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

Installation Restoration Research Program

RDX and HMX Sorption
in Thin Disk Soil Columns

by   Dan M. Townsend, D. Dean Adrian,
     Louisiana State University

Tommy E. Myers, WES

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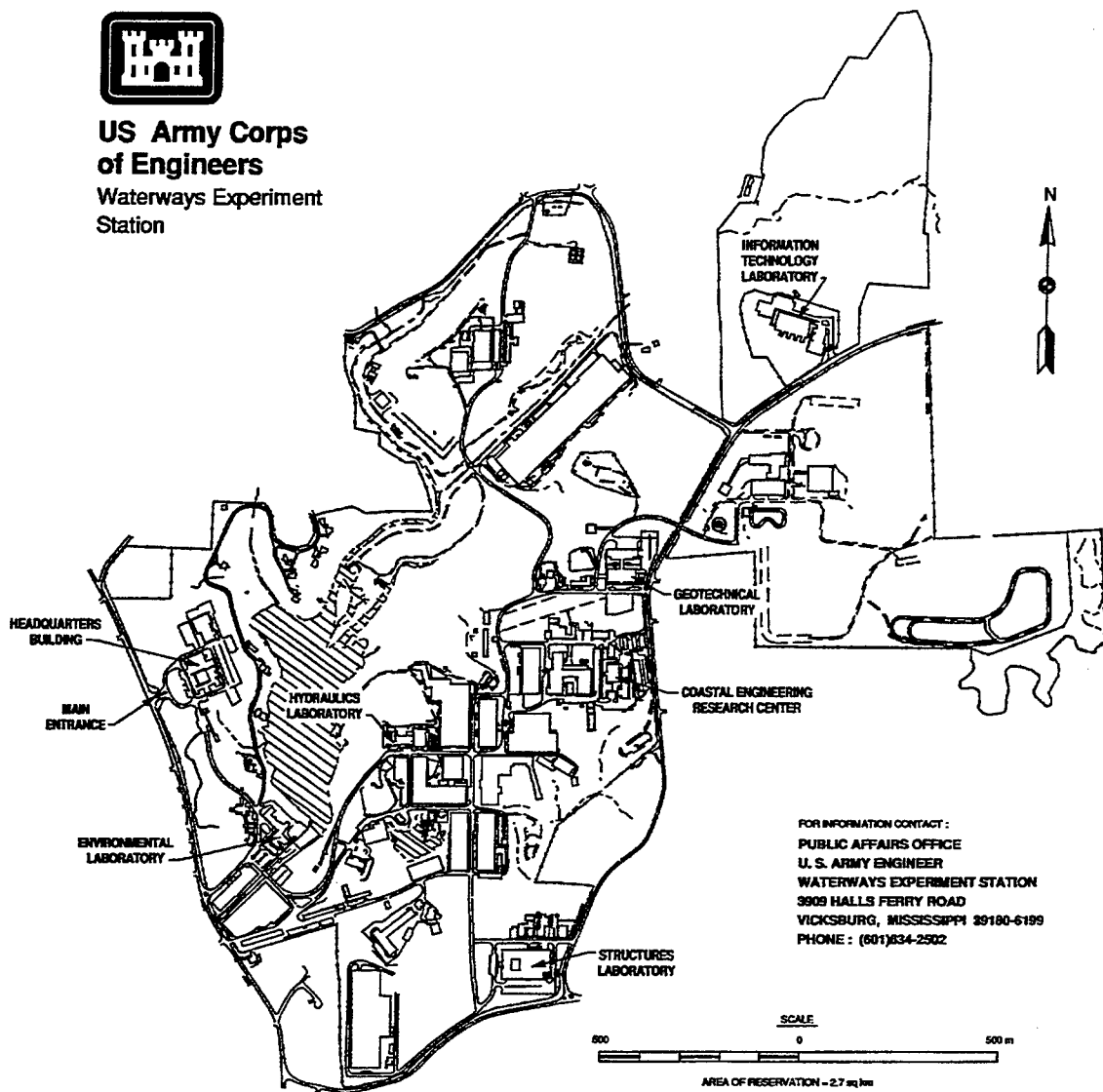Vicksburg, MS   39180-6199

Final report

**US Army Corps
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STRUCTURES
LABORATORY

SCALE

500   0   500 m

AREA OF RESERVATION = 2.7 sq km

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Preface

The work reported was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) for Headquarters, U.S. Army Corps of Engineers (HQUSACE). Funding was provided by the HQUSACE Installation Restoration Research Program (IRRP), Work Unit AF25-GW-003. Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, HQUSACE. The Technical Monitors for this work unit were Messrs. George O'Rourke and David Becker. The IRRP Program Manager was Dr. M. John Cullinane.

This report was prepared by Mr. Dan M. Townsend, Contract-Graduate Student, Louisiana State University, Baton Rouge, LA, assigned to the Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL); Mr. Tommy E. Myers, ERB, EED, EL; and Dr. D. Dean Adrian, Louisiana State University, Baton Rouge, LA. Mr. C. J. McGrath, Water Quality and Contaminant Modeling Branch (ES-Q), Environmental Processes and Effects Division (EPED), EL, and Dr. James M. Brannon, Ecosystem Processes and Effects Branch (EPEB), EPED, EL, were technical reviewers for this report. Chemical analyses were performed by Ms. Erika McCormick and Ms. Karen Myers, Environmental Chemistry Branch, EED, EL. Mr. Andrew J. Green, AScI Corporation, assisted with soil column operation and sampling.

The work was conducted under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, and Dr. John W. Keeley, Director, EL.

Dr. Robert W. Whalin was Technical Director of WES. Commander was COL Bruce K. Howard, EN.

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> Report IRRP-96-8, U.S. Army Engineer Waterways Experiment
> Station, Vicksburg, MS.

1 Introduction

Background

The fate and transport of explosives through porous media have become of greater concern recently, due in part to the increased number of military installation closings. Many of these installations were involved in the manufacture and packing of munitions. As a result of these operations, subsurface contamination by explosives poses a potential threat to groundwater resources at many of these munition plants (Spaulding and Fulton 1988; Pugh 1982). Containment and remediation efforts are under way at many of these sites.

At many military installations, 2,3,5-trinitro-1,3,5-triazine (RDX) and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) subsurface contamination is present in addition to contamination by 2,4,6-trinitrotoluene (TNT). Information on RDX and HMX subsurface transport is more limited than information on TNT subsurface transport and is inadequate for accurate transport modeling. Because transport models are used for planning containment and remediation measures and evaluation of natural attenuation, additional research concerning subsurface transport processes potentially affecting RDX and HMX is needed.

Process Overview

Many processes affect the fate and transport of RDX and HMX in soils and groundwater (McGrath 1995). These processes include, but are not limited to, convection, hydrodynamic dispersion, biodegradation, abiotic transformations, soil sorption, dissolution, and diffusion. The majority of the available literature on RDX and HMX has focused on sorption and irreversible disappearance of these compounds.

RDX sorption

The sorption of RDX on soils has been studied by several researchers (Sikka et al. 1980; Leggett 1985; Ainsworth et al. 1993; Selim and Iskandar 1994; Myers et al. in preparation). Each of these researchers found that RDX

was extremely mobile and could be described well using a linear equilibrium approach. Leggett (1985) noted that sorption values for RDX on bentonite were similar to sorption values for RDX on natural sediments, suggesting that the clay content of natural soils and sediments is important to the sorption of RDX. Reported linear equilibrium distribution coefficients (K_d) for RDX range from <1 to 7.8 L/kg (Townsend and Myers 1996).

HMX sorption

The information on HMX sorption is more limited than the information on RDX sorption. The available information on HMX sorption suggests that HMX is mobile, although not as mobile as RDX. Nonlinear or nonequilibrium HMX sorption (breakthrough curve tailing) has been observed (Myers et al. in preparation; Pennington et al. 1995). Linear equilibrium distribution coefficients (K_d) for HMX as high as 13 L/kg have been reported (Townsend and Myers 1996).

RDX disappearance

Disappearance of RDX from soils and sediments has been noted by several investigators (Sikka et al. 1980; McCormick, Cornell, and Kaplan 1981; Pennington et al. 1995; Myers et al. in preparation). Each of these investigators suggested that RDX disappearance may be attributed to biological transformation, that is, biodegradation. However, with the exception of McCormick, Cornell, and Kaplan (1981), RDX transformation products were not analyzed. In the absence of measured transformation products, mass balance calculations can be misinterpreted since discrepancies in RDX mass cannot be unequivocally attributed to transformation.

An anaerobic biodegradation scheme (Figure 1) has been proposed (McCormick, Cornell, and Kaplan 1981). According to this scheme, RDX is biodegraded via successive reduction of nitro groups. After several steps of reduction and ring cleavage, methanol, formaldehyde, and hydrazines are produced. The work of McCormick, Cornell, and Kaplan (1981) suggests products that have not been analyzed in laboratory transport experiments are also produced.

Sikka et al. (1980) monitored the concentrations of RDX in water samples over time. The results showed that little or no loss of RDX occurred in water samples alone or in water samples in the presence of yeast extract. In samples amended with 1 percent sediment, significant loss of RDX, which could not be accounted for as adsorption to the sediment, was observed.

An elution curve for a field-contaminated soil (Pennington et al. 1995) suggested RDX disappearance. An RDX first-order disappearance rate constant of approximately 0.1 hr^{-1} was obtained from the elution curve.

