t_{1/2}$, hr
+500 mV			
5	0.66	0.0005	1,386
6	0.76	0.005	139
7	0.53	NS[1]	NS
8	0.002	NS	NS
+250 mv			
5	0.75	0.04	17.3
6	0.21	NS	NS
7	0.55	NS	NS
8	0.46	NS	NS
-150 mV			
5	0.006	NS	NS
6	0.99	0.05	15.4
7	0.95	0.02	30.1
8	0.0008	NS	NS
[1] NS indicates that the rate constant was not significantly ($p < 0.05$) different from zero.			

reduced conditions. Under highly aerobic conditions, sorption was highest at pH 8. Moderately reducing conditions result in the highest adsorption of HMX by soil over a wide range of pHs.

Redox potential and pH significantly affected HMX stability. HMX was relatively stable under most Eh/pH conditions. HMX was most stable at +500 mV, pH 6 with 96 percent of the added HMX remaining in the system. HMX was least stable in the -150-mV test at pH 6 where 25 percent remained in the system (Figure 12), mirroring results observed in culture studies (McCormick, Cornell, and Kaplan 1984a). These results indicate that HMX in soil is relatively stable under a wide variety of redox and pH conditions and least stable under highly reducing conditions at pH 6.

Production of the transformation product MN-HMX was strongly related to redox potential (Figure 13). The -150-mV pH 6 and 8 treatments showed the highest aqueous concentration by Day 21 of sampling. These results are consistent with those of McCormick, Cornell, and Kaplan (1984a), who saw only negligible HMX transformation under aerobic conditions. McCormick, Cornell,

Figure 11.   Mass of HMX remaining (aqueous and soil phases) 21 days after addition of HMX at various Eh and pH conditions

Table 6
Mean *Kds* (L/kg) (standard error (n = 3)) for Day 21 HMX Water and Soil Concentrations

pH	+500 mV	+250 mV	-150 mV
5	6.13 (0.42)	16.7 (5.6)	1.80 (0.02)
6	4.32 (0.86)	23.8 (8.2)	1.25 (0.28)
7	10.1 (0.84)	19.8 (1.7)	4.41 (2.4)
8	37.7 (2.8)	20.0 (4.0)	1.97 (0.16)
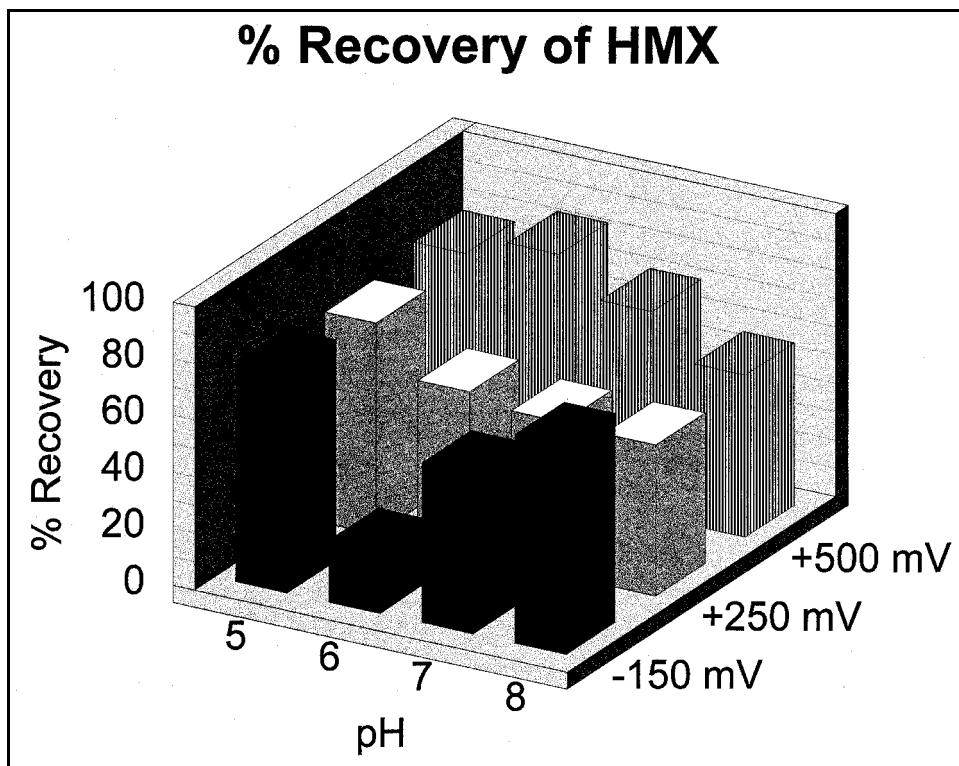
Figure 12. Percent recovery of HMX (aqueous plus soil) 21 days after addition of HMX

