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# **Laboratory Studies of Soil Sorption/ Transformation of TNT, RDX, and HMX**

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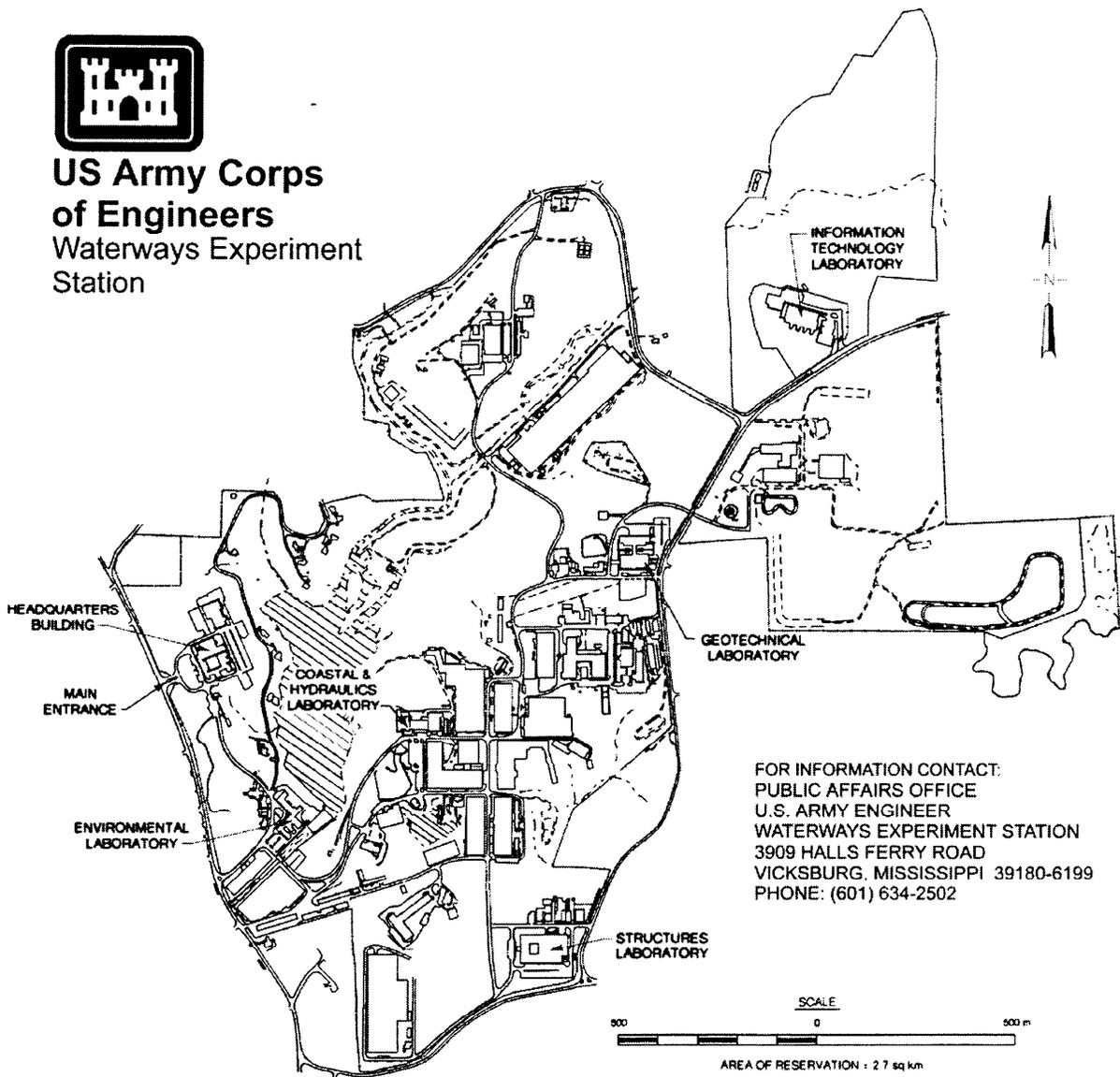
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# Preface

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The work reported herein 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-002. Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, HQUSACE. The HQUSACE Technical Monitors for Work Unit AF25-GW-003 were Messrs. David Becker and George O'Rourke. The IRRP Program Manager was Dr. M. John Cullinane.

This report was prepared by Mr. Tommy E. Myers, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES; Drs. James M. Brannon and Judith C. Pennington, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL; Mr. Dan M. Townsend, Contract-Graduate Student, ERB; Dr. William M. Davis, EPEB; Mr. Michael K. Ochman and Ms. Charolett A. Hayes, AScI Corporation; and Ms. Karen F. Myers, Environmental Chemistry Branch (ECB), EED. Dr. Ning H. Tang, University of Puerto Rico, Mayaguez, Puerto Rico, and Ms. Trudy J. Olin, Environmental Resources Engineering Branch, EED, were technical reviewers for this report. Ms. Barbara A. Tardy, ERB, and 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 Ms. Ann B. Strong, Chief, ECB, and under the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, Dr. Richard E. Price, Chief, EPED, and Dr. John Harrison, Director, EL.

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# 1 Introduction

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## Background

Many Department of Army (DOA) and other Department of Defense (DOD) installations are tasked with the cleanup of soils and groundwater contaminated with explosives. Subsurface contamination with the explosives 2,4,6-trinitrotoluene (TNT), 2,3,5-trinitro-1,3,5-triazine (RDX), and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is often associated with the operation of munitions manufacturing, loading, assembling, and packing facilities (Pereira et al. 1979; Spangford et al. 1982; Jones et al. 1982). To support DOA and DOD cleanup goals, technical guidance in numerical modeling of natural and engineered remediation alternatives is needed. Important components of this guidance involve development of descriptors for the processes affecting subsurface transport of explosives.

Processes affecting groundwater contaminant transport include, but are not limited to, convection, hydrodynamic dispersion, biodegradation, abiotic transformations, soil sorption, facilitated transport by organic and inorganic colloids, dissolution, and diffusion (in water films surrounding soil particles, interaggregate pores, and intraparticle pores) (McGrath 1995). All processes do not affect TNT, RDX, and HMX transport equally at all sites, so it is important to identify key processes and conditions under which these processes dominate transport phenomena. Site-specific application of well-conceived and properly formulated models requires improved understanding of process mechanisms and factors affecting process mechanisms so that relevant processes can be identified for simulation.

## Research Need

Sorption of explosives such as TNT, RDX, and HMX by soils and drilling muds has been investigated in laboratory batch studies (Leggett 1985; Loehr 1989; Pennington and Patrick 1990; Brannon et al. 1992; Ainsworth et al. 1993; Comfort et al. 1995; Xue, Iskandar, and Selim 1995) and column studies (Comfort et al. 1995; Selim, Xue, and Iskandar 1995; Townsend, Myers, and Adrian 1995; Townsend, Myers, and Adrian 1996). Results from these studies

have varied. Leggett (1985) found that a two-site modification of the Langmuir equation (curvilinear model) provided best fit for equilibrium sorption of TNT to commercial drilling muds. Pennington and Patrick (1990) also observed curvilinear-equilibrium sorption of TNT to 15 soils and found that the Langmuir equation without modification provided excellent fit. Ainsworth et al. (1993) described curvilinear-equilibrium TNT sorption to sterilized soils including the soils studied by Pennington and Patrick (1990) and found that the Freundlich equation provided best fit. Xue, Iskandar, and Selim (1995) found that TNT sorption for bentonite clay could be described well using linear, Freundlich, Langmuir, and modified Langmuir (Leggett 1985) isotherms, although the Freundlich model provided a slightly better fit than the other models. Comfort et al. (1995) found that TNT sorption to a silty clay loam was best described by a Freundlich isotherm. However, Loehr (1989) and Brannon et al. (1992) described anomalous soil sorption of TNT that was ill-defined and inconsistent with standard sorption equations.

Interpretation of batch data on TNT sorption is confounded by formation of TNT transformation products (TPs) such as 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,6-diamino-4-nitrotoluene (2,6-DANT), 2,4-diamino-6-nitrotoluene (2,4-DANT), and triaminotoluene (TAT) (Figure 1). Transformation of TNT occurs in soils (Greene, Kaplan, and Kaplan 1985; Kaplan et al. 1985; Loehr 1989; Pennington and Patrick 1990; Ainsworth et al. 1993; Price, Brannon, and Hayes 1995; Townsend, Myers, and Adrian 1995), but in most cases the available batch sorption studies do not account for transformation. When transformation of a sorbing analyte is neglected, sorption can be overestimated and even misinterpreted. If sorbed concentrations are calculated by difference, composite-equilibrium coefficients for a mixed system of sorbed TNT, sorbed transformation products, dissolved TNT, and dissolved transformation products are obtained. Also, if radiolabeled TNT is used and TNT mass balance is developed by counting the radiolabeled species, there is no way to distinguish between TNT and TNT TPs unless additional chemical analyses of individual species are conducted.

Ainsworth et al. (1993) calculated sorption isotherms from directly measured sorbed and dissolved TNT concentrations and thereby eliminated the potential error made when calculating sorbed TNT concentrations by difference. The Ainsworth et al. (1993) data collaborate the curvilinear isotherms previously reported by Leggett (1985) and Pennington and Patrick (1990). Although the soils used by Ainsworth et al. (1993) were sterilized, some TNT transformation was observed. Consequently, their results include competition for sorption sites by TNT and TNT TPs. Competitive sorption among TNT and TNT TPs is a confounding factor that is almost always present except in highly artificial systems.

Information on TNT sorption kinetics is also limited. Kinetic information is needed to evaluate the local equilibrium assumption, an assumption often used to simplify transport models (Valocchi 1985). Groundwater contaminant transport models based on equilibrium constants are only valid if sorption is completely reversible and fast with respect to pore water velocities. Batch sorption studies

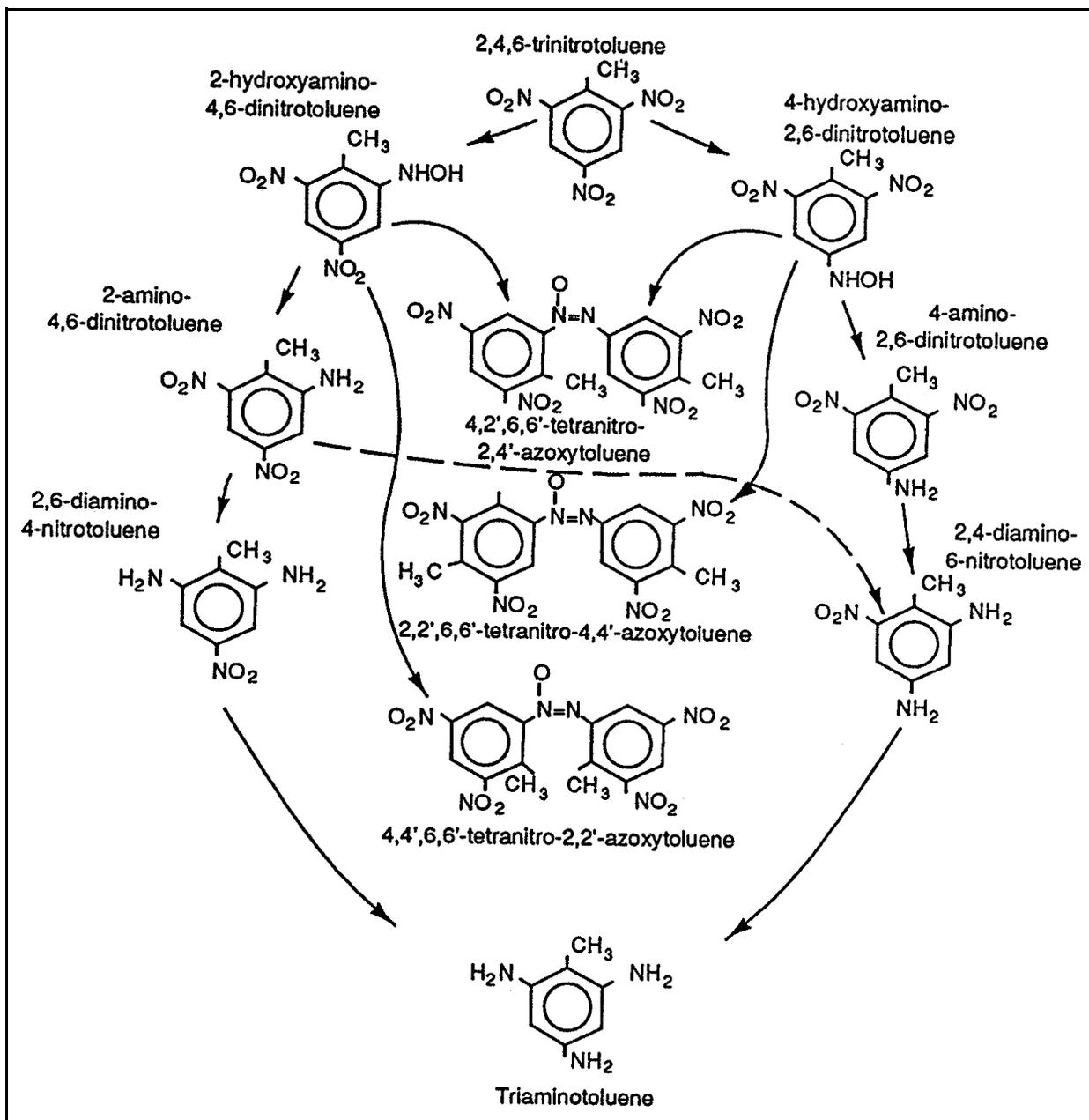


Figure 1. Reduction pathways for 2,4,6-trinitrotoluene (modified from McGrath 1995)