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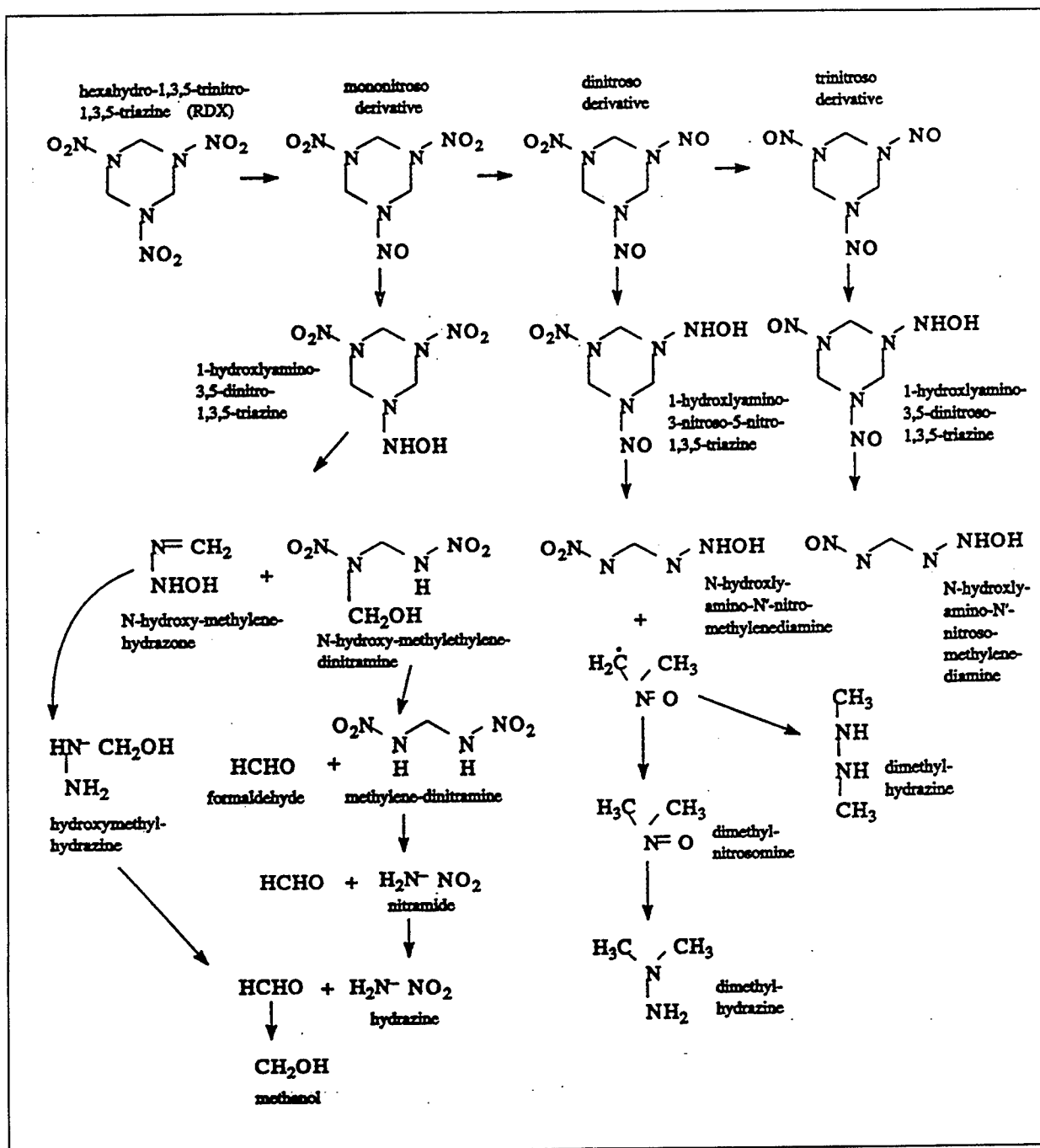
Figure 1. RDX transformation pathway scheme (from McGrath 1995, after McCormick, Cornell, and Kaplan 1981)

Myers et al. (in preparation) conducted aerobic RDX batch experiments with one of the soils used in this study (Yokena clay) under both biotic and abiotic conditions. Differences in RDX recoveries between the biotic (63 percent) and the abiotic (91 percent) tests suggested significant amounts of RDX biodegradation. Myers et al. (in preparation) also conducted column studies with the same soils used in this study. Mass balance analysis indicated

significant RDX disappearance in the silt and clay and no RDX disappearance in the sand. First-order disappearance rate constants for the silt and clay were 6×10^{-3} and 14×10^{-3} hr^{-1}, respectively.

HMX disappearance

Less information is available on HMX disappearance than on RDX disappearance. There is evidence that disappearance of HMX in soils occurs. Pennington et al. (1995) observed HMX disappearance in an experiment with a field-contaminated soil. An HMX first-order disappearance rate constant of 0.09 hr^{-1} was obtained from the experiment. Myers et al. (in preparation) performed laboratory column experiments with HMX using the same soils used in this study. Mass balance analysis indicated that HMX, like RDX, underwent disappearance in the silt and clay, but not in the sand. First-order disappearance rate constants for the silt and clay were 32×10^{-3} and 4×10^{-3} hr^{-1}, respectively.

Objectives

The objectives of this study were as follows:

a. Use thin disk soil columns to obtain RDX and HMX breakthrough curves for three soils of varying grain-size distributions.

b. Determine RDX and HMX sorption and disappearance parameters from the breakthrough curves.

c. Evaluate nonequilibrium effects using a pause in flow technique.

2 Materials and Methods

Soils

Three soils were used in this study: Tunica silt from Vicksburg, MS, Yokena clay from Vicksburg, MS, and Ottawa sand obtained from U.S. Silica Company, Ottawa, IL. The Tunica silt and Yokena clay soils were previously described by Pennington and Patrick (1990). Soil properties are listed in Table 1, and particle size distributions are shown in Figures 2, 3, and 4.

Table 1
Soil Properties[1]

Properties	Soils		
	Tunica Silt	Yokena Clay	Ottawa Sand
Percent sand	4	2	93
Percent silt	82	36	7
Percent clay	14	62	0
pH	4.54	5.71	**
EC[2]	0.72	2.45	**
FOC[3]	0.006	0.024	**
CEC[4]	17.2	124.9	**
Fe[5]	252	1,252	**
Al[6]	196	160	**
Mn[7]	152	59.6	**
Ca[8]	1.10	0.954	**