and Kaplan (1984b) found that HMX persisted in activated sludge except under anaerobic conditions where reduction to mononitroso, dinitroso, and trinitroso derivatives occurred. Soil concentrations of MN-HMX were also highest in the -150-mV system, reaching a concentration of 7.3 mg in the pH 6 test (Figure 13).
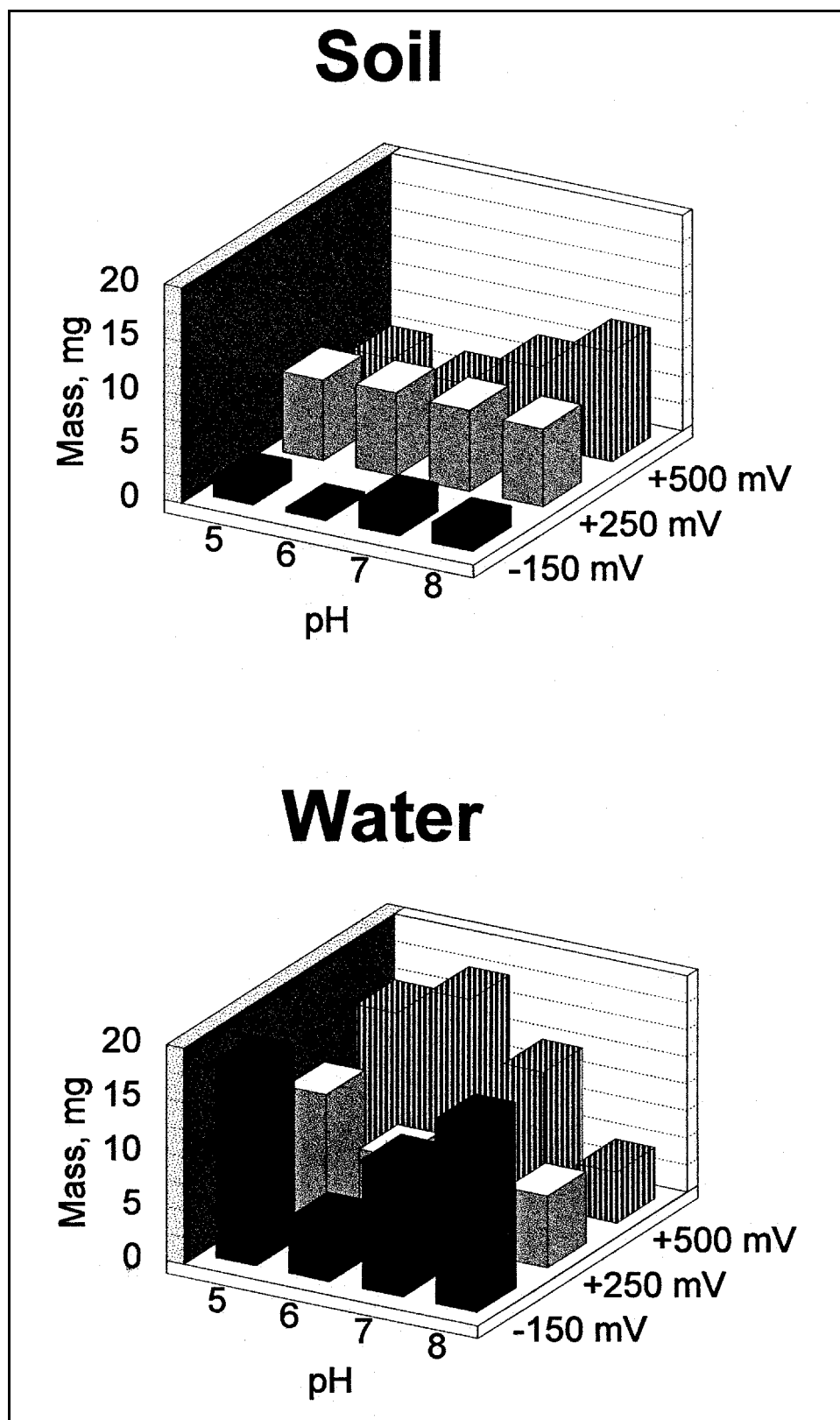
Figure 13.   Mass of MN-HMX remaining (aqueous and soil phases) 21 days after addition of 26 mg HMX at various Eh and pH conditions