have shown TNT solution concentrations approach steady state in 24 hr (Pennington and Patrick 1990) to 96 hr (Ainsworth et al. 1993). The long equilibration times for TNT solution concentrations that have been reported are related to TNT transformation, competition for sorption sites, and reequilibration with dissolved TNT (Pennington and Patrick 1990; Ainsworth et al. 1993). Xue, Iskandar, and Selim (1995) found little deviation between TNT sorption and desorption isotherms for bentonite clay, indicating reversibility and satisfaction of local equilibrium conditions. Townsend, Myers, and Adrian (1995) found that a linear equilibrium sorption term coupled with a first-order transformation

rate term could adequately describe TNT column elution curves. In spite of the long equilibration times observed in batch tests, Ainsworth et al. (1993) were able to model column elution curves for average pore water velocities as high as 0.01 cm/sec using the local equilibrium assumption.

Information on RDX and HMX soil sorption is limited relative to information on TNT. Leggett (1985) reported linear sorption of RDX and HMX to drilling muds. Ainsworth et al. (1993) also observed linear sorption of RDX to a variety of sterilized soils in equilibrium batch tests. Their batch kinetic results showed RDX sorption was faster than TNT (equilibrium attained in 4 hr). Their column experiments confirmed application of the local equilibrium assumption and a linear isotherm model to continuous flow systems. Xue, Iskandar, and Selim (1995) also described RDX adsorption with a linear isotherm. Townsend, Myers, and Adrian (1996) found that RDX and HMX column elution curves could be adequately described using linear equilibrium sorption. Loehr (1989), however, reported ill-defined sorption of RDX and HMX to two soils that was inconsistent with standard isotherm equations. Brannon et al. (1992) also described anomalous soil sorption of RDX.

Information gaps on sorption and generation of transformation products from TNT, RDX, and HMX are even more serious than those for the parent compounds. Development of model descriptors for transformation products is important because some transformation products are toxic (Won, DiSalvo, and Ng 1976). In addition, TPs compete with parent compounds for sorption sites and may significantly affect mass balance, depending on transformation rates. TNT transformation products from reductive processes have been identified (Figure 1). However, information on TNT transformation rates is limited. Information is available on the types of RDX transformation products to expect (McCormick, Cornell, and Kaplan 1981), but little is known about generation rates and sorption properties of RDX transformation products. For HMX, there is little information on transformation products.

Thus, few aspects of explosives sorption to soils and aquifer materials are unequivocally accepted. Much of what is known is based on incompletely characterized batch experiments involving sorption and transformation. Complementary batch and column studies of TNT, RDX, and HMX that demonstrate the applicability of batch sorption isotherms to continuous flow systems are scant. Studies of this nature are critical to development of accurate and relevant descriptors of sorption and transformation processes for TNT, RDX, and HMX. The present understanding of sorption and transformation process rates for explosives is inadequate and limits development of accurate models of TNT, RDX, and HMX subsurface transport.

## Scope and Objectives

This report describes laboratory experiments conducted to improve the state-of-knowledge and explore difficulties in mathematical formulation of key

processes affecting subsurface transport of explosives. Attention is given to transformation and sorption processes affecting transport in sterilized and unsterilized soils. Batch tests were conducted to obtain information on sorption/transformation kinetics under abiotic, biotic, anaerobic, and aerobic conditions over a range of soil types. Soil column experiments were conducted to determine the relative significance of sorption and transformation of explosives for selected soils and to evaluate transport model structure for sorption/transformation sinks.

## 2 Materials and Methods

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Table 1 shows the experimental matrix for batch and column experiments. Three soils were investigated in batch and column experiments. One soil, Yokena clay, was common to both batch and column experiments.

### Batch Kinetic Tests

Two sets of batch experiments were conducted to examine the adsorption and transformation kinetics of TNT, 4A-DNT, and RDX. Experimental conditions for each set of experiments are described below.

#### Batch experiment-1

The first experiment examined biotic and abiotic adsorption kinetics of TNT, 4A-DNT, and RDX for soils under aerobic conditions. Three soils free of explosives contamination (West End, D Street, and Yokena clay) were selected to represent a range of properties associated with sorption processes, i.e., clay content, total organic carbon (TOC), and cation exchange capacity (CEC). West End and D Street soils are aquifer materials from Rocky Mountain Arsenal, Denver, CO. Yokena clay is a soil from the Vicksburg, MS, area that is high in clay content, CEC, and TOC. Soils were characterized for particle size distribution using the methods of Day (1956) as modified by Patrick (1958). Total organic carbon was determined by American Public Health Association (1989) Method 5310 D. Cation exchange capacity was determined by the ammonium saturation method (Plumb 1981). Extracts were analyzed according to U.S. Environmental Protection Agency (USEPA) Standard Method 350.1 (USEPA 1982). Soil properties are listed in Table 2.

Three replicates for each sampling time for each soil were prepared. Abiotic samples of each soil were prepared for sampling at intervals of 2 hr, 6 hr, 12 hr, 24 hr, 3 days, 7 days, and 14 days. Biotic samples were prepared for the same sampling intervals with additional samples added for sampling at 1 min, 5 min, 15 min, and 1 hr.

<b>Table 1 Experimental Matrix</b>			
	<b>Batch-1</b>	<b>Batch-2</b>	<b>Columns</b>
<b>Explosives</b>			
TNT	✓	✓	✓
RDX	✓		✓
HMX			✓
<b>Conditions</b>			
Aerobic-biotic	✓	✓	
Aerobic-abiotic	✓	✓	
Anaerobic-biotic		✓	✓
Anaerobic-abiotic		✓	
<b>Soils</b>			
Yokena clay	✓	✓	✓
WES-silt			✓
Ottawa sand			✓
D Street	✓		
West End	✓		
<b>TNT TPs</b>			
2-DNT	✓	✓	✓
4-DNT	✓	✓	✓
2,4-DANT	✓	✓	✓
2,6-DANT	✓	✓	✓

<b>Table 2 Soil Properties</b>						
<b>Soil</b>	<b>pH</b>	<b>% TOC<sup>1</sup></b>	<b>Particl Size</b>			<b>CEC<sup>2</sup> (meq/100 g)</b>
			<b>% Sand</b>	<b>% Silt</b>	<b>% Clay</b>	
West End	7.7	0.177	72.5	20.0	7.5	45.7
D Street	7.7	0.172	95.0	50.0	0.0	1.78
Yokena clay	5.3	2.400	2.0	64.0	34.0	38.9
WES-silt	5.3	0.567	2.5	90.0	7.5	12.4
Ottawa sand	--- <sup>3</sup>	---	92.5	7.5	0.0	---

<sup>1</sup> Total organic carbon.  
<sup>2</sup> Cation exchange capacity.  
<sup>3</sup> --- not measured.

Samples for testing under aerobic-abiotic conditions were sealed and treated to prevent microbial degradation by soil microorganisms during testing. The soils were irradiated with a gamma-ray source at Louisiana State University for 16 hr. This exposure time ensures at least one megarad of radiation to all parts of the sample. The source consisted of an annular array of Co-60 rods and plates clad in stainless steel centered in a pit under 5.5 m of water. The total activity of the source was 3071 Curies on July 30, 1986.

Four grams dry weight of soil were weighed into 25-ml glass centrifuge tubes, and 16 ml of distilled water was added to each tube. This was followed by spiking tube contents with either RDX, TNT, or 4A-DNT. To each of the tubes for RDX testing, 16 µg (1 µg/ml) of radiolabeled [2,4,6-<sup>14</sup>C]1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX) (Chemsyn Science Laboratories) having a specific activity of 7.75 mCi/mmol, a chemical purity greater than 97.6 percent as determined by high performance liquid chromatography (HPLC), and a radiochemical purity greater than 99 percent as determined by radio-HPLC were added in an acetone carrier. To each of the tubes for TNT and 4A-DNT testing, 80 µg (5 µg/ml) of cold material were added with acetone or methanol carrier, respectively.

The tubes were placed on a reciprocating box shaker for 24 hr at 180 excursions/min to ensure adequate mixing. Samples were removed from the shaker at the intervals described earlier and centrifuged for 20 min at 10,000 rpm. After centrifugation, samples spiked with RDX were quantified by counting 1 ml of aqueous sample in 15 ml of UltimaGold Liquid Scintillation Cocktail (Packard Instruments Company, Inc., Meriden, CT) in a Packard TriCarb 2500 Liquid Scintillation (LS) Analyzer. Each sample was counted using the external standard method for 2 min through two cycles and the disintegrations per minute averaged.

Aqueous samples from tubes spiked with TNT and 4A-DNT were analyzed by HPLC for TNT, 4A-DNT, 2A-DNT, 2,4-DANT, 2,6-DANT, and trinitrobenzene (TNB). Samples were extracted by mixing 1 ml of sample with 1 ml of acetonitrile, filtering the mixture through a 0.5-µm filter, then storing the filtrate in amber 2-ml vials in a refrigerator until it was analyzed by HPLC.

Two grams of soil from each sample amended with TNT and 4A-DNT (2 hr and higher) were extracted for 12 hr with 10 ml of acetonitrile then centrifuged for 15 min at 10,000 rpm. Five milliliters of the centrifugate were combined with 5 ml of distilled water, shaken, and allowed to stand for 15 min. Samples were then filtered through a 0.5-µm polytetrafluoroethylene (PTFE) filter, and a 2-ml portion was stored in amber vials in a refrigerator until analyzed by HPLC. Residual soil RDX concentrations in samples amended with RDX were extracted and analyzed by HPLC for the 24-hr and 14-day samples. A 3-g portion of wet soil was extracted for 18 hr in a sonic bath with 10 ml of acetonitrile. The extracts were diluted 1:1 with calcium chloride solution (5 g/l), filtered through a 0.5-µm PTFE membrane filter, and analyzed by HPLC. A portion of each soil sample was also analyzed for percent solids.

## Batch experiment-2

The second experiment focused on Yokena clay TNT adsorption and transformation kinetics. TNT adsorption/transformation kinetics were investigated under four conditions at higher initial solution concentrations than were used in batch experiment 1. Treatments included aerobic-biotic, aerobic-abiotic, anaerobic-biotic, and anaerobic-abiotic. In the abiotic experiments,  $\text{HgCl}_2$  (4.25 g/l) was used to eliminate biological activity.

To each 500-ml polycarbonate centrifuge tube, 90 g clay and 360 ml distilled water were added. Tubes for the aerobic-biotic and -abiotic treatments were spiked immediately following the addition of water. Soils for the anaerobic-biotic and -abiotic treatments were sealed after addition of deoxygenated distilled water and mechanically shaken for 10 days to allow development of anaerobic conditions prior to spiking. Redox potential measurements taken with a platinum electrode following 24 hr of equilibration on two dedicated replicates showed that a moderately reducing redox potential of +380 mV was attained in the anaerobic clay soil. The  $\text{HgCl}_2$  was added to the abiotic-anaerobic treatment following the 10-day anaerobic incubation.