[1] Adapted from Pennington and Patrick (1990).
[2] Electrical conductivity (dS m^{-1}).
[3] Fraction organic carbon.
[4] Cation exchange capacity (cmol$_c$ kg^{-1}).
[5] Oxalate extractable metals (mg kg^{-1}).
Note: ** = not measured.
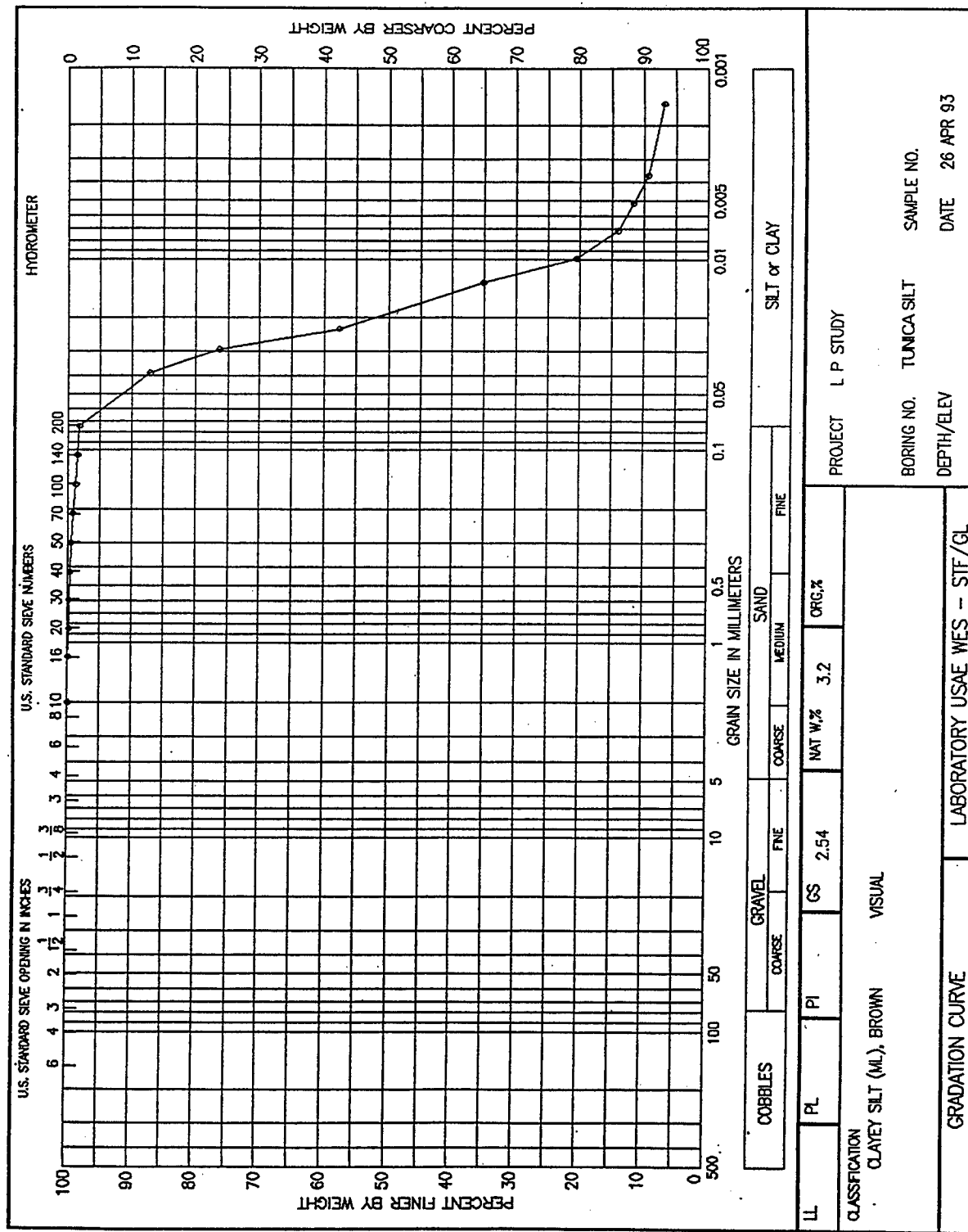
Figure 2. Tunica silt particle size distribution
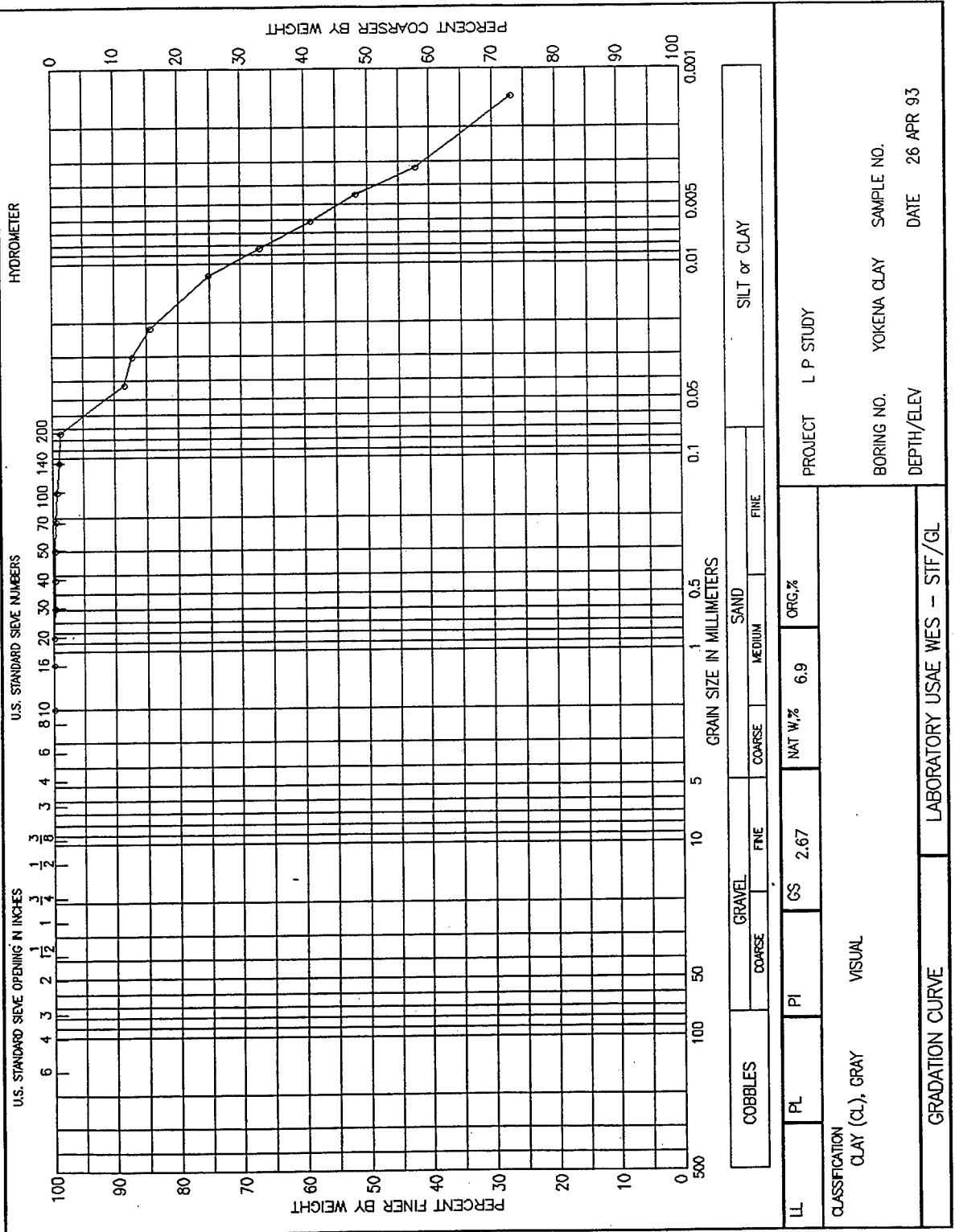
Figure 3.   Yokena clay particle size distribution
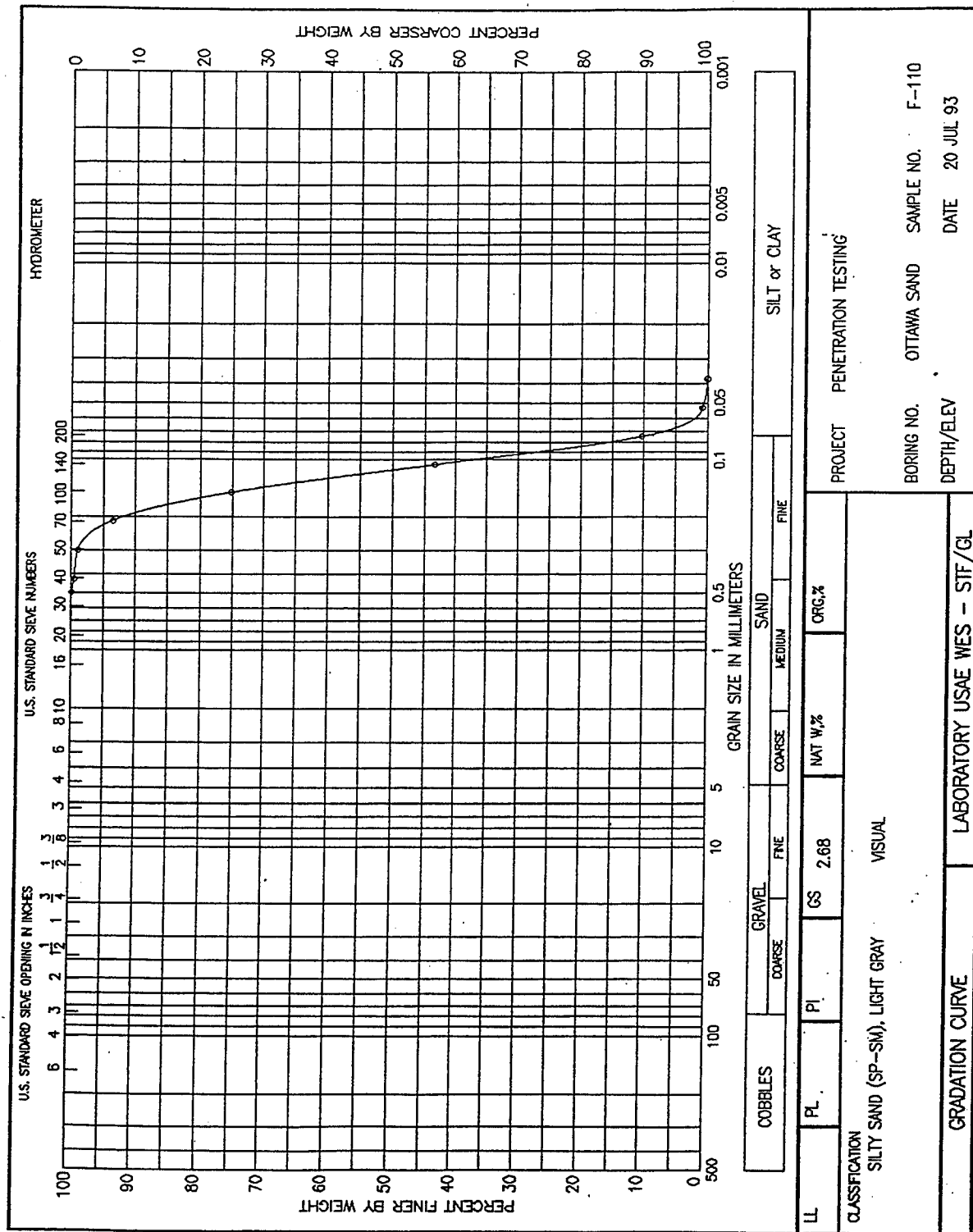
Figure 4. Ottawa sand particle size distribution

Thin Disks

Experiments were conducted in stainless steel columns (Figure 5) 0.32 cm
in length, with a 4.45-cm inside diameter. Stainless steel porous plates
(0.64 cm thick, 100 μm nominal pore diameter, Mott Metallurgical, Farming-
ton, CT) were placed on the inlet and outlet sides of the soil layer. These
plates were used to distribute flow across the soil surface. Rubber O-rings
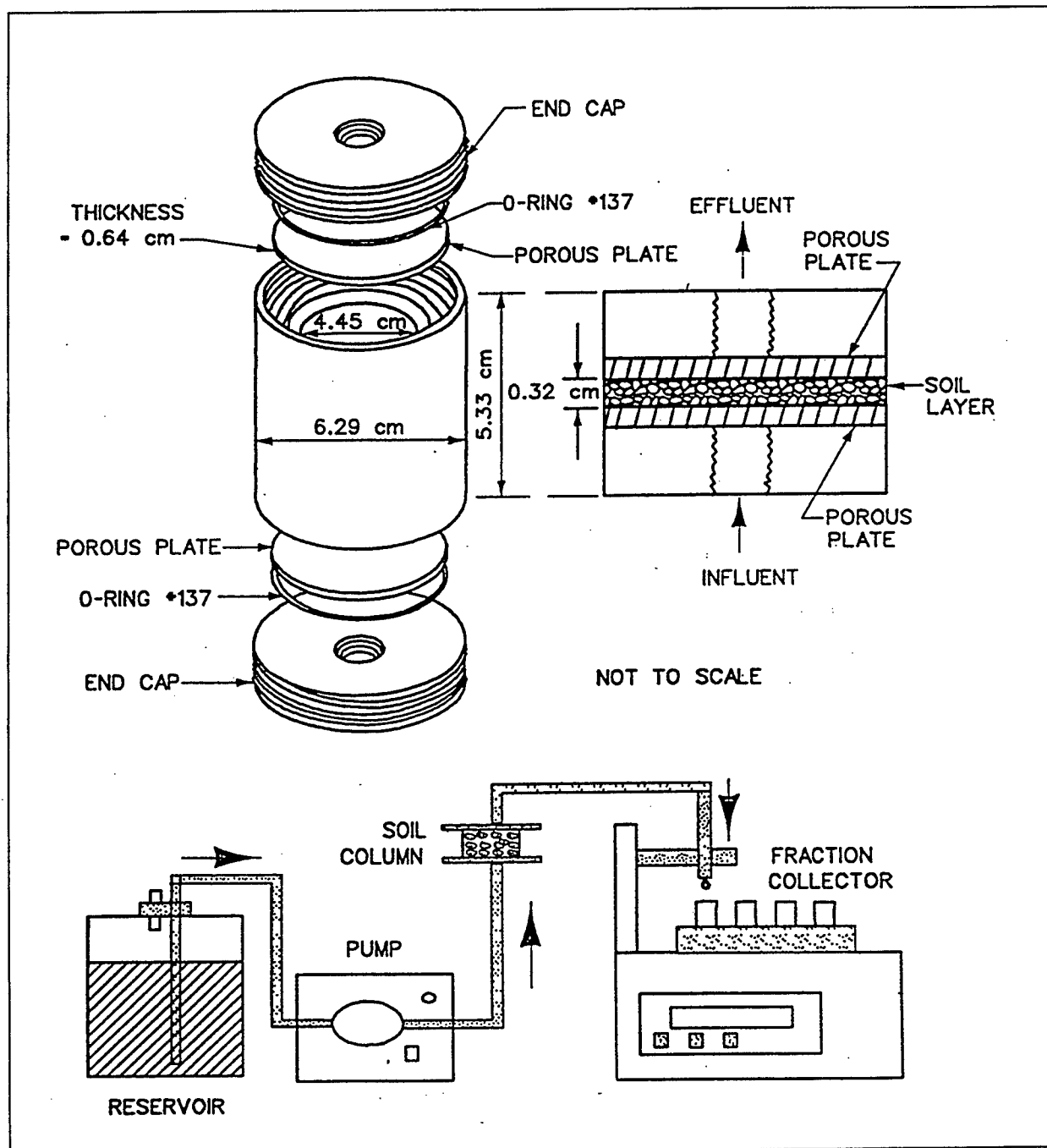
Figure 5. Thin disk schematic and experimental apparatus

(Mississippi Rubber Specialty Company, Vicksburg, MS) were used to seal the end caps. The end caps were connected to stainless steel inlet and outlet tubing.

Disk Loading

In large length-to-diameter columns, the usual column loading procedure is to pack the soil in increments and scarify the surface to minimize bedding planes. Packing was impractical for thin disk columns. Therefore, another loading procedure was developed.