4   Conclusions

RDX added to soils was least stable under highly reduced conditions. Oxidizing (+500-mV) and moderately reducing (+250-mV) conditions did not significantly affect RDX stability except at the higher pH level of 8 at +250 mV. The pH had a marked effect on mineralization in the anaerobic reactors with 80 percent of the radioactivity recovered as $^{14}CO_2$ at pH 7 compared with 18 percent at pH 5 and 8. Anaerobic conditions 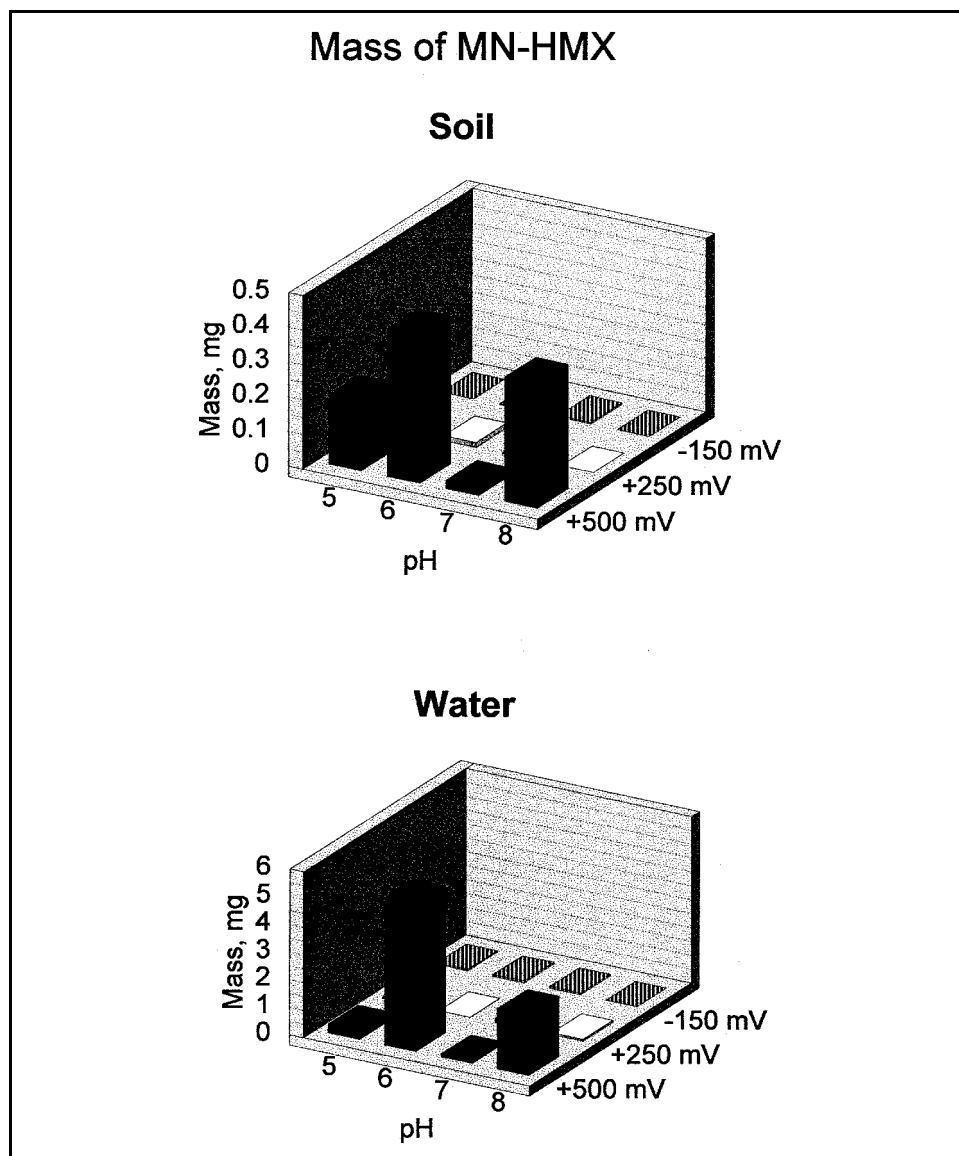promoted increased transformation of RDX to MNX. RDX sorption was affected by Eh and pH. Anaerobic conditions decreased soil sorption, and at +250 mV, sorption was highest at pH 8.