The aqueous phase in each treatment was spiked with TNT to provide an initial TNT concentration of 100  $\mu\text{g/ml}$ . All treatments were duplicated. The tubes were sealed, placed on a reciprocating horizontal shaker at 180 excursions per minute and sampled at intervals of 5 min, 15 min, 30 min, 45 min, 60 min, 2 hr, 6 hr, 12 hr, 24 hr, 48 hr, and 72 hr. Aerobic sampling was conducted by removing tubes from the shaker and pipeting 5 ml of slurry into a 25-ml glass centrifuge tube. Tubes were centrifuged at 10,000 rpm for 20 min after which the aqueous phase was removed, diluted 1:1 with acetonitrile, and filtered through a 0.5- $\mu\text{m}$  PTFE filter. Filtered samples were stored in 2-ml glass amber vials at 10 °C until analyzed for TNT, 2A-DNT, 4A-DNT, 2,4-DANT, 2,6-DANT, and TNB by HPLC. Anaerobic samples were handled in a similar manner except that all operations prior to dilution of the filtered sample with acetonitrile were conducted under a nitrogen atmosphere in a glove box.

## Soil Column Sorption/Transformation Tests

Soil column experiments were conducted in stainless steel columns (Figure 2) 15.24 cm in length, with a 4.45-cm inside diameter. Three uncontaminated soils were used, WES-silt (soil from the Vicksburg, MS, area), Yokena clay (soil from the Vicksburg, MS, area), and Ottawa sand (U.S. Silica Company, Ottawa IL) (Table 2). Columns were loaded in two approximately equal lifts. The soil surface was scarified between lifts to minimize bedding planes. Flow (upflow mode) was set to provide an average pore velocity of about  $1 \times 10^{-4}$  cm/sec using constant-volume metering pumps (Fluid Metering, Inc., Model QG6-0-SSY). Operating parameters for the columns are provided in Table 3. Soil specific gravity was determined according to methods described in U.S. Army Corps of Engineers (1970). Bulk density and porosity were calculated from air-dried

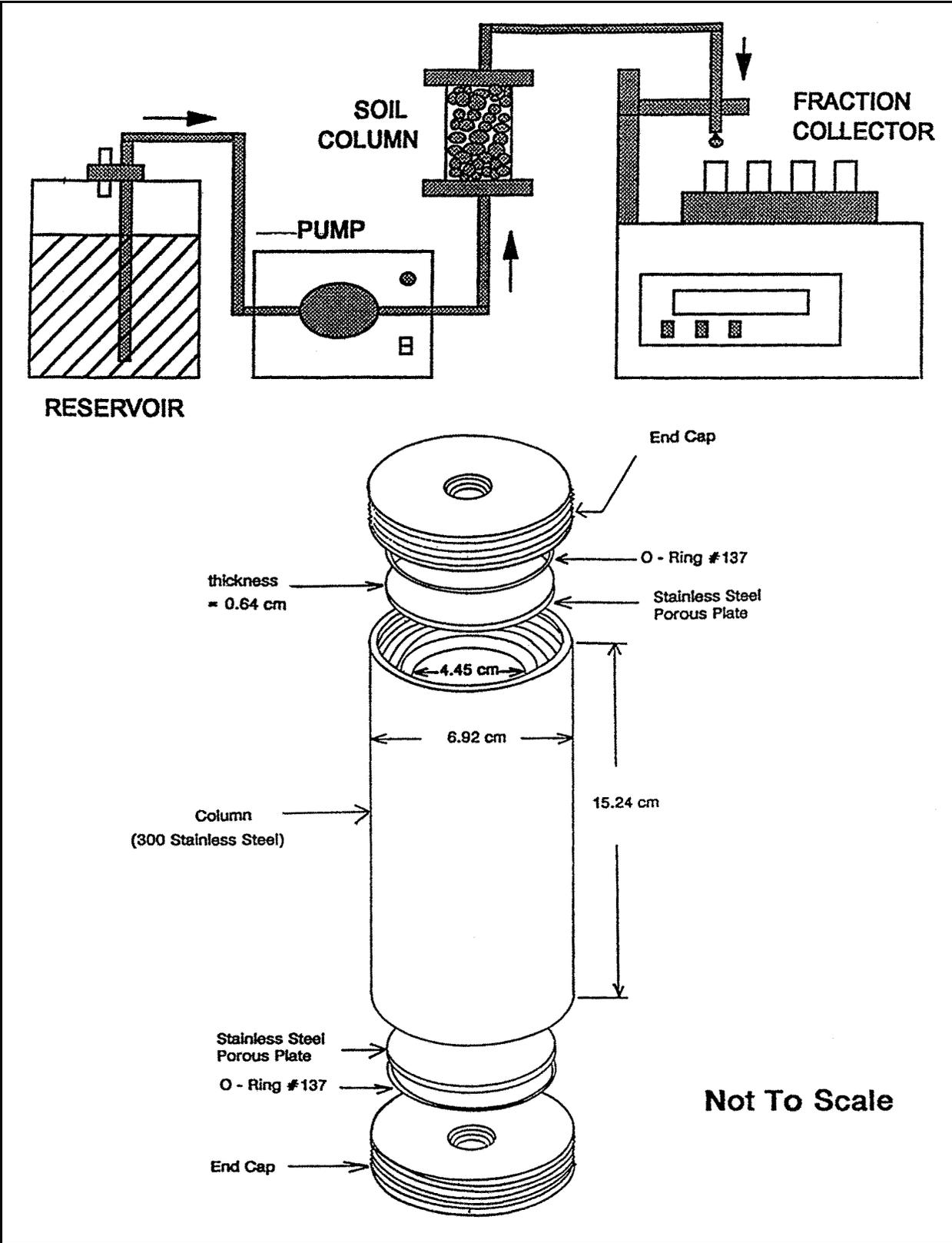


Figure 2. Soil column test apparatus and soil column schematic

<b>Column</b>	<b>v, cm/sec</b>	<b>D, cm<sup>2</sup>/sec</b>	<b>ρ<sub>b</sub>, g/cm<sup>3</sup></b>	<b>n</b>	<b>SG</b>
WES-silt	1.29 × 10 <sup>-4</sup>	4.40 × 10 <sup>-5</sup>	1.017	0.60	2.54
Yokena clay	1.15 × 10 <sup>-4</sup>	7.28 × 10 <sup>-5</sup>	0.990	0.63	2.67
Ottawa sand	1.59 × 10 <sup>-4</sup>	2.23 × 10 <sup>-5</sup>	1.425	0.47	2.68

Note: v = Average pore water velocity. D = Dispersion coefficient. ρ<sub>b</sub> = Bulk density.  
N = Porosity. SG = Specific gravity.

water content, total soil weight loaded, specific gravity, and column inside dimensions.

After soil loading, de-aired, distilled-deionized water was pumped at steady flow through the columns for 5 to 7 days (approximately 5 to 7 pore volumes) to allow the hydraulic properties of the columns to stabilize and to fully develop anaerobic conditions. Laboratory synthesized polluted groundwater (PGW) was then pumped into the columns at steady flow to provide a step input loading sufficient to displace four pore volumes. The contaminated water was prepared by shaking a highly contaminated soil from the Naval Surface Warfare Center (NSWC), Crane, IN (Crane conveyor soil), with distilled-deionized water for 24 hr at a liquid-to-solids ratio of 2:1. Solids-liquid separation was accomplished by centrifugation and filtration (1 μm binderless, glass fiber). Two batches of contaminated water were prepared. The first batch was used in the Yokena clay column experiment, and the second batch was used in the WES-silt and Ottawa sand column experiments. TNT, HMX, RDX, 2A-DNT, 4A-DNT, 2,6-DANT, 2,4-DANT, and TNB concentrations in the contaminated water were monitored during step input loading, and no significant changes were observed in either batch (Table 4). After step input loading, columns were eluted with de-aired, distilled-deionized water at the same flow used for the step input loading.

At the end of the column elution experiments, the columns were sectioned, and the sectioned soil samples were analyzed for TNT, RDX, HMX, 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT using the dual column method (Jenkins and Walsh 1987). A 3-g portion of wet soil was extracted for 18 hr in a sonic bath with 10 ml of acetonitrile. The extracts were diluted 1:1 with calcium chloride solution (5 g/l), filtered through a 0.5-μm PTFE membrane filter, and analyzed on the two HPLC systems described in the next section. A portion of each soil sample was also analyzed for percent solids.

### **Explosives analysis**

Column eluate samples were collected in 10- to 40-ml increments in amber glass vials (40 ml) using an Eldex Laboratories, Inc., Model UFC fraction

<b>Table 4</b>								
<b>Step Input Polluted Groundwater Contaminant Concentrations (mg/l)</b>								
<b>Day</b>	<b>TNT</b>	<b>2A-DNT</b>	<b>4A-DNT</b>	<b>RDX</b>	<b>HMX</b>	<b>TNB</b>	<b>2,4-DANT</b>	<b>2,6-DANT</b>
<b>WES-Silt</b>								
0	69.9	2.98	2.40	39.6	3.16	0.305	0.250	0.054
1	70.2	2.95	2.39	39.8	3.14	0.320	0.231	0.041
2	69.2	2.94	2.38	39.5	3.13	0.369	0.225	0.028
3	68.0	2.91	2.36	39.0	3.08	0.415	0.232	0.033
4	67.9	3.00	2.42	39.5	3.12	0.421	0.239	0.041
<b>Yokena Clay</b>								
0	110	3.23	2.92	64.7	5.56	0.300	<0.200	<0.200
1	110	3.25	2.91	64.7	5.53	0.336	<0.200	<0.200
3	108	3.13	2.78	63.8	5.43	0.372	<0.200	<0.200
<b>Ottawa Sand</b>								
0	69.9	2.98	2.40	39.6	3.16	0.305	0.250	0.054
1	70.2	2.95	2.39	39.8	3.14	0.320	0.231	0.041
2	69.2	2.94	2.38	39.5	3.13	0.369	0.225	0.028
3	68.0	2.91	2.36	39.0	3.08	0.415	0.232	0.033
4	67.9	3.00	2.42	39.5	3.12	0.421	0.239	0.041

collector. Samples were preserved with methanol (1:1) within 12 hr of collection and stored at 4 °C in capped vials until analyzed. Column eluate samples were analyzed by HPLC for TNT, TNB, RDX, HMX, 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT using the dual column confirmation method developed by Jenkins, Miyares, and Walsh (1988). The sample extracts were filtered through a 0.5-µm PTFE membrane filter and analyzed independently on two HPLC systems (Millipore/Waters Chromatography Division, Milford, MA). The first HPLC system consisted of a 600E system controller, a 712 Wisp Auto Injector, and a 486 Tunable Absorbance Detector. The second HPLC system consisted of an HPLC Module I. The column for the first system was an Ultracarb 5 ods 20 (250- by 3.2-mm) column (Phenomenex, Torrance, CA) eluted with 1:1 methanol/water at 0.5 ml/min. The column for the second system was an HPLC-CN (Supelco 25-cm by 4.6-mm) column eluted with 1:1 methanol/water at 2.0 ml/min.

## Dispersion coefficients

Following the elution of explosives, column dispersion coefficients were determined using a chloride tracer. For WES-silt and Ottawa sand, a constant input of sodium chloride solution at approximately 87 mg/l as Cl<sup>-</sup> was pumped into the columns until the initial Cl<sup>-</sup> concentration was achieved in the effluents. For Yokena clay, a known mass of chloride (500 µl at 100,000 mg/l as NaCl) was introduced at the column inlet to simulate an instantaneous pulse or slug. Chloride concentrations in column eluates were measured potentiometrically using a chloride selective ion electrode (Orion 9417B) in conjunction with a double junction, sleeve-type reference electrode (Orion 90-02). Potentials were measured on an ion-selective meter (Orion 720A). Nonlinear curve fitting (TableCurve, Jandel Scientific, Corte Madera, CA) of conservative tracer transport models was used to estimate dispersion coefficients.