Soils were placed in the columns as slurries, and water was allowed to drain by gravity. To keep soil particles from being trapped in the column threads during this process, an insert, which was a 6.5-cm-long polyvinyl chloride pipe with exterior threads, was designed to protect the column threads. Soil loading was a trial and error process, and the slurry density had to be adjusted for each soil.

Tunica silt

Using measured specific gravity, water content, and an assumed porosity (0.65), the mass of Tunica silt needed for a 0.32-cm soil layer was estimated at 4.55 g. This amount of soil was mixed with distilled-deionized (DDI) water in a clean, oven-dry beaker to give a 6:1 mass of water to mass of soil slurry. The column was clamped to a stand and leveled. After the thread protection insert was in place, the slurry was transferred to the column using a glass stirring rod. The beaker was rinsed thoroughly so as to transfer as much of the soil as possible. The water was allowed to drain under gravity, which took about 20 min. The entire loading process had to be repeated several times until a satisfactory layer was produced. Upon producing a satisfactory layer, a porous plate was placed on top of the soil layer and an end cap was screwed into the disk, holding the porous plate firmly against the soil layer. Soil left on the inside of the column insert was rinsed into the beaker used for the slurry transfer. This beaker was then placed in an oven at 110 °C and dried until all the water was evaporated. It was then weighed on an analytical balance. The soil mass in the column was calculated by difference.

Yokena clay

The mass of Yokena clay needed to give a 0.32-cm soil layer was estimated using specific gravity, water content, and an assumed porosity (0.65). This was calculated to be 4.88 g. On the first loading attempt, an 8:1 water to soil ratio was used, and the slurry was transferred to the column using the same procedure as with the Tunica silt soil. The slurry was allowed to drain

under gravity, which took approximately 75 min. Upon inspection, it was noted that the clay apparently had swelled, making the soil layer thicker than the desired 0.32 cm. The same procedure was followed in a second loading attempt. The water took longer to drain, but the results were similar to the first loading attempt. Loading was also attempted using a slight vacuum to remove water. This procedure produced a very uneven surface on the soil layer.

Because of the swelling, various amounts of soil were used to get a 0.32-cm layer. After several attempts, it was determined that approximately 3.8 g of soil were needed. However, a smooth, even layer was still not achieved. Therefore, using about 3.8 g of soil, the water to soil ratio was changed from 8:1 to approximately 10:1. The slurry was placed on a stir plate and mixed with a magnetic stir bar. This allowed the clay to swell before addition to the column. The slurry was stirred for approximately 4 hr and then transferred to the column as before. A smooth, even layer was obtained using the 10:1 water to Yokena clay, 4 hr of stirring, and gravity drainage.

Ottawa sand

An estimated mass of 9.25 g of Ottawa sand needed to produce a 0.32-cm layer was calculated using its specific gravity, water content, and an assumed porosity (0.30). With the regular slurry transfer procedure, the sand settled too fast, resulting in an uneven layer.

Because of the high settling velocity, a different loading procedure was developed for sand. The column outlet valve was shut off, and water was added to the column. The sand was then sprinkled into the standing water. After addition of the sand, the valve was opened, and the water was allowed to drain. The layer produced was smooth and even, but it was more than 0.32 cm thick. The mass of soil added was reduced to 8.0 g, and a smooth, even layer at the desired thickness was obtained.

Contaminated Feed Solution Preparation

Contaminated feed solution was prepared using field-contaminated soil from the Naval Surface Warfare Center in Crane, IN. The soil (labeled Crane Sifter-Conveyor) contained a RDX concentration of approximately 11,200 mg/kg and a HMX concentration of approximately 1,250 mg/kg (Pennington et al. 1995). Two batches were prepared during the project.

Crane Sifter-Conveyor soil (250 g) and DDI water (500 mL) were placed in a 1,000-mL, high-density polyethylene bottle. Four soil-water suspensions were prepared. The bottles were taped shut, placed in a tumbler, and tumbled for approximately 18 hr at 25 rpm.

After tumbling, the soil-water suspensions were centrifuged at 4,000 rpm in a bucket centrifuge (Model PR-7000, International Equipment Company, Needham Heights, MA) for 30 min. Supernatants were decanted and centrifuged again at 9,000 rpm in a bench centrifuge (Model SS-3 automatic, Sorvall, Inc., Newtown, CT) for 30 min. Finally, the supernatant was filtered through a 0.45-μm membrane filter (Type HA, Millipore Corporation, Bedford, MA).

Filtrates were combined into two amber-colored glass jars. A 5-mL aliquot was pipetted from each jar and preserved with an equal amount of acetonitrile for a reference standard. Both the preserved samples and the contaminated feed solution were stored at approximately 4 °C. Contaminated feed solution samples were preserved for analysis periodically throughout the course of the experiments (Appendix A).

Thin Disk Column Tests

Breakthrough curves

DDI water was pumped (upflow mode) through three soil columns (Tunica silt, Yokena clay, and Ottawa sand) using constant-volume metering pumps (Model QG6-2-SSY, Fluid Metering Inc., Oyster Bay, NY) until target flows were obtained (approximately 1.8 to 2.3 mL/hr). When these flows were achieved, the pumps were stopped, and DDI water was replaced with contaminated feed solution. The pumps were restarted with the contaminated feed solution which was pumped through the disks for a number of pore volumes (see following paragraph), defined as step inputs. Column operating parameters and average feed solution concentrations are shown in Tables 2 and 3, respectively.

Table 2
Column Operating Parameters

Column	V^1, cm/s	ρ^2, g/cm^3	n^3	SG^4
Tunica silt	4.96×10^{-5}	0.888	0.65	2.54
Yokena clay	5.61×10^{-5}	0.719	0.73	2.67
Ottawa sand	9.44×10^{-5}	1.610	0.40	2.68

[1] Average pore water velocity.
[2] Bulk density.
[3] Porosity.
[4] Specific gravity of soil.

Contaminated feed solution was pumped through the Tunica silt and Yokena clay columns for 160 and 211 pore volumes, respectively (284 and 329 hr, respectively). Contaminated feed solution was pumped through the Ottawa sand column for 51 pore volumes (48 hr).

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Table 3			
Average Feed Solution Concentrations (mg/L)			
Parameter[1]	Tunica Silt	Yokena Clay	Ottawa Sand
RDX	33.6	33.6	30.9
HMX	2.47	2.47	2.18
TNT	63.2	63.2	58.8
TNB	0.27	0.27	0.184
DNB	< 0.02	< 0.02	< 0.02
TETRYL	< 0.05	< 0.05	< 0.05
4A-DNT	0.145	0.145	0.110
2A-DNT	2.23	2.23	1.97
2,6-DNT	< 0.020	< 0.020	< 0.020
2,4-DNT	0.028	0.028	0.026
AZOXY	< 0.100	< 0.100	< 0.100
3,5-DNA	0.054	0.054	0.051
2,6-DANT	< 0.100	< 0.100	< 0.100
2,4-DANT	< 0.200	< 0.200	< 0.200
[1] See Appendix B for full chemical names.			

After the step inputs of contaminated feed solution were applied to the columns, the pumps were stopped, and contaminated feed solution was replaced with DDI water. The pumps were restarted with DDI water which was pumped through the Tunica silt and Yokena clay columns for 100 hr (56 and 66 pore volumes), respectively. DDI water was pumped through the Ottawa sand column for 68 hr (75 pore volumes). The pumps were stopped, and the columns were sealed after the addition of DDI water.

All column tests were performed at room temperature (18 to 24 °C).

Pause in flow

After allowing each of the sealed soil columns to sit undisturbed for 8 weeks, DDI water was again pumped through the columns for an additional 24 hr to investigate rate-limited desorption. Afterwards, the pumps were turned off, and the columns were disassembled. The entire soil layer was taken from each soil column for chemical analysis (Jenkins, Miyares, and Walsh 1988).

Sampling procedure

During the thin disk column tests, samples were collected using fraction collectors (Model UFC, Eldex Laboratories, Inc., Napa, CA). Samples were collected hourly during the majority of the experiment. A portion of each sample (1.5 mL) was spiked with an equal volume of acetonitrile for preservation.

Chemical Analysis

Samples were analyzed for 2,3,5-trinitro-1,3,5-triazine (RDX) and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) on two independent HPLC systems using the dual column confirmation method developed by Jenkins, Miyares, and Walsh (1988). The first system consisted of a 600E system controller, a 712 Wisp Auto Injector, and a 486 Tunable Absorbance Detector (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-18 (Supelco 25 cm × 4.6 mm) column eluted with 1:1 methanol/water at 1.2 mL/min. The second HPLC system consisted of an HPLC Module I (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-CN (Supelco 25 cm × 4.6 mm) column eluted with 1:1 methanol/water at 1.2 mL/min.

Chloride Tracer

A 500-mg/L as Cl⁻ solution was pumped through an empty column until chloride concentrations reached the initial concentration. Because sample volumes were smaller than that needed for analysis with a dip-type chloride ion probe, chloride concentrations were indirectly measured using an in-line conductivity electrode (Mfr. #018010, Orion Research, Inc., Boston, MA) which was attached at the end of the outlet tubing. Conductivity readings were taken using a conductivity meter (Model 35, Yellow Springs Instrument Co., Inc., Yellow Springs, OH). The conductivity curve was used to estimate the effective hydraulic residence time of the apparatus without soil, which is needed for modeling (see section on Complete-mix Analytical Model in Chapter 3).

Treatment of Observed Data

It is useful to normalize soil column data by dividing the observed effluent concentrations by the influent concentration and to convert time to the number of pore volumes eluted. To do the latter, the following relationship is used:

$$T = \frac{ut}{L} \tag{1}$$

where

T = pore volumes eluted

L = column length, cm

u = average pore water velocity, cm/s

t = time, s

3   Results and Discussion

Breakthrough Curves (BTCs)

RDX

The normalized Tunica silt RDX BTC (Figure 6) shows that RDX concentrations reached a steady state after about 40 pore volumes were eluted. Steady-state concentrations were about 105 percent of the initial concentration. The BTC was approximately symmetrical with minimal scattering of data. The washout portion of the BTC shows that RDX concentrations returned to near the detection limit (0.020 mg/L) after about 40 pore volumes were eluted. Mass balance (Table 4) indicated that the RDX mass introduced to Tunica silt was completely recovered in the effluent. The approximate symmetry of the BTC and the total elution of sorbed RDX indicate a reversible, linear sorption process (Brusseau and Rao 1989).