RDX in groundwater moving into an area of intense reduction would not persist under normal pH conditions. RDX moving into moderately reducing or oxidizing conditions would be highly mobile and persistent.

HMX added to soils was least stable under highly reducing conditions, especially at pH 6.   Eh and pH conditions affected the sorption characteristics of HMX. Highly anaerobic conditions decreased soil sorption, whereas moderately reducing conditions promoted sorption at all pH values. Under highly oxidizing conditions, a high pH (pH 8) increased HMX sorption. Results of these investigations imply that HMX moving into groundwater would be persistent except when under highly reducing conditions and a pH near 6.

References

Brannon, J. M. (1983). "The transformation, fixation, and mobilization of arsenic and antimony in contaminated sediments," Ph.D. diss., Louisiana State University, Baton Rouge, LA.

Burton, D. T., and Turley, S. D. (1995). "Reduction of hexahydro-1,3,5,-trinitro-1,3,5-triazine (RDX) toxicity to the cladoceran *Ceriodaphnia dubia* following photolysis in sunlight," *Bull. Environ. Contam. Toxicol.* 55, 89-95.

Cataldo, D. A., Harvey, S. D., Fellow, R. J., Bean, R. M., and McVeety, B. D. (1990). "An evaluation of the environmental fate and behavior of munitions material (TNT, RDX) in soil and plant systems: Environmental fate and behavior of TNT," Final Report, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Cholakis, J. M., Wong, L. C. K., Van Goethem, D. L., Minor, J., Short, R., Sprinz, H., and Ellis, H. V., III. (1980). "Mammalian toxicological evaluation of RDX," Contract No. DAMD17-78-C-8027, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Crawford, R. L. (1995). *Biodegradation of nitroaromatic compounds - Biodegradation of nitrated munition compound and herbicides by obligately anaerobic bacteria.* J. C. Spain, ed., Plenum Press, New York.

Etnier, E. L. (1986). "Water quality criteria for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)," Final Report, AD-ORNL-6178, Oak Ridge National Laboratory, Oak Ridge, TN.

Fair, G. M., Geyer, J. C., and Okun, D. A. (1968). "Water and wastewater engineering, 2." *Water purification and wastewater treatment and disposal.* John Wiley and Sons, Inc., New York.

Greene, B., Kaplan, D. L., and Kaplan, A. M. (1985). "Degradation of pink water compounds in soil - TNT, RDX, HMX," NATICK Technical Report 85-046, U.S. Army Natick Research and Development Center, Natick, MA.

Hansen, E., Stone, J., Shetley, P., and Bruce, B. (1984). "Cornhusker Army Ammunition Plant, sampling and analysis - Phase III," U.S. Army Toxic and Hazardous Materials Agency, Report No. DRXTH-AS-CR-84288, Aberdeen Proving Ground, MD.

Hoffsommer, J. C., Kaplan, L. A., Glover, D. J., Kubose, D. A., Dickinson, C., Goya, H., and Sitzmann, M. E. (1978). "Biodegradability of TNT: A three-year pilot plant study," NSWC/WOL- 77-136, Naval Surface Weapons Center, Silver Spring, MD.

Layton, D., Mallon, B., Mitchell, W., Hall, L., Fish, R., Perry, L., Snyder, G., Bogen, K., Malloch, W., Ham, C., and Dowd, P. (1987). "Data base assessment of the health and environmental effects of conventional weapons demilitarization: Explosives and their co-contaminants," Report No. 83, Lawrence Livermore National Laboratory, Livermore, CA.

Leggett, D. C. (1985). "Sorption of military explosive contaminants on bentonite drilling muds," CRREL Report 85-18, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

McCormick, N. G., Cornell, J. H., and Kaplan, A. M. (1984a). "The anaerobic biotransformation of RDX, HMX, and their acetylated derivatives," NATICK Technical Report 85-007, U.S. Army NATICK Research and Development Center, Natick, MA.