A semi-infinite advection-dispersion model was fitted to the salt elution curves for WES-silt and Ottawa sand columns. The semi-infinite model for a constant input is given below (van Genuchten and Alves 1982).

$$C_T = \frac{C_o}{2} \left[ \operatorname{erfc} \left( \frac{(1 - T)L}{2 \left( \frac{DTL}{v} \right)^{\frac{1}{2}}} \right) + \exp \left( \frac{vL}{D} \right) \operatorname{erfc} \left( \frac{(1 + T)L}{2 \left( \frac{DTL}{v} \right)^{\frac{1}{2}}} \right) \right] \quad (1)$$

where

$C_T$  = chloride concentration at  $L$  and  $T$ , mg/l

$C_o$  = initial chloride concentration, mg/l

$T$  = pore volumes eluted (dimensionless time), dimensionless

$L$  = column length, cm

$D$  = dispersion coefficient, cm<sup>2</sup>/sec

$v$  = average pore water velocity, cm/sec

From nonlinear curvefitting of Equation 1 with the dispersion coefficient as the only adjustable parameter, dispersion coefficients of  $4.40 \times 10^{-5}$  cm<sup>2</sup>/sec and  $2.23 \times 10^{-5}$  cm<sup>2</sup>/sec were obtained for the WES-silt and Ottawa sand columns, respectively. Figure 3 shows the observed and fitted chloride elution curves for WES-silt and Ottawa sand.

A semi-infinite model for a slug input was fitted to the salt elution curve for the Yokena clay column. This model is given below (Levenspiel 1972).

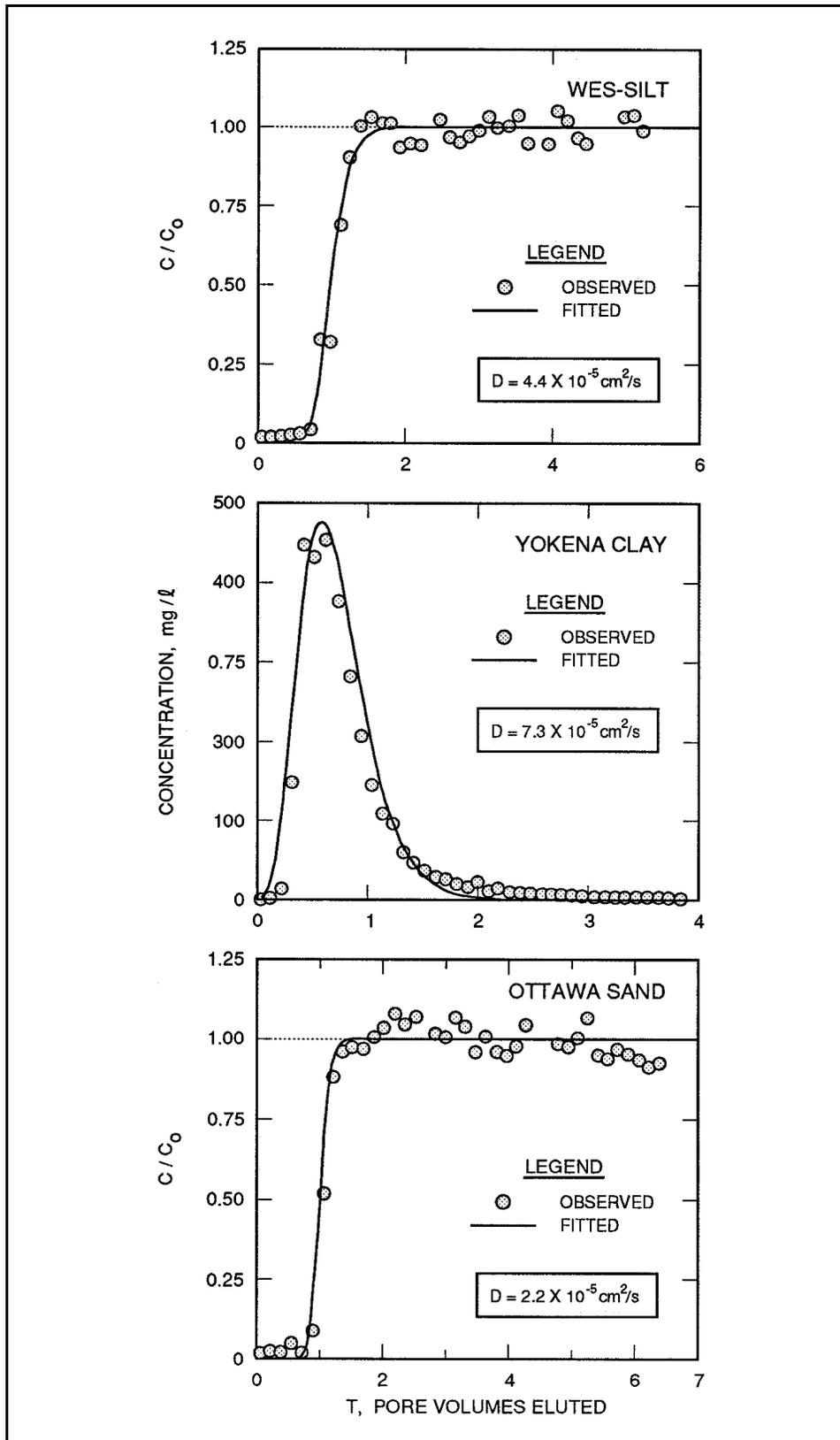


Figure 3. Observed and fitted chloride elution curves

$$C_T = \left[ \frac{M}{A \sqrt{\frac{4\pi DTL}{v}}} \right] \exp\left( - \frac{Lv (1 - T)^2}{4DT} \right) \quad (2)$$

where

$C_T$  = chloride concentration at  $L$  and  $T$ ,  $\mu\text{g}/\text{cm}^3$

$M$  = chloride input mass,  $\mu\text{g}$

$A$  = pore area,  $\text{cm}^2$

$D$  = dispersion coefficient,  $\text{cm}^2/\text{sec}$

$T$  = pore volumes eluted (dimensionless time), dimensionless

$L$  = column length,  $\text{cm}$

$v$  = average pore water velocity,  $\text{cm}/\text{sec}$

From nonlinear curve fitting of Equation 2 with the dispersion coefficient as the only adjustable model parameter, a dispersion coefficient of  $7.28 \times 10^{-5} \text{ cm}^2/\text{sec}$  was obtained for the Yokena clay soil column. Figure 3 shows the observed and fitted Yokena clay chloride elution curve.

## 3 Results and Discussion

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### Batch Tests Results

#### Batch experiment-1 (aerobic soils)

**TNT.** Disappearance of solution phase TNT under biotic conditions was rapid for the West End and Yokena clay soils (Figure 4), with most of the disappearance occurring within the first 15 min. Initial disappearance of solution phase TNT in these soils is probably due to adsorption to the soil phase. Solution phase TNT concentrations for D Street soil tended to increase and then decrease. Since the concentrations were near or above the initial spiked concentration (5 mg/ℓ), there was little TNT adsorption by the D Street soil. After the initially rapid adsorption in the West End and Yokena clay soils, disappearance of solution phase TNT continued, but at a slower rate. TNT solution phase concentrations after 6 hr were very close to the 2-hr values for West End and Yokena clay soils. The slow decrease between 2 and 6 hr may be due to gradual formation of transformation products (Pennington and Patrick 1990; Ainsworth et al. 1993). Solution concentrations of TNT under abiotic conditions are not reported because sampling was limited to 120 and 360 min in the initial 360-min period where most concentration changes occurred.

Soil phase TNT concentrations (Figure 5) under biotic conditions decreased for Yokena clay and West End soils over time. Virtually all of the soil phase TNT for the Yokena Clay soil disappeared within 12 hr. The rate of disappearance in soil phase TNT under biotic conditions for the West End soil was relatively steady and less than the rate for Yokena clay soil. Soil phase TNT concentrations for D Street soil started out low and tended to remain low as would be expected from the solution phase data. Soil phase losses cannot be accounted for as TNT transformation to 2A-DNT, 4A-DNT, 2,6-DANT, 2,4-DANT, or TNB. These TPs were below detection limits, 0.25 mg/kg and 0.02 mg/ℓ, in both soil and solution phases, respectively. Soil phase TNT concentrations (Figure 5) under abiotic conditions were more variable than trends observed under biotic conditions. Trends for the Yokena Clay and D Street soils under abiotic conditions were generally similar to those observed under biotic conditions. Soil phase TNT concentrations in West End soil were

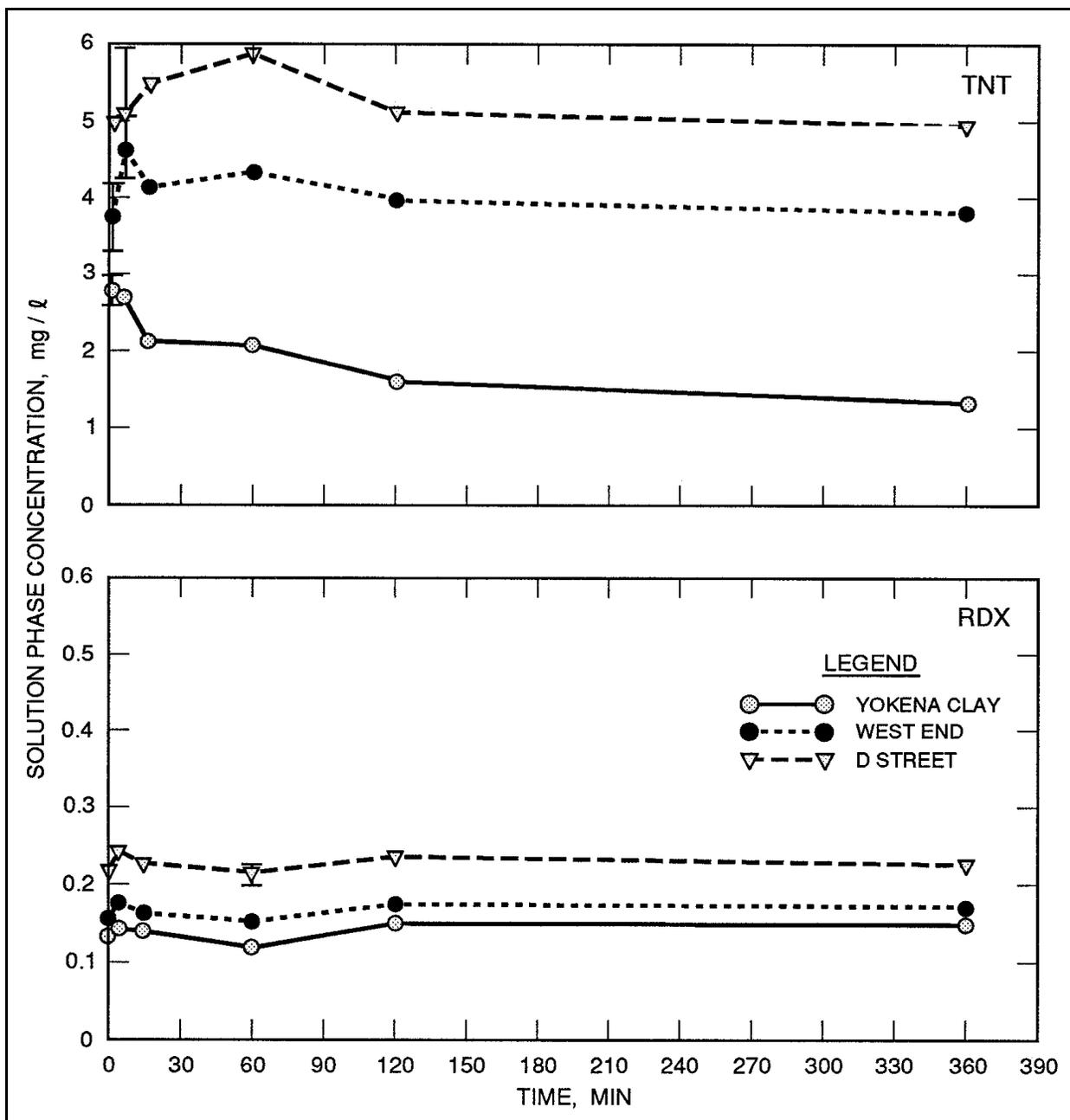


Figure 4. Batch solution phase concentration of TNT and RDX in aerobic soil under biotic conditions

generally lower under abiotic conditions. The reason for the rise in soil concentrations at 336 hr in all soils is not readily apparent.