The normalized Yokena clay RDX BTC (Figure 6) shows that RDX concentrations reached a steady state after about 20 pore volumes were eluted, and steady-state concentrations were about 102 percent of the intitial concentration. The BTC showed minimal scattering of data. The washout portion of the BTC showed that RDX concentrations decreased to near the detection limit after about 40 pore volumes were eluted. Mass balance (Table 4) indicated that virtually all of the RDX mass introduced to Yokena clay was recovered in the effluent, although trace amounts of RDX remained in the soil after completion of the experiment. Since the rising and falling limbs of the BTC were not symmetrical, a nonequilibrium process or nonlinear sorption affected RDX transport in Yokena clay.

The normalized Ottawa sand RDX BTC (Figure 6) shows that RDX concentrations reached a steady state after about 50 pore volumes were eluted, and steady-state concentrations were about 103 percent of the initial concentration. The BTC was symmetrical and showed virtually no data scattering. Mass balance (Table 4) indicated that the RDX mass introduced to Ottawa sand was completely recovered in the effluent. The symmetry of the BTC and the total elution of sorbed RDX indicate a reversible, linear sorption process.

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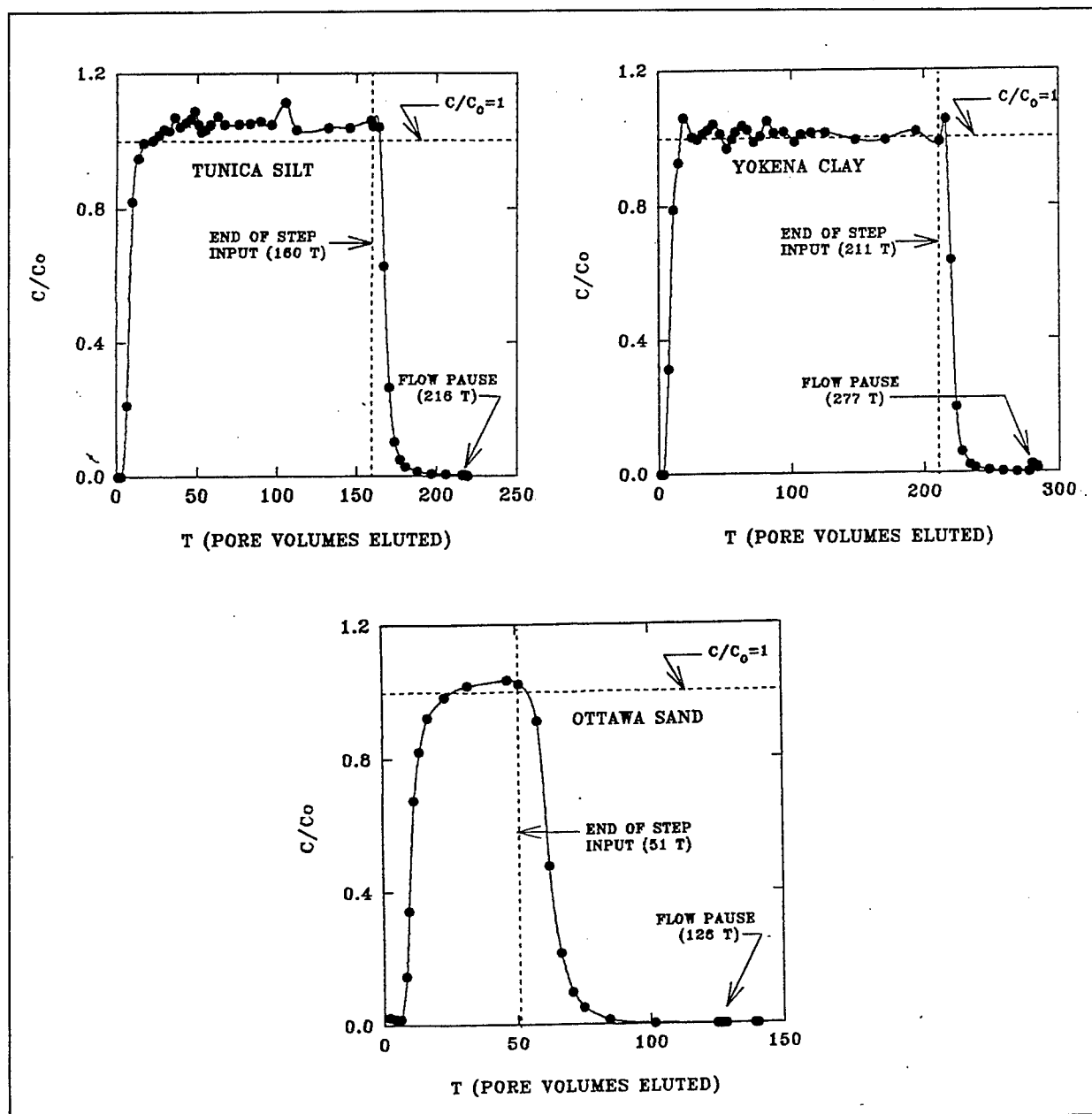
Figure 6.   Normalized RDX breakthrough curves

HMX

The normalized Tunica silt HMX BTC (Figure 7) was similar to the
Tunica silt RDX BTC. HMX concentrations reached a steady state after about
40 pore volumes were eluted, and steady-state concentrations were about
105 percent of the initial concentration. Mass balance (Table 4) indicated that
the HMX mass introduced to Tunica silt was completely recovered in the
effluent. The washout portion of the BTC showed a return of HMX concen-
trations to below the detection limit (0.020 mg/L) after approximately

Table 4
Mass Balances for RDX and HMX

Column	Parameter	Mass in, mg	Mass out, mg	Residual Mass, mg	Mass Balance percent
Tunica silt	RDX	17.30	18.16	0	105.0
	HMX	1.27	1.29	0	101.6
Yokena clay	RDX	25.31	25.80	0.01	102.0
	HMX	1.86	2.00	0.05	110.2
Ottawa sand	RDX	3.13	3.21	0	102.6
	HMX	0.221	0.232	0	105.0

50 pore volumes were eluted. The approximate symmetry of the BTC and the total elution of HMX indicate a reversible, linear sorption process.

The normalized Yokena clay HMX BTC (Figure 7) was similar to the Yokena clay RDX BTC. HMX concentrations reached a steady state after about 20 pore volumes were eluted, and steady-state concentrations were about 110 percent of the initial concentration. The washout portion of the BTC showed that HMX concentrations returned to below the detection limit after about 70 pore volumes were eluted. Mass balance (Table 4) indicated that virtually all of the HMX mass introduced to Yokena clay was recovered in the effluent, although trace amounts of HMX remained in the soil after completion of the experiment. Since the rising and falling limbs of the BTC were not symmetrical, a nonequilibrium process or nonlinear sorption affected HMX transport in Yokena clay.

The normalized Ottawa sand HMX BTC (Figure 7) was nearly identical to the Ottawa sand RDX BTC. The Ottawa sand HMX required about 50 pore volumes of elution to reach a steady state at about 105 percent of the initial concentration and required about 50 pore volumes of washout for HMX concentrations to return to below the detection limit. Mass balance (Table 4) indicated that the HMX mass introduced to Ottawa sand was completely recovered in the effluent. The symmetry of the BTC and the total elution of sorbed HMX indicate a reversible, linear sorption process.

Implications of BTCs

RDX and HMX BTCs showed consistent trends with minimal scattering of data. Each BTC reached a steady-state concentration greater than the influent RDX and HMX concentrations, indicating a consistent experimental error of uncertain origin. Total recovery of RDX and HMX mass, essentially all of which was recovered in the effluent, showed that disappearance of RDX and HMX was minimal. In contrast, Myers et al. (in preparation) obtained RDX

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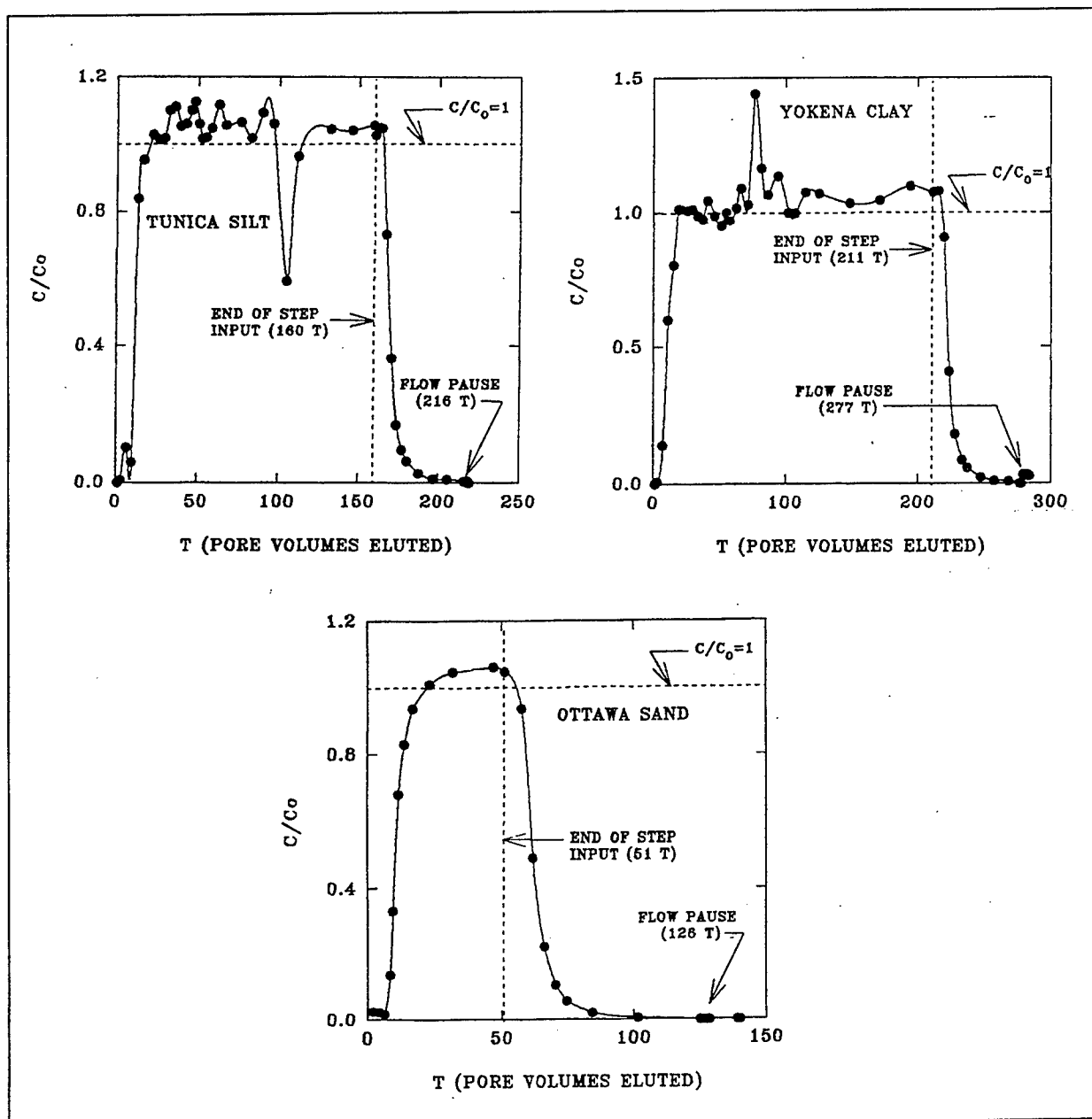
Figure 7. Normalized HMX breakthrough curves

mass balances of 67, 62, and 108 percent for Tunica silt, Yokena clay, and Ottawa sand, respectively, and HMX mass balances of 97, 55, and 109 percent for Tunica silt, Yokena clay, and Ottawa sand, respectively. The soil columns used by Myers et al. (in preparation) were longer (15.2 cm) than the ones used here (0.32 cm). The longer columns used by Myers et al. (in preparation) were probably more anaerobic than the columns used here, suggesting that RDX and HMX disappearance is dependent on redox conditions.