_____. (1984b). "The fate of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and related compounds in anaerobic denitrifying continuous culture systems using simulated wastewater," TR-85/008, U.S. Army Natick Research and Development Laboratory, Natick, MA.

Merck and Co. (1983). *The Merck index*. 10th ed., Rahway, NJ, 292-293.

Patrick, W. H., Jr., Williams, B. G., and Moraghan, J. T. (1973). "A simple system for controlling redox potential and pH in soil suspensions," *Soil Science Soc. Am. Proc.* 37, 331-332.

Pennington, J. C., and Patrick, W. H., Jr. (1990). "Adsorption and desorption of 2,4,6-trinitrotoluene by soils," *Journal of Environmental Quality* 19, 559-567.

Rosenblatt, D. H. (1981). "Environmental risk assessment for four munitions-related contaminants at Savanna Army Depot Activity," Technical Report 8110, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Selim, H. M., Xue, S. K., and Iskandar, I. K. (1995). Transport of 2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine in soils," *Soil Science* 160(5), 328-339.

Sikka, H., C., Banerjee, S., Pack, E. J., and Appleton, H. T. (1980). "Environmental fate of RDX and TNT," Technical Report 81-538, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Spalding, R. F., and Fulton, J. W. (1988). "Groundwater munition residues and nitrate near Grand Island, Nebraska, U.S.A.," *Journal of Contaminant Hydrology* 2, 139-153.

Spanggord, R. J., Mill, T., Chou, T., Mabey, W. R., Smith, J. H., and Shonh, L. (1980). "Environmental fate studies on certain munition wastewater constituents - Final Report, Phase II - Laboratory studies," Technical Report Project No. LSU 7934, Defense Technical Information Center, Alexandria, VA.

U.S. Environmental Protection Agency. (1990). "Test methods for evaluating solid wastes," SW-846, Washington, DC.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 1998	3. REPORT TYPE AND DATES COVERED Final report

4. TITLE AND SUBTITLE

Transformation of RDX and HMX Under Controlled Eh/pH Conditions

5. FUNDING NUMBERS

6. AUTHOR(S)

Cynthia B. Price, James M. Brannon, Sally L. Yost

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199; DynTel Corporation, 3530 Manor Drive, Vicksburg, MS 39180-5693

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report IRRP-98-2

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The presence of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in soil and groundwater can present serious environmental problems. An understanding of the processes that control the mobility and transformation of RDX and HMX in soils and water is needed in order to fully evaluate any problems with release of these explosives. The objective of this study was to determine the effects of redox potential (Eh) and pH on RDX and HMX transformation in soil.

Laboratory investigations included testing at three redox potentials and four pH levels. A 10:1 (water:soil) suspension spiked with 10 mg of RDX/L or HMX/L was used. The aqueous phase was sampled for RDX, HMX, and transformation products over a period of time. Soils were analyzed at completion of the test incubations.

Results in the RDX tests showed that RDX was least stable under highly anaerobic conditions (-150 mV). Oxidizing (+500 mV) and moderately reducing (+250 mV) conditions did not significantly affect RDX stability. Radiolabeled RDX recovery tests showed pH to have a marked effect on mineralization in the anaerobic reactors. At pH 7, 80 percent of the radioactivity was recovered as $^{14}CO_2$ as compared with much lower percentages at pH 5 and 8.

(Continued)

14. SUBJECT TERMS

Groundwater
HMX transformation
pH
RDX transformation
Redox potential
Soil

15. NUMBER OF PAGES

32

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

13. (Concluded).

Results in the HMX tests showed that HMX was least stable under highly reducing conditions, specifically at pH 6. Soil sorption of HMX was affected by Eh and pH. Decreased HMX sorption occurred under highly anaerobic conditions, and increased sorption occurred under highly oxidizing conditions, especially at a pH of 8.

The data obtained in this study indicate that RDX in groundwater moving into an area of intense reduction would not persist under neutral pH conditions. RDX moving into areas of oxidizing or moderately reducing conditions would be mobile and persistent. HMX moving into groundwater would be mobile and persistent under all Eh and pH conditions with the exception of highly reducing conditions at or near a pH of 6.