Biotic TNT recoveries are shown in Figure 6. Recovery calculations included TNT sorbed and in solution plus transformation products sorbed and in solution. At the beginning of the test, TNT recoveries were 100 percent or greater from all three biotic soils. Recoveries decreased in all biotic soils as time of exposure increased, decreasing to 60 or 70 percent for West End and D Street

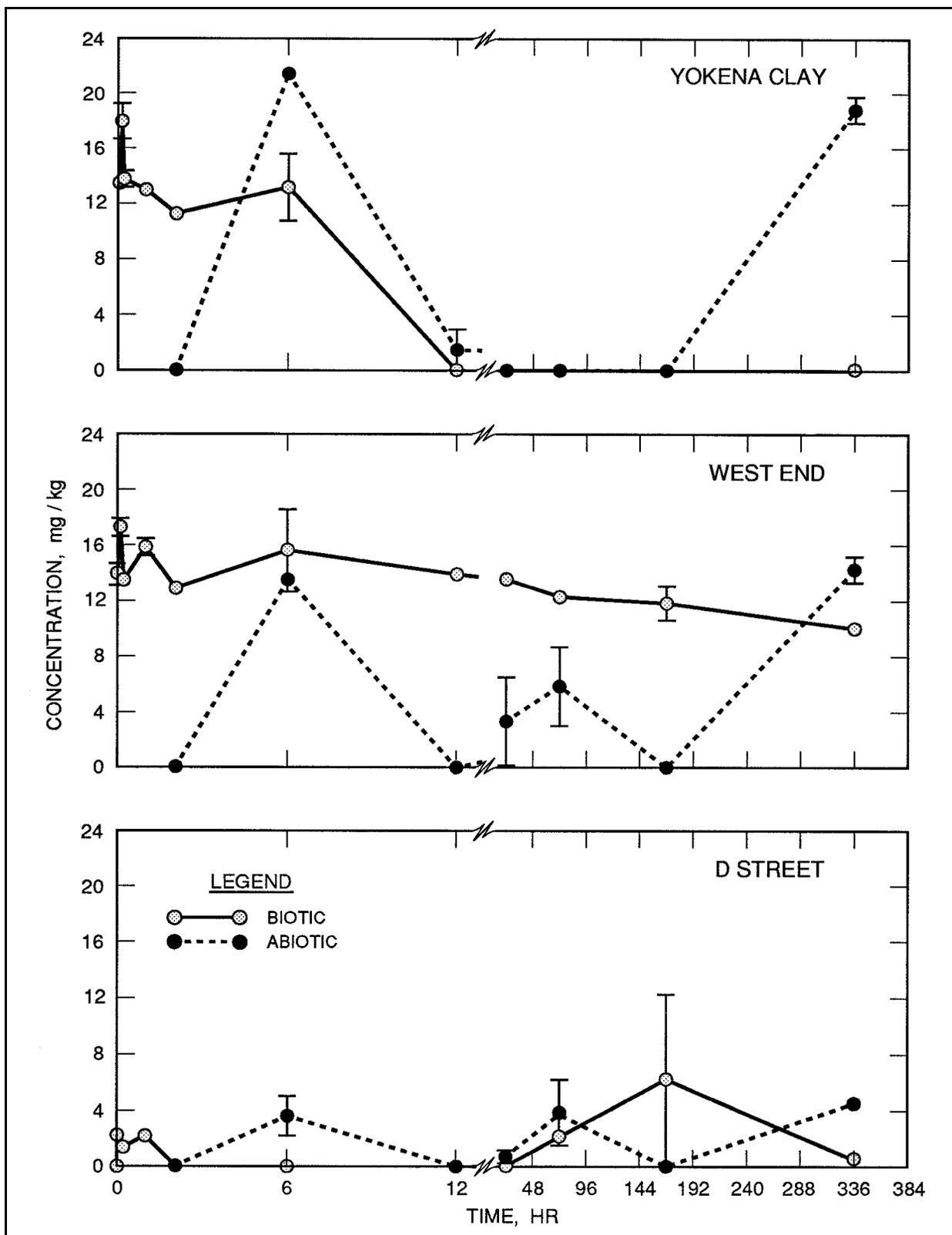


Figure 5. Batch soil phase concentrations of TNT in aerobic soil solution under biotic and abiotic conditions

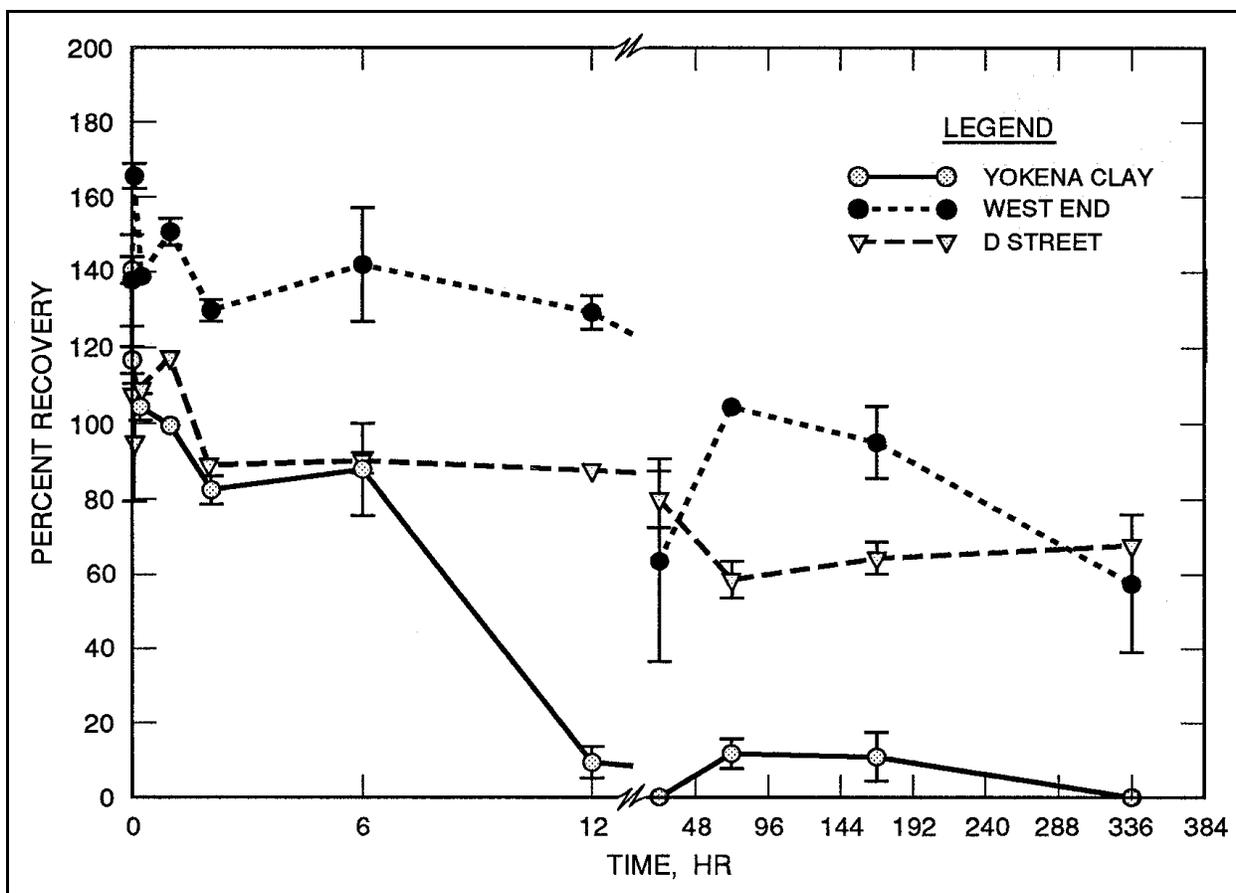


Figure 6. Batch percent recovery of TNT from tests of aerobic soil under biotic conditions

soils following 14 days of exposure. Recoveries in the Yokena clay soil were less than 10 percent for all sampling times after 12 hr. TNT recoveries in abiotic soils were as variable as soil phase TNT concentrations and showed similar trends.

The biotic data presented in Figure 4 suggest correlation of initial TNT disappearance (adsorption) to soil clay content and to a lesser degree soil organic carbon. Biotic solution phase concentrations were highest in the D Street soil (no clay, 0.172-percent organic carbon) and lowest in the Yokena clay soil (34.0-percent clay, 2.4-percent organic carbon). Solution phase concentrations in the West End soil (7.5-percent clay, 0.0174-percent organic carbon) were intermediate between D Street and Yokena clay soils. The biotic recoveries in Figure 6 show somewhat similar trends. Recoveries for the Yokena clay soil were significantly less than the recoveries for the West End and D Street soils. However, recoveries for West End soil were initially higher than recoveries for D Street soil. After 14 days, recoveries for West End and D Street soils were similar. The data in Figure 6 also suggest some unexplained problem with the West End soil data because initial percent recoveries are well above 100 percent.

The abiotic data in Figure 5 are too inconsistent for interpretation with regard to abiotic TNT disappearance relative to biotic TNT disappearance. Such inconsistencies in TNT sorbed concentrations in abiotic soils have been noted previously (Brannon et al. 1992) and remain unexplained.

**4A-DNT.** Batch data for 4A-DNT tended to be less variable under abiotic conditions than under biotic conditions (Figure 7). Solution concentrations of 4A-DNT had already stabilized in abiotic West End and D Street soils by the time the first sample was taken (2 hr). In the abiotic Yokena clay soil, solution concentrations of 4A-DNT decreased from the initial concentration of 5 mg/ℓ to 2 mg/ℓ at 2 hr and then to approximately 1 mg/ℓ at the 14-day sampling time.

Solution phase concentrations of 4A-DNT in biotic soils showed an initial decrease followed by an increase. In the D Street soil, biotic solution phase concentrations decreased and eventually returned to approximately the initial solution concentration. For the West End soil, biotic solution phase concentrations decreased and then increased, but the standard error (error bars in Figure 7) for the biotic results encompassed the abiotic results. Thus, it is difficult to distinguish between abiotic and biotic results for West End soil. For the Yokena clay soil, there was an initial decrease in solution phase concentrations followed by an increase to a concentration that was higher than the abiotic concentration. Thereafter, biotic and abiotic solution phase concentrations of 4A-DNT were similar for the clay soil. Comparison of biotic and abiotic data for the three soils investigated is therefore difficult. The decreases followed by increases in biotic soils cannot be explained. However, biotic and abiotic solution phase concentrations were similar at starting, middle, and end points.

The abiotic data in Figure 7 suggest correlation of solution phase 4A-DNT concentrations to soil clay content and to a lesser degree soil organic carbon. Abiotic solution phase concentrations for the D Street soil (no clay, low soil organic carbon) showed no tendency to change from the initial concentration (5 mg/ℓ). The West End soil (7.5-percent clay, low soil organic carbon) showed a small decrease in solution phase concentration of 4A-DNT. The Yokena clay soil (34.0-percent clay, high soil organic carbon) showed a decrease of over 50 percent from the initial solution phase concentration at 2 hr and a tendency to gradually decrease.

Soil phase concentrations of 4A-DNT showed differences for abiotic and biotic conditions and for different soil types (Figure 8). Soil phase concentrations of 4A-DNT under abiotic conditions tended to be more stable and show less overall change than under biotic conditions. In addition, abiotic concentrations tended to be higher than biotic concentrations. The Yokena clay soil showed the largest difference, and the sandy D Street soil showed the least difference, with the exception of one data pair (6 hr). As with TNT, most of the soil phase 4A-DNT in the biotic clay soil disappeared within 12 hr. This disappearance from the soil phase suggests that if biological reactions are not directly involved, they at least enhance the abiotic disappearance of 4A-DNT.