RDX and HMX BTCs in the Yokena clay were somewhat asymmetrical, indicating the presence of a nonequilibrium process or nonlinear sorption. Nonequilibrium behavior can be attributed to diffusive mass-transfer resistances (transfer to and from immobile water regions) and rate-limited sorption reactions. Sorption isotherm nonlinearity and sorption-desorption nonsingularity can also cause BTCs to appear as if nonequilibrium processes were operative (Brusseau et al. 1989). However, as shown by the pause in flow data discussed in the next section, the Yokena clay RDX and HMX BTC asymmetries are due to diffusive mass transfer resistance to and from immobile water regions.

Pause in Flow

The effects of nonequilibrium processes on BTCs include early breakthrough, BTC tailing, and, as mentioned in the preceding section, BTC asymmetry. If nonequilibrium effects are slight, column experiments may not be able to discern the presence of these effects. An interruption in flow during an otherwise continuous flow experiment tends to magnify nonequilibrium effects and can be used to investigate nonequilibrium processes (Brusseau et al. 1989).

A pause in flow may be incorporated into the study on the frontal portion of the BTC or on the distal portion of the BTC (during washout). A pause in flow on the frontal portion of the BTC will show a decrease in concentration during the flow pause if a nonequilibrium process is present. A pause in flow on the washout portion of the BTC will show an increase in concentration during the flow pause if a nonequilibrium process is present. In either case, concentrations will remain constant during the flow pause if equilibrium conditions are predominate.

In the present experiment, flow to each column was stopped during washout, and the columns were sealed for 8 weeks. After this pause in flow, washout was restarted.

RDX

In Tunica silt, normalized RDX concentrations were approximately 0.003 immediately before the flow pause (Figure 8). When flow was restarted, RDX concentrations increased slightly and then began to decrease with continued flow. In Yokena clay, normalized RDX concentrations were approximately 0.0015 immediately before the flow pause (Figure 8). When flow was restarted, normalized RDX concentrations increased to approximately 0.025, and then decreased with continued flow. In the Ottawa sand, RDX concentrations were below detection limits both before and after the flow pause (Figure 8).
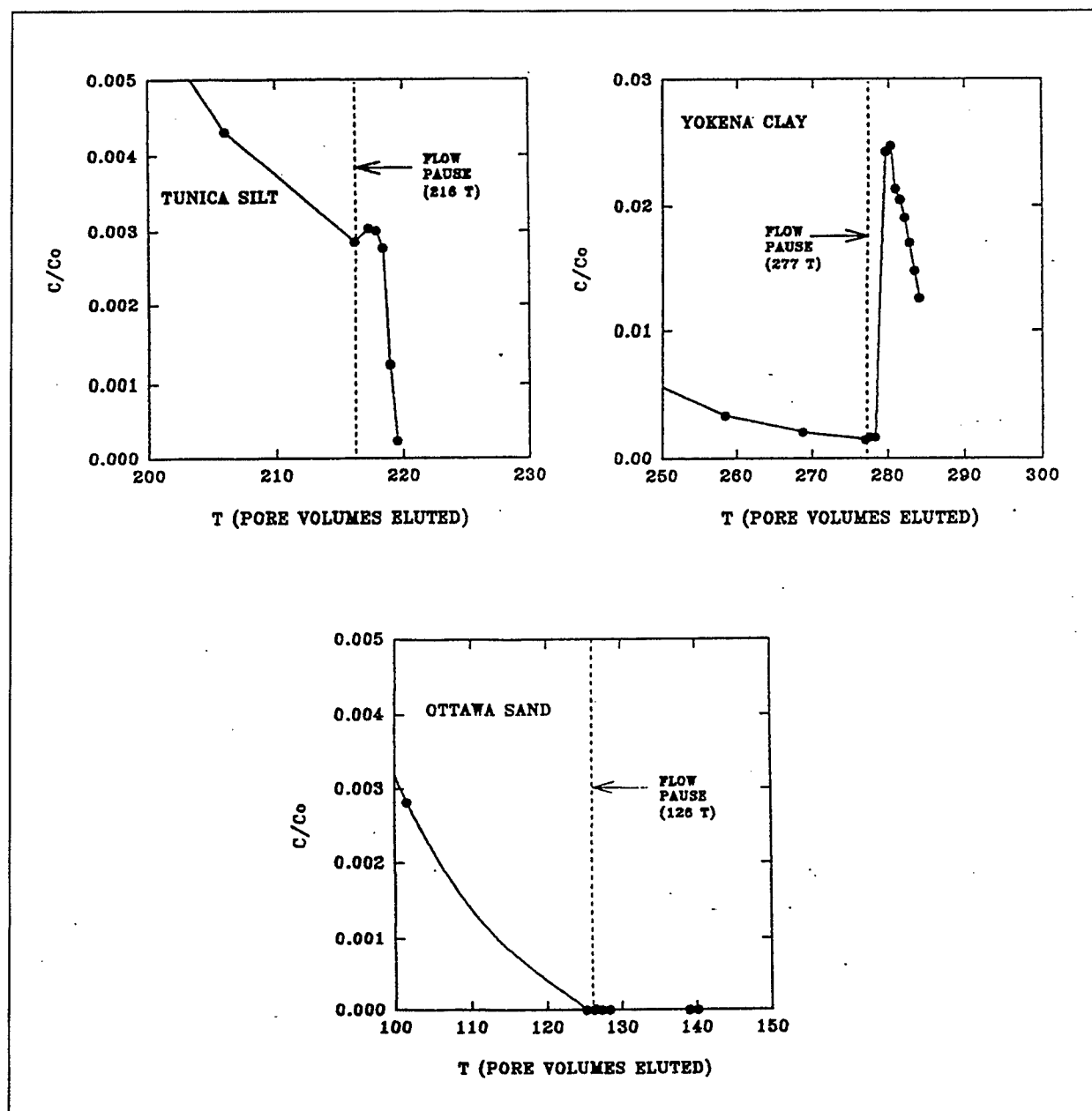
Figure 8.   Normalized RDX breakthrough curves describing flow pause

HMX

In Tunica silt, normalized HMX concentrations were approximately 0.005 immediately before the flow pause (Figure 9). When flow was restarted, normalized HMX concentrations increased to approximately 0.0065. With continued flow, HMX concentrations decreased to below detection limit. In Yokena clay, HMX concentrations were below detection limit immediately before the flow pause and increased to approximately 0.036 when flow was

Figure 9.   Normalized HMX breakthrough curves describing flow pause

restarted (Figure 9).   HMX concentrations then decreased with continued flow.   Ottawa sand HMX concentrations were below detection limit both before and after the pause in flow (Figure 9).
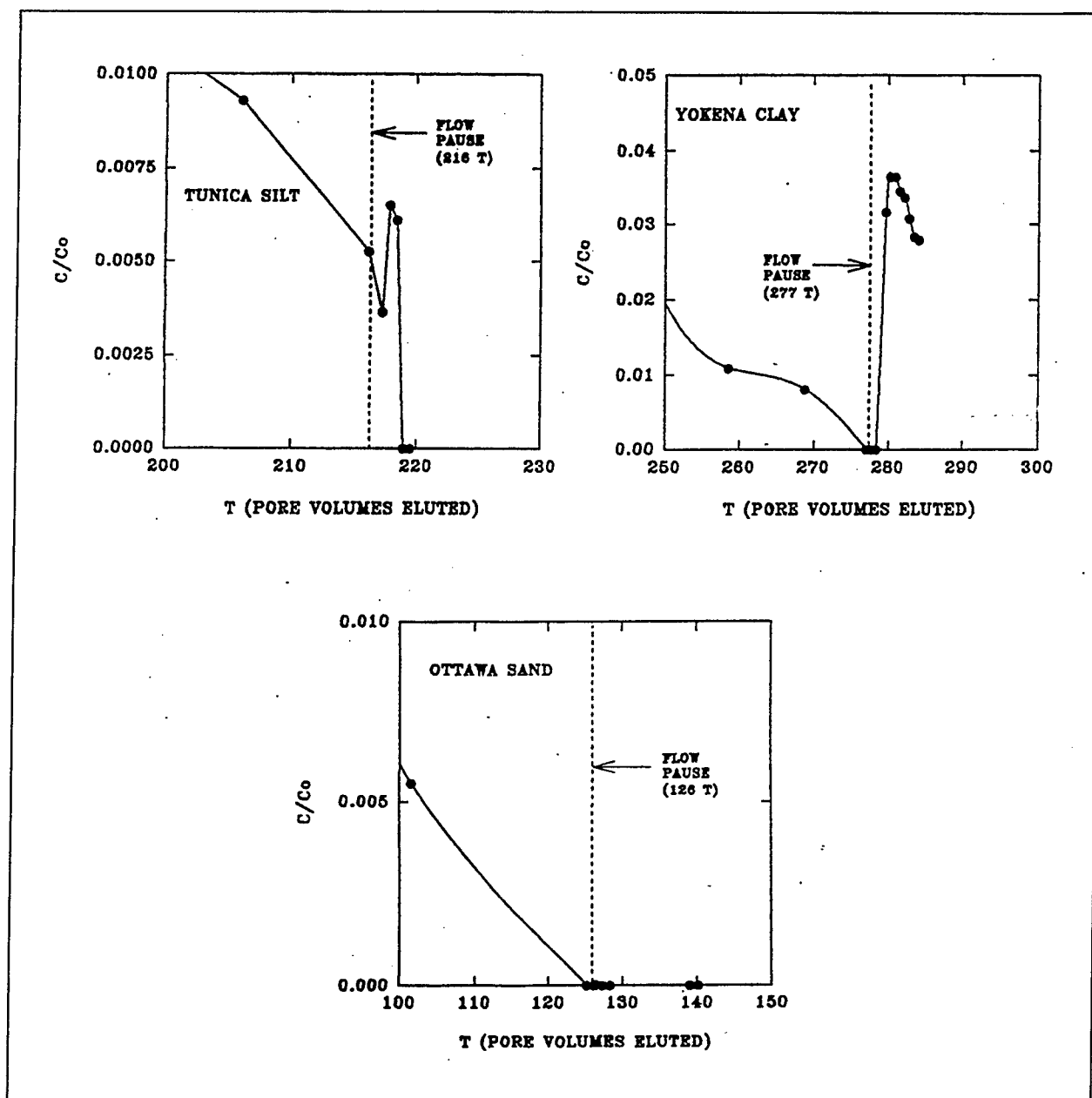
Implications of flow pause

The flow pause data is evidence that RDX in Yokena clay and HMX in Yokena clay and Tunica silt were affected by a nonequilibrium process.

Increases in HMX concentrations during the flow pause were somewhat higher than increases in RDX concentrations during the flow pause, suggesting that nonequilibrium processes may be more important for HMX than for RDX. Nonequilibrium effects were more pronounced in Yokena clay than in Tunica silt. Evidence of HMX nonequilibrium (i.e., BTC tailing) has been observed by other researchers (Pennington et al. 1995; Myers et al. in preparation). Evidence of RDX nonequilibrium in the literature is generally lacking.

Diffusive mass transfer with immobile water regions is probably the cause of nonequilibrium effects observed in these data, although a rate-limited sorption reaction (i.e., chemical nonequilibrium) cannot be completely ruled out. The immobile water concept has been employed by numerous researchers to explain nonequilibrium effects observed in the transport of contaminants. For instance, BTC tailing of 2,4,5-trichlorophenoxyacetic acid in unsaturated soil columns was attributed to diffusion through immobile water regions (van Genuchten, Wierenga, and O'Connor 1977). The nonequilibrium effects observed for transport of chloride, bromide, carbon tetrachloride, tetrachlorethylene, bromoform, o-dichlorobenzene, and hexachloroethane in a saturated aquifer was attributed to diffusive exchange with immobile water regions (Goltz and Roberts 1986). Diffusion through immobile water regions also affected transport of trichloroethene, bromoform, and chloride in sandy loam soil columns (Hutzler et al. 1986).

Complete-mix Analytical Model

A complete-mix model (Townsend, Myers, and Adrian 1995) developed for thin disk breakthrough curves was used to obtain RDX and HMX transport parameters. The model is similar to one derived by Skopp and McCallister (1986). In a complete-mix model, hydrodynamic dispersion is neglected. The concentration inside the soil layer is assumed to be equal to the concentration exiting the soil layer. The model of Townsend, Myers, and Adrian (1995) includes linear equilibrium sorption and first-order reaction.

From conservation of mass (Equation 2) and a linear sorption isotherm (Equation 3), Equation 4 is derived for the initial condition C(0) = 0.

$$QC_o - QC - \mu nVC = nV\frac{dC}{dt} + \rho V\frac{dS}{dt} \tag{2}$$

$$S = K_d C \tag{3}$$

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - \exp\left(-\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right) \right] \tag{4}$$

where

C = effluent solute concentration, mg/L

C_o = influent solute concentration, mg/L

θ_H = hydraulic residence time, hr

μ = transformation rate constant, hr^{-1}

n = porosity

ρ = bulk density, kg/L

K_d = distribution coefficient, L/kg

Equation 4 is the basic equation describing reactive, sorptive contaminant transport through a complete-mix soil system. This equation has several practical limitations. For instance, difficulties arise in taking measurements directly at the soil layer boundary. In general, columns have an inlet and an outlet associated with them, which are usually not part of the main model. The solute must first travel through the inlet portion of the column before coming into contact with the soil layer and, upon leaving the soil layer, must travel through an outlet before being collected for analysis. In traditional columns, the inlet and outlet travel time is usually much smaller than the residence time in the soil and is often neglected. With thin disk columns, the inlet and outlet residence times are significant and therefore must be considered.

To determine the total inlet-outlet (inlet plus outlet) residence time (t_o), a chloride tracer study was performed on a blank column. It was assumed that both the inlet and outlet could be modeled as plug flow. Inlet-outlet residence time (t_o) was measured with a tracer study, and the model was modified to account for this travel time as follows:

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - \exp\left(-\left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} \right] (t - t_o) \right) \right] \tag{5}$$

where

t_o = inlet-outlet residence time, hr

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Equation 5 describes solute travel through the complete thin disk apparatus during the step input of the feed solution.

After the end of the feed solution step input, DDI water was pumped through to wash the disk out. Changing the conditions at the inlet to C = 0 for t > t_1 yields:

$$C = C_{t_1} \exp\left\{ -\left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} \right] (t - t_1) \right\}$$

(6)

where

C_{t1} = Effluent concentration at time t_1

t_1 = time at the end of the step input plus t

Parameter Estimation

For the purpose of fitting Equations 5 and 6 to the BTCs, the initial RDX and HMX concentrations were assumed to be the mean of the steady-state concentrations measured in the column effluents rather than the RDX and HMX concentrations measured in the feed solutions. Since complete recovery of RDX and HMX was observed for each column, disappearance rate constants were not applicable to these data. Therefore, only linear equilibrium distribution coefficients (K_d) were obtained by fitting Equations 5 and 6 to the adjusted BTCs (Table 5). Good fits were obtained for each column for RDX (Figure 10) and HMX (Figure 11).

Table 5
Fitted Disappearance and Sorption Parameters for RDX and HMX

Column	Parameter	μ^1, hr^{-1}	K_d^2, L/kg
Tunica silt	RDX	0	2.5
	HMX	0	3.6
Yokena clay	RDX	0	5.7
	HMX	0	8.5
Ottawa sand	RDX	0	1.35
	HMX	0	1.45

[1] First-order disappearance rate constant.
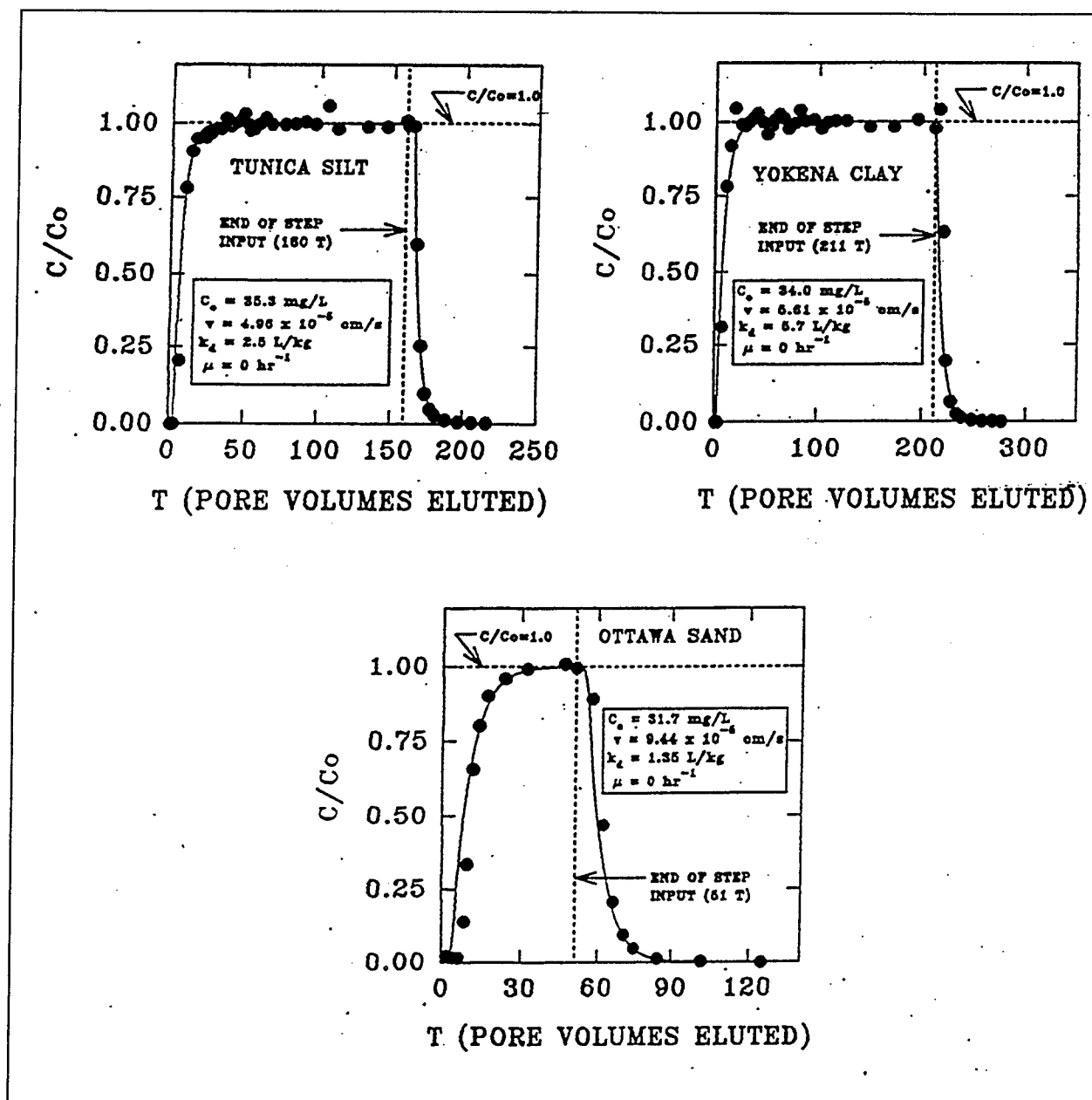[2] Linear equilibrium distribution coefficient.