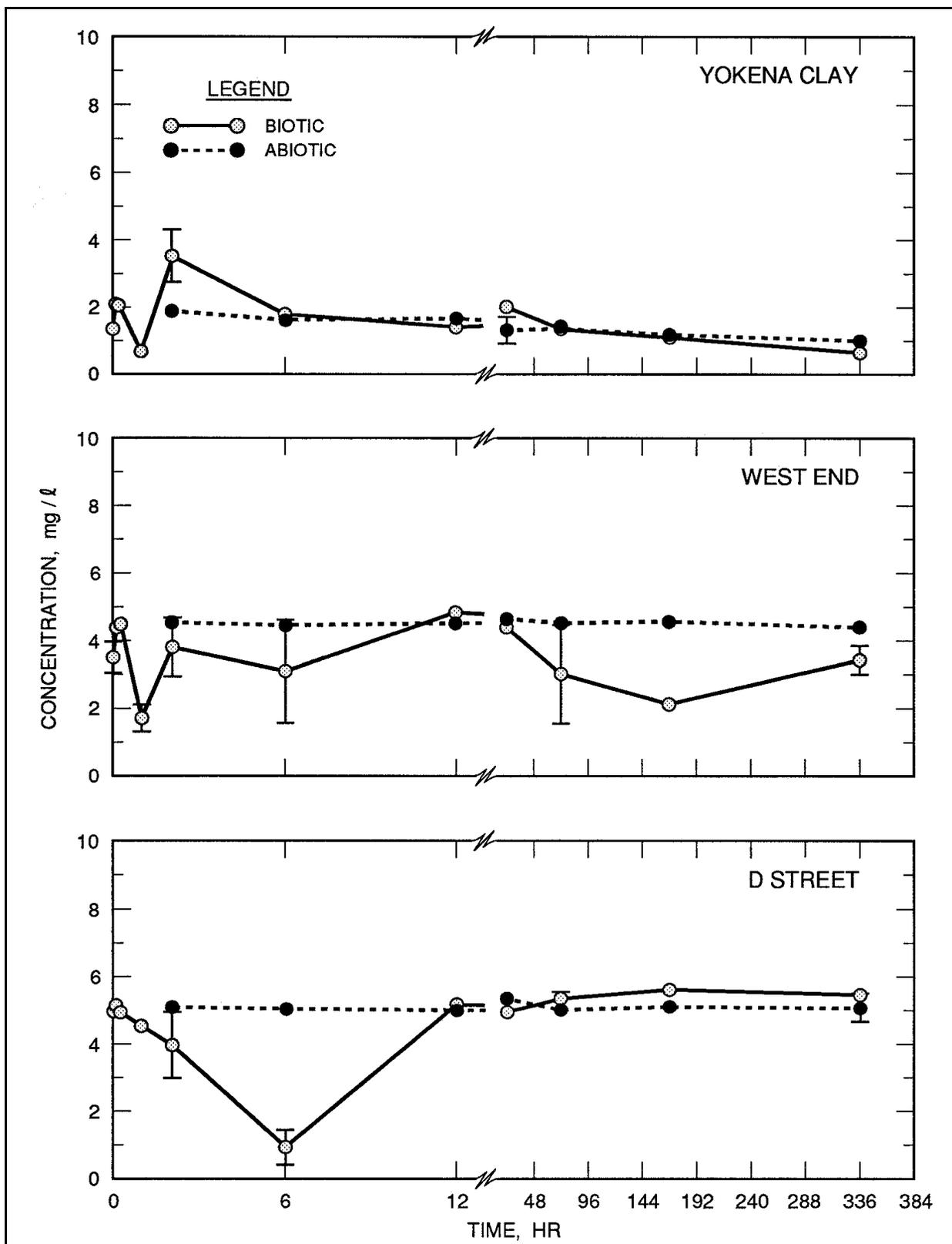


Figure 7. Batch solution phase concentrations of 4A-DNT in aerobic soil under biotic and abiotic conditions

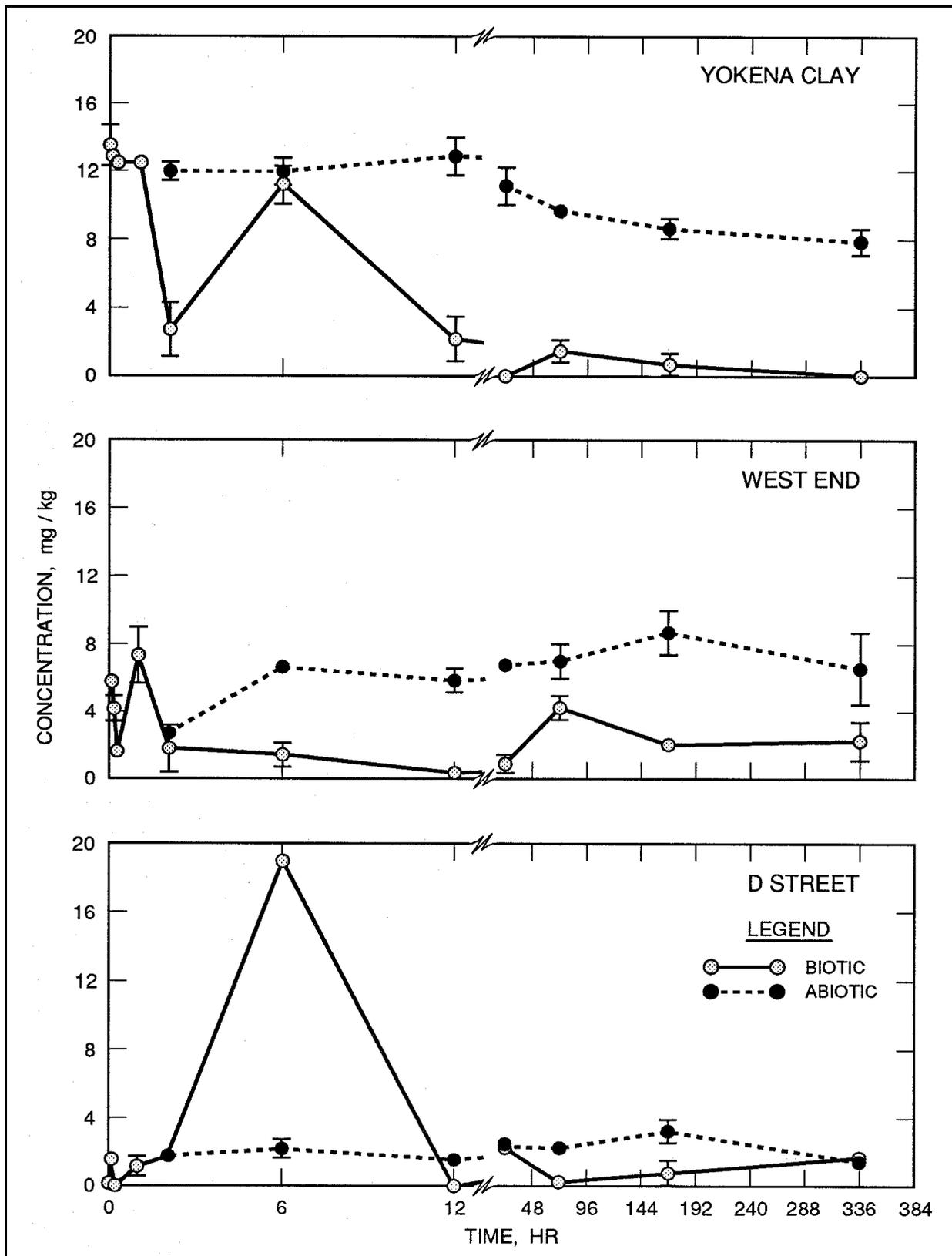


Figure 8. Batch soil phase concentrations of 4A-DNT in aerobic soil under biotic and abiotic conditions

Initial soil phase concentrations of 4A-DNT (Figure 8) were lowest in the D street soil and highest in the Yokena clay soil. Thus, initial soil sorption of 4A-DNT showed a dependency on soil properties, especially clay content.

Recoveries of 4A-DNT (Figure 9) were generally higher than those observed for TNT (Figure 6). Recoveries of 4A-DNT were similar under biotic and abiotic conditions for the D Street soil and lower under biotic conditions for the Yokena clay and West End soil. Highest 4A-DNT recoveries were associated with the soil with the lowest clay content, and lowest 4A-DNT recoveries were associated with the soil with the highest clay content. The differences between abiotic and biotic recoveries show that sterilization can reduce but cannot eliminate 4A-DNT disappearance in soils containing clay. In the soil containing no clay, there was little difference in recoveries between abiotic and biotic tests.

The 4A-DNT data showed that 4A-DNT sorbed and/or transformed. When TNT transforms to 4A-DNT, 4A-DNT will compete with TNT for sorption sites. It is likely that transformation products similar to 4A-DNT, such as 2A-DNT, 2,6-DANT, 2,4-DANT, and TAT, will also compete with TNT for sorption sites, and there could be an interaction between transformation and competitive sorption.

**RDX.** Adsorption of RDX under biotic conditions was rapid for all soils (Figure 4), with most of the adsorption occurring within the first 15 min. Stable solution concentrations of RDX were maintained under both biotic and abiotic conditions in all three soils for 14 days in all but the biotic Yokena clay soil (Figure 10). In the Yokena clay soil, concentrations gradually decreased after the 48-hr sampling period. Recoveries of added radiolabeled RDX measured at 1 and 14 days (Table 5) in the biotic soils reflected decreasing solution concentrations in the biotic Yokena clay soil. Recoveries of RDX were evaluated only after the 14-day incubation in the abiotic incubation. RDX recoveries were based on counting radioactivity in extracted samples. Recovery of added RDX in the abiotic Yokena clay soil following 14 days of exposure was 91.0 percent, significantly ( $p < 0.05$ ) higher than the 63.4-percent recovery following 14 days of exposure in the biotic soils. Recoveries in the biotic D Street and West End soils did not significantly differ between the 1- and 14-day incubations. Recoveries in abiotic D Street and West End soils after 14 days were comparable with recoveries in the 14-day biotic soils.

The difference between biotic and abiotic RDX recoveries at 14 days in Yokena clay suggests significant sorption/transformation in the biotic tests. RDX is biodegraded under anaerobic conditions to hydrazine and methanol, but aerobic biodegradation of RDX does not occur (McCormick, Cornell, and Kaplan 1981). However, microanaerobic regions may exist around soil particles due to the biological and chemical oxygen demand of soils. These microanaerobic regions could provide the reducing conditions needed for RDX biodegradation. Methanol produced by RDX biodegradation in microanaerobic regions would be converted to carbon dioxide and lost from the system. Biodegradation of RDX is also possible in the abiotic tests since gamma