Figure 10. Normalized observed and fitted RDX breakthrough curves

RDX

The Tunica silt RDX BTC was described well by the model (Figure 10). The Yokena clay RDX BTC was described reasonably well by the model (Figure 10), although the observed data reached steady state slightly before the model prediction. The Ottawa sand RDX BTC was also described reasonably well by the model (Figure 10), although the observed BTC showed slightly later breakthrough than the model predicted. Linear equilibrium distribution coefficients (K_d) for RDX were 2.5, 5.7, and 1.35 L/kg for the

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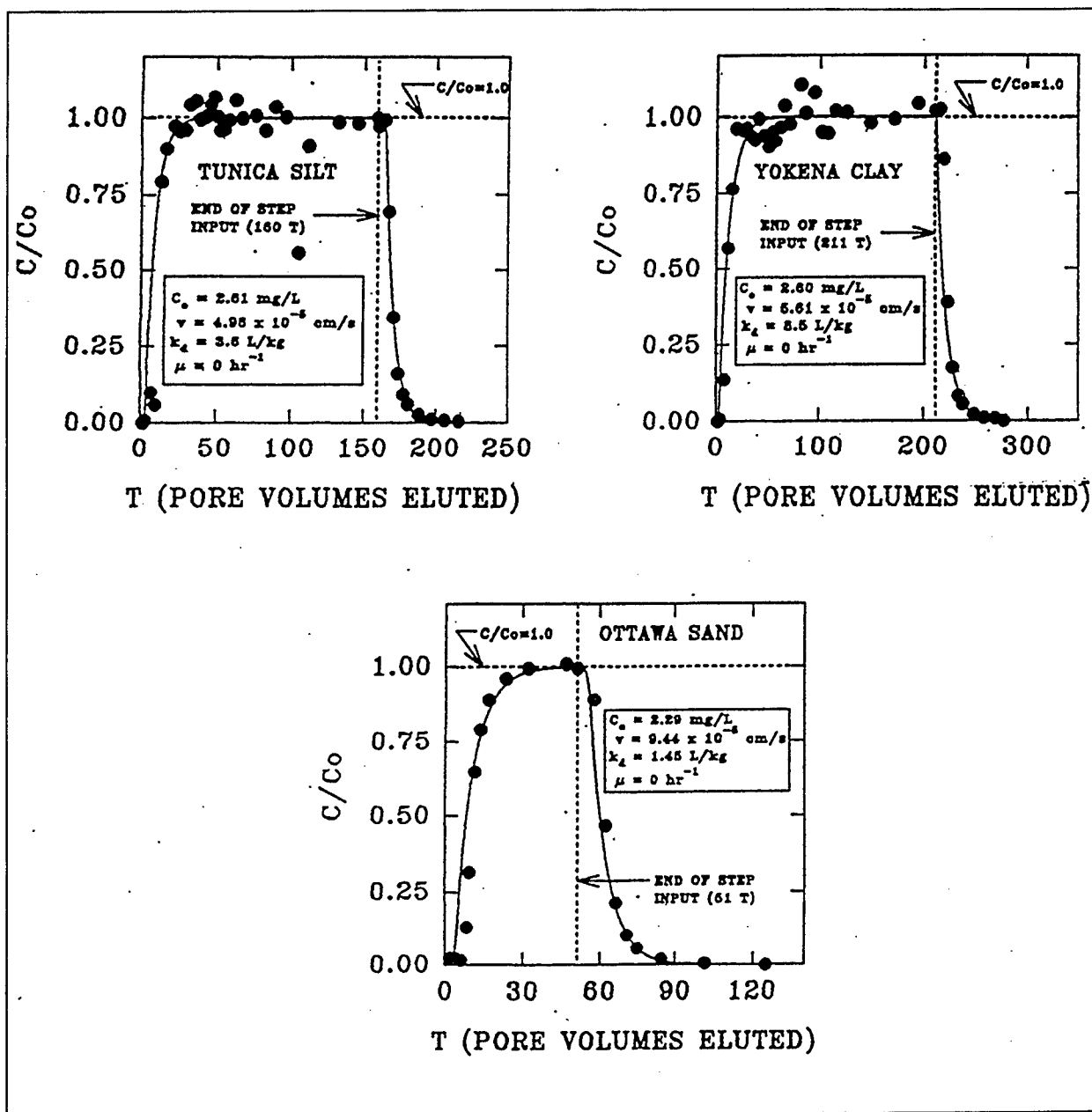Figure 11. Normalized observed and fitted HMX breakthrough curves

Tunica silt, Yokena clay, and Ottawa sand, respectively. These coefficients are in good agreement with those reported in previous works (Townsend and Myers 1996, McGrath 1995).

HMX

The Tunica silt HMX BTC was described well by the model, although there was more scatter of data in the Tunica silt HMX BTC than in the Tunica

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silt RDX BTC. The Yokena clay HMX BTC showed slightly earlier break-through than the model predicted but was otherwise described well. The Ottawa sand HMX BTC, like the Ottawa sand RDX BTC, showed slightly later breakthrough than the model predicted but was otherwise described well. Unlike earlier studies (Pennington et al. 1995; Myers et al. in preparation), no HMX BTC tailing was observed for any of the soils. Linear equilibrium distribution coefficients (K_d) for HMX were 3.6, 8.5, and 1.45 L/kg for the Tunica silt, Yokena clay, and Ottawa sand, respectively. These coefficients are in good agreement with those reported in previous works (Townsend and Myers 1996; McGrath 1995).

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4 Conclusions and Recommendations

Conclusions

The thin disk soil columns provided well-behaved RDX and HMX break-through curves that could be simulated using a complete-mix model with linear equilibrium sorption. Good mass balances were obtained (101 to 110 percent). Agreement between observed and model breakthrough curves suggests that linear equilibrium sorption in transport models for RDX and HMX will capture the main effects of this process, even at high solution concentrations, for the conditions and soils investigated. However, some degree of nonequilibrium may affect both RDX and HMX, as evidenced by the flow pause.

HMX tended to sorb more strongly than RDX in all three soils. This agrees with earlier works (Leggett 1985; Myers et al. in preparation).

Neither RDX nor HMX disappearance was observed in this study. The lack of observed RDX and HMX disappearance may be due to aerobic soil conditions in the thin disk columns that preclude reductive transformations.

Recommendations

Many questions regarding RDX and HMX transport in soils remain to be answered. The following aspects of RDX and HMX transport in the subsurface must be addressed:

a. It should not be assumed that RDX and HMX transformations are inoperative, especially under reducing conditions. Chemical analytical procedures for measuring RDX and HMX transformation products should befurther developed and future experiments should include ananalysis for these products.

b. The influence of redox conditions on RDX and HMX disappearance rates and pathways should be studied systematically before RDX and HMX migration through soils can be fully understood.

c. Column experiments over a wide range of pore water velocities are needed to provide information on film effects, mobile-immobile water diffusion limitations, other mass transfer limitations, and the general applicability of linear equilibrium models for RDX and HMX.

d. Column experiments incorporating a pause in flow, along with tracer experiments incorporating a similar pause in flow, may be used to further investigate nonequilibrium processes for RDX and HMX. These types of experiments may be able to distinguish between physical and chemical nonequilibrium.

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Appendix A
Feed Solution Concentrations

Tunica Silt and Yokena Clay Feed Solution Concentrations (mg/ℓ)

Day	RDX	HMX	TNT	TNB	DNB	TETRYL	AZOXY	4A-DNT	2A-DNT	2,6-DNT	2,4-DNT	3,5-DNA	2,6-DANT	2,4-DANT
0	33.7	2.50	64.4	0.258	<0.020	<0.050	<0.100	0.154	2.26	<0.020	0.024	0.053	<0.100	<0.200
5	33.9	2.49	64.6	0.265	<0.020	<0.050	<0.100	0.197	2.27	<0.020	0.028	0.050	<0.100	<0.200
7	33.3	2.45	62.9	0.234	<0.020	<0.050	<0.100	0.068	2.19	<0.020	0.031	0.053	<0.100	<0.200
10	33.5	2.47	62.6	0.250	<0.020	<0.050	<0.100	0.157	2.21	<0.020	0.028	0.056	<0.100	<0.200
15	34.0	2.46	62.6	0.296	<0.020	<0.050	<0.100	0.166	2.22	<0.020	0.028	0.055	<0.100	<0.200
17	33.4	2.45	62.0	0.429	<0.020	<0.050	<0.100	0.101	2.25	<0.020	0.030	0.052	<0.100	<0.200
18	32.8	2.40	60.8	0.349	<0.020	<0.050	<0.100	0.162	2.20	<0.020	0.029	0.053	<0.100	<0.200

Ottawa Sand Feed Solution Concentrations (mg/ℓ)

Day	RDX	HMX	TNT	TNB	DNB	TETRYL	AZOXY	4A-DNT	2A-DNT	2,6-DNT	2,4-DNT	3,5-DNA	2,6-DANT	2,4-DANT
0	31.2	2.20	59.3	0.180	<0.020	<0.050	<0.100	0.129	1.98	<0.020	0.026	0.053	<0.100	<0.200
3	30.5	2.17	58.3	0.185	<0.020	<0.050	<0.100	0.065	1.95	<0.020	0.025	0.049	<0.100	<0.200
5	30.6	2.16	58.0	0.194	<0.020	<0.050	<0.100	0.144	1.97	<0.020	0.025	0.049	<0.100	<0.200

Appendix B
Chemical Abbreviations

RDX: 2,3,5-trinitro-1,3,5-triazine

HMX: Oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

TNT: 2,4,6-trinitrotoluene

DNB: 1,3-dinitrobenzene

TNB: 1,3,5-trinitrobenzene

4A-DNT: 4-amino-2,6-dinitrotoluene

2A-DNT: 2-amino-4,6-dinitrotoluene

2,6-DNT: 2,6-dinitrotoluene

2,4-DNT: 2,4-dinitrotoluene

3,5-DNA: 3,5-dinitroaniline

2,6-DANT: 2,6-diamino-4-nitrotoluene

2,4-DANT: 2,4-diamino-6-nitrotoluene

AZOXY: Composite of 4,2',6,6'-tetranitro-2,4'-azoxytoluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 4,4',6,6'-tetranitro-2,2'-azoxytoluene

TETRYL: Methyl-2,4,6-trinitrophenylnitramine

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13. ABSTRACT *(Maximum 200 words)*

Subsurface contamination by 2,3,5-trinitro-1,3,5-triazine (RDX) and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) has prompted remediation and containment efforts at many Army installations. To fully evaluate the potential for natural attenuation to eliminate or substantially reduce remediation requirements, information on sorption and natural disappearance is needed. This study was conducted to determine RDX and HMX sorption and disappearance coefficients from breakthrough curves (BTCs) for three soils--a silt loam, a clay, and Ottawa sand. Thin disk soil columns (0.32-cm soil length) were used to obtain RDX and HMX BTCs.

Approximately symmetrical RDX and HMX BTCs were obtained for each soil. The BTCs were modeled assuming complete-mixing, first-order disappearance, and linear equilibrium sorption. This model produced excellent curve fits, with only slight discrepancies between the model and the observed data. Good mass balances were observed for both RDX (102 to 105 percent) and HMX (102 to 110 percent).

RDX and HMX tended to sorb weakly to the soils used in this study. Linear equilibrium distribution coefficients (K_d) for RDX ranged from 1.35 to 5.7 L/kg. Linear equilibrium distribution coefficients for HMX ranged from 1.45 to 8.5 L/kg.

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Although a linear equilibrium model could be used to simulate RDX and HMX sorption in the soils, a planned interruption in flow during the otherwise continuous flow experiments revealed evidence of nonequilibrium conditions in the clay and silt. Nonequilibrium effects were more pronounced in the clay than in the silt.

BTCs and mass balances indicated that transformation and irreversible soil binding of RDX and HMX were minimal in these studies.