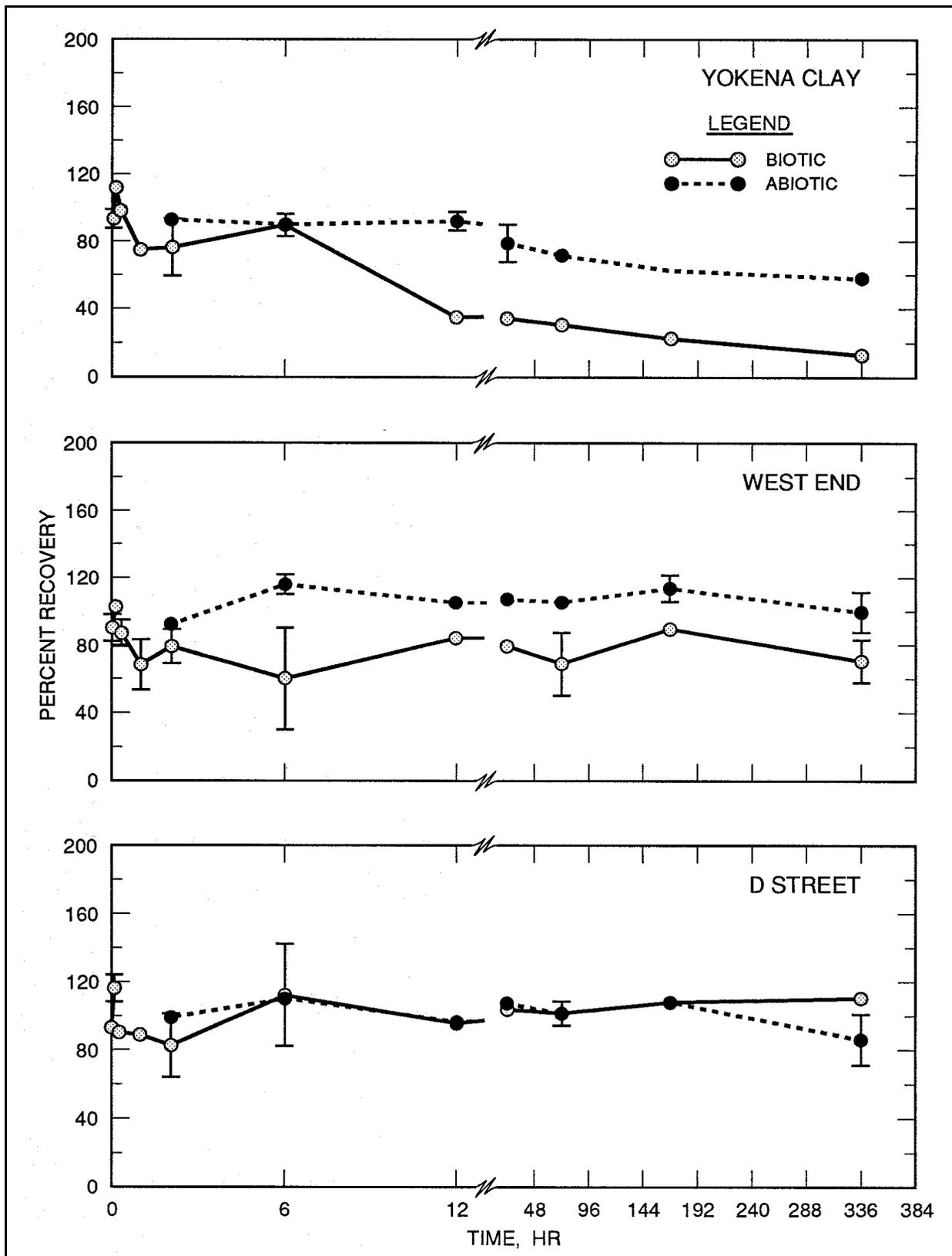


Figure 9. Batch percent recovery of 4A-DNT from tests of abiotic soil under biotic and abiotic conditions

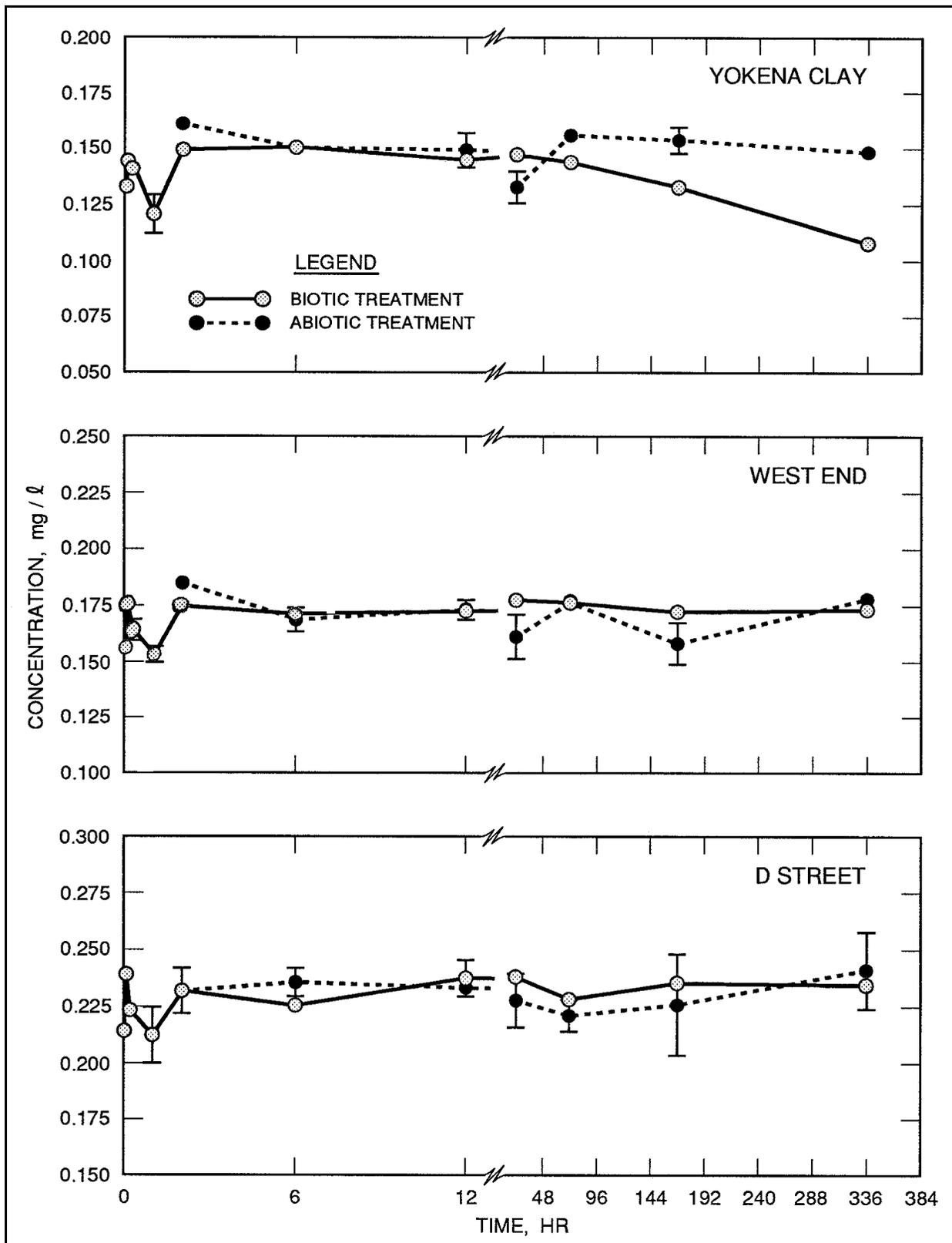


Figure 10. Batch solution phase concentrations of RDX in aerobic soil under biotic and abiotic conditions

<b>Table 5</b>			
<b>Percent Recovery of RDX Under Biotic and Abiotic Conditions</b>			
<b>Time, days</b>	<b>D Street</b>	<b>West End</b>	<b>Yokena Clay</b>
<b>Biotic Conditions</b>			
1	92.6 (2.3)	104.2 (2.0)	101.5 (2.7)
14	92.5 (2.2)	103.8 (1.0)	63.4 (1.7)
<b>Abiotic Conditions</b>			
14	97.7 (11.3)	98.9 (2.9)	91.0 (1.0)
Note: Standard error in parenthesis.			

radiation does not kill spores. In long test periods, spores can gradually repopulate sterilized soils with biota. If this is true, the design of the abiotic tests is compromised because a key variable—biological activity—is uncontrolled.

### **Batch experiment-2 (anaerobic and aerobic soils)**

The second batch experiment focused on Yokena clay soil where the most pronounced changes in TNT concentration and appearance of transformation products were noted. TNT sorption/transformation in the Yokena clay soil under aerobic conditions was further investigated at higher initial concentrations (100 mg/ℓ) under biotic and abiotic conditions.

In aerobic tests, adsorption was rapid under both biotic and abiotic conditions and resulted in similar concentrations of TNT in solution during the first 2 hr of exposure (Figure 11). Over the longer term, TNT solution concentrations in biotic tests were lower than in abiotic tests (Figure 12). This is due in part to transformation of TNT to 2A-DNT and 4A-DNT. Transformation products (2A-DNT, 4A-DNT) were not found in the abiotic treatment under aerobic conditions (Figure 13). The appearance of 2A-DNT and 4A-DNT, reductive transformation products, is evidence of microanaerobic regions around soil particles, as previously discussed for anaerobic RDX biodegradation in aerobic tests. As would be expected for aerobic testing, accumulation of reductive transformation products was low and accounts for only a small percentage of TNT disappearance.

Adsorption of TNT under anaerobic conditions (redox potential of +380 mV) was also explored at higher initial concentrations (100 mg TNT/ℓ) under biotic and abiotic conditions (Figure 14). Unlike the situation under aerobic conditions, anaerobic solution TNT concentrations in the abiotic treatment were much higher than in the biotic treatment. TNT concentrations in the biotic treatment decreased rapidly to about 5 mg/ℓ, then recovered to about 10 mg/ℓ, and essentially disappeared from solution after 24 hr of exposure. TNT

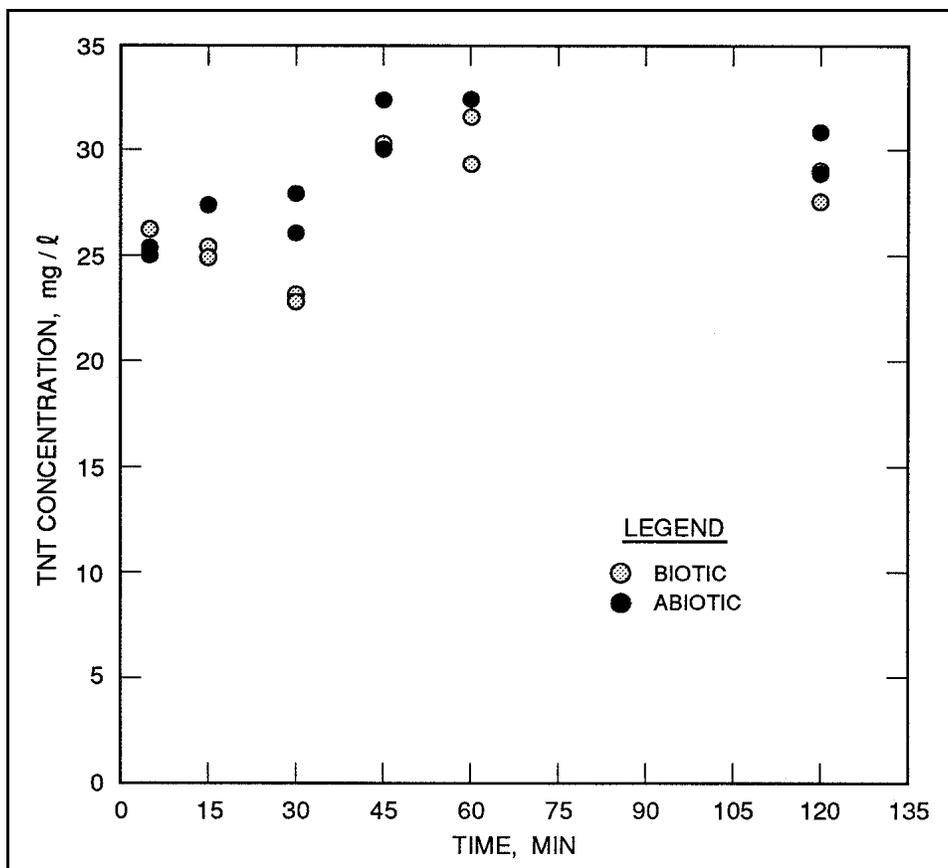


Figure 11. Batch solution TNT concentrations in aerobic clay soil under biotic and abiotic conditions during 2 hr of testing

concentrations in the abiotic treatment also declined rapidly (to about 10 mg/l), recovered to about 42 mg/l, then gradually declined until 24 hr of exposure, after which concentrations were steady. The disappearance of TNT in the biotic treatment was accompanied by the rapid appearance of 2A-DNT and 4A-DNT in solution. The appearance of trace concentrations of diamino compounds, 2,4-DANT and 2,6-DANT, was also observed. Concentrations of the 2A-DNT and 4A-DNT peaked at 12 hr, then began a gradual decline. Transformation products (2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT) were not detected in the abiotic treatment.

The TNT and TNT TPs solution phase data under anaerobic conditions are evidence of rapid adsorption, competitive sorption, and transformation. Rapid disappearance of TNT from solution occurred in both abiotic and biotic tests. Thus, the initial disappearance is probably adsorption. In both tests, there was a recovery of TNT in solution. In the biotic tests, as TNT concentrations in solution recovered, 2A-DNT and 4A-DNT increased. In the abiotic tests, TNT solution concentrations also increased but were not accompanied by identifiable TPs. Both the biotic and abiotic data therefore indicate competitive sorption with native soil constituents.

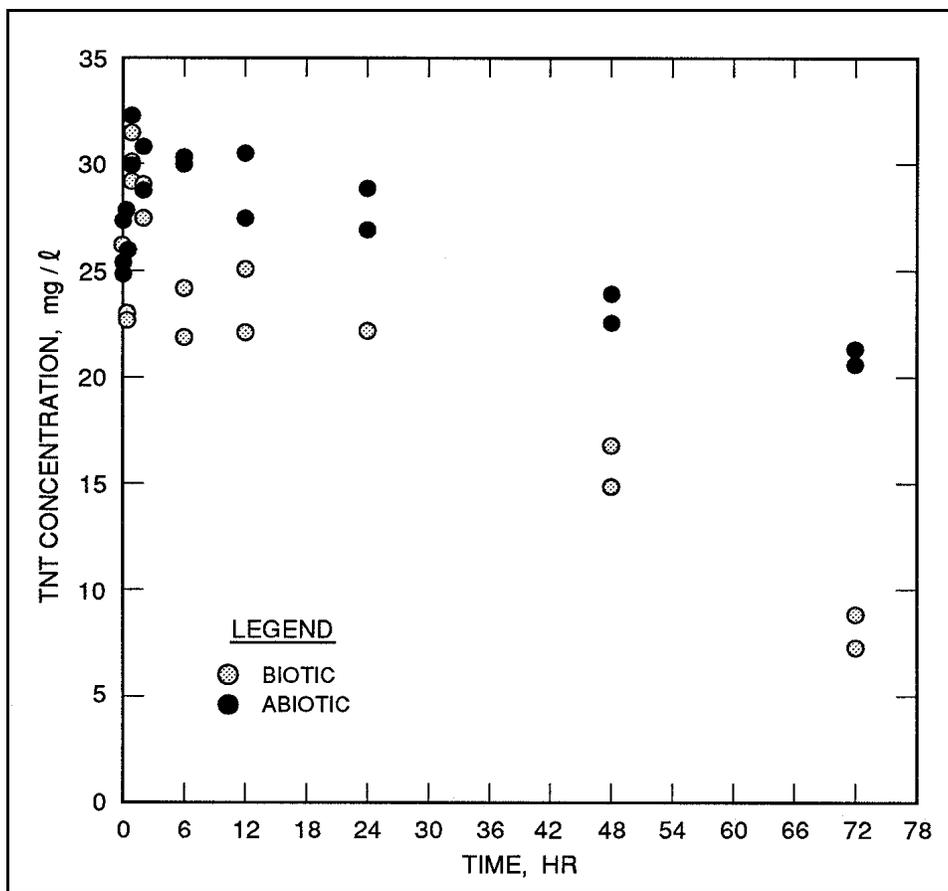


Figure 12. Batch solution TNT concentrations in aerobic clay soil under biotic and abiotic conditions during 72 hr of testing

The appearance of 2A-DNT and 4A-DNT in the biotic tests and lack of appearance in the abiotic tests is unequivocal evidence of biological TNT reductive transformation. This appears to occur in the soil phase. The decline in 2A-DNT and 4A-DNT with time in the biotic tests indicates sorption of TNT TPs as TNT disappears, since a concomitant appearance of 2,6-DANT and 2,4-DANT was not observed in the aqueous phase. The gradual decline of solution phase TNT in the abiotic tests suggests a slow abiotic transformation process.

## Column Test Results

### TNT

Trace quantities of TNT ( $C/C_o \leq 0.018$ , 1.2 mg/l or less) were detected in water exiting the WES-silt soil column over the course of eluting 20 pore volumes (Figure 15). Trace quantities of TNT ( $C/C_o \leq 0.010$ , 1.1 mg/l or less) were also present in the water exiting the Yokena clay soil column (Figure 15). The peak exit concentration for TNT relative to the TNT concentration in the PGW introduced to the WES-silt soil column was reduced by a factor of

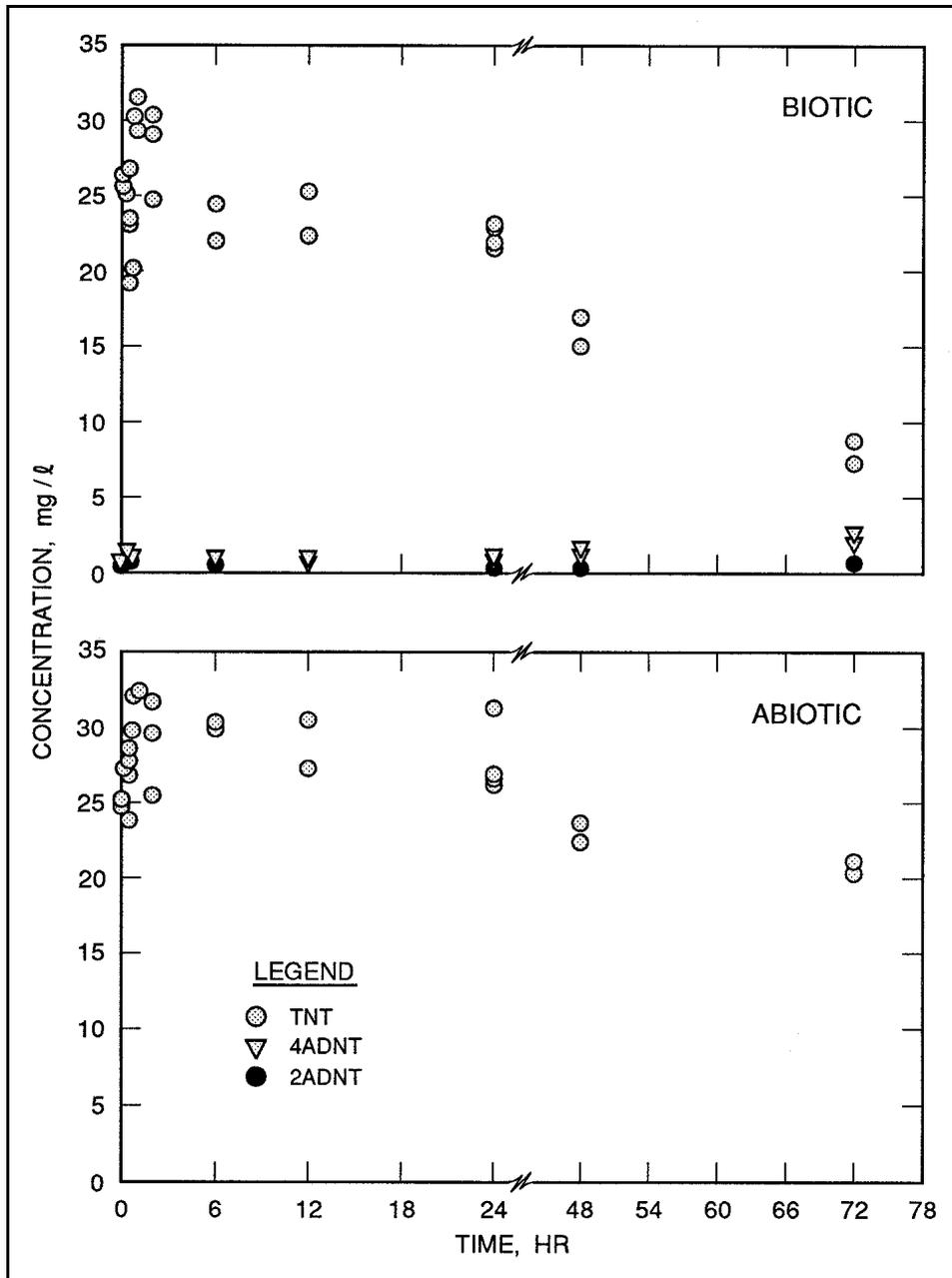


Figure 13. Batch solution concentrations of TNT, 2A-DNT, and 4A-DNT in aerobic clay soil under biotic and abiotic conditions

approximately 55. For Yokena clay soil, the peak exit concentration for TNT relative to the TNT concentration in the PGW introduced to the soil column was reduced by a factor of approximately 100. In contrast to WES-silt and Yokena clay, peak concentrations of TNT exiting the Ottawa sand column (Figure 15) were only slightly below the TNT concentration in the PGW.

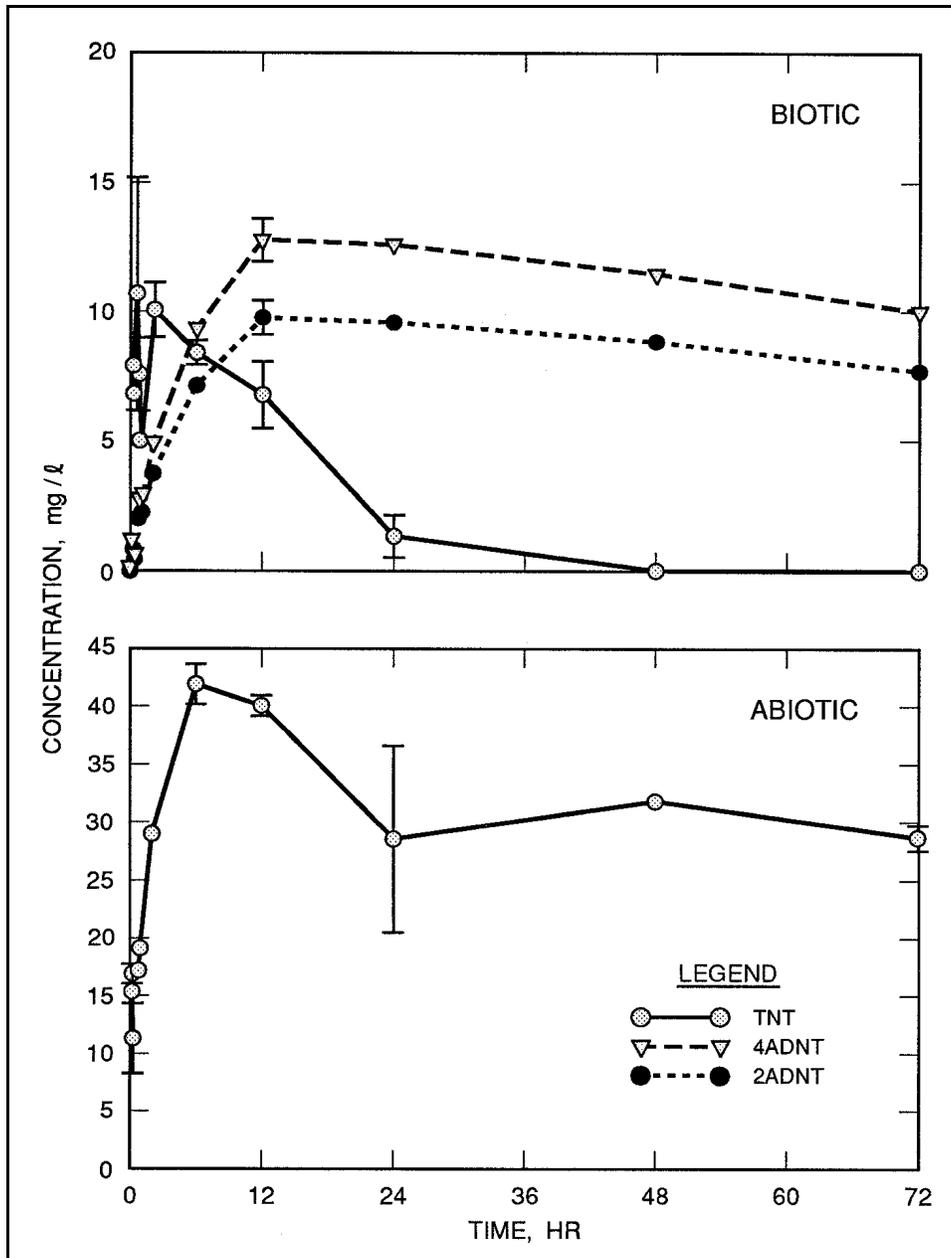


Figure 14. Batch solution phase concentrations of TNT, 2A-DNT, and 4A-DNT in anaerobic clay soil under biotic and abiotic conditions

Exit concentrations in the WES-silt column relative to concentrations in the PGW for 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT are shown in Figure 16. The appearance of 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT concentrations greater than the initial concentrations of these products indicated TNT transformation (reduction) during passage through the WES-silt soil. Peak exit concentrations of 2,6-DANT and 2,4-DANT relative to concentrations in the PGW were much greater than peak exit concentrations of 2A-DNT and 4A-DNT relative to concentrations in the PGW. Since 2A-DNT, 4A-DNT, 2,6-DANT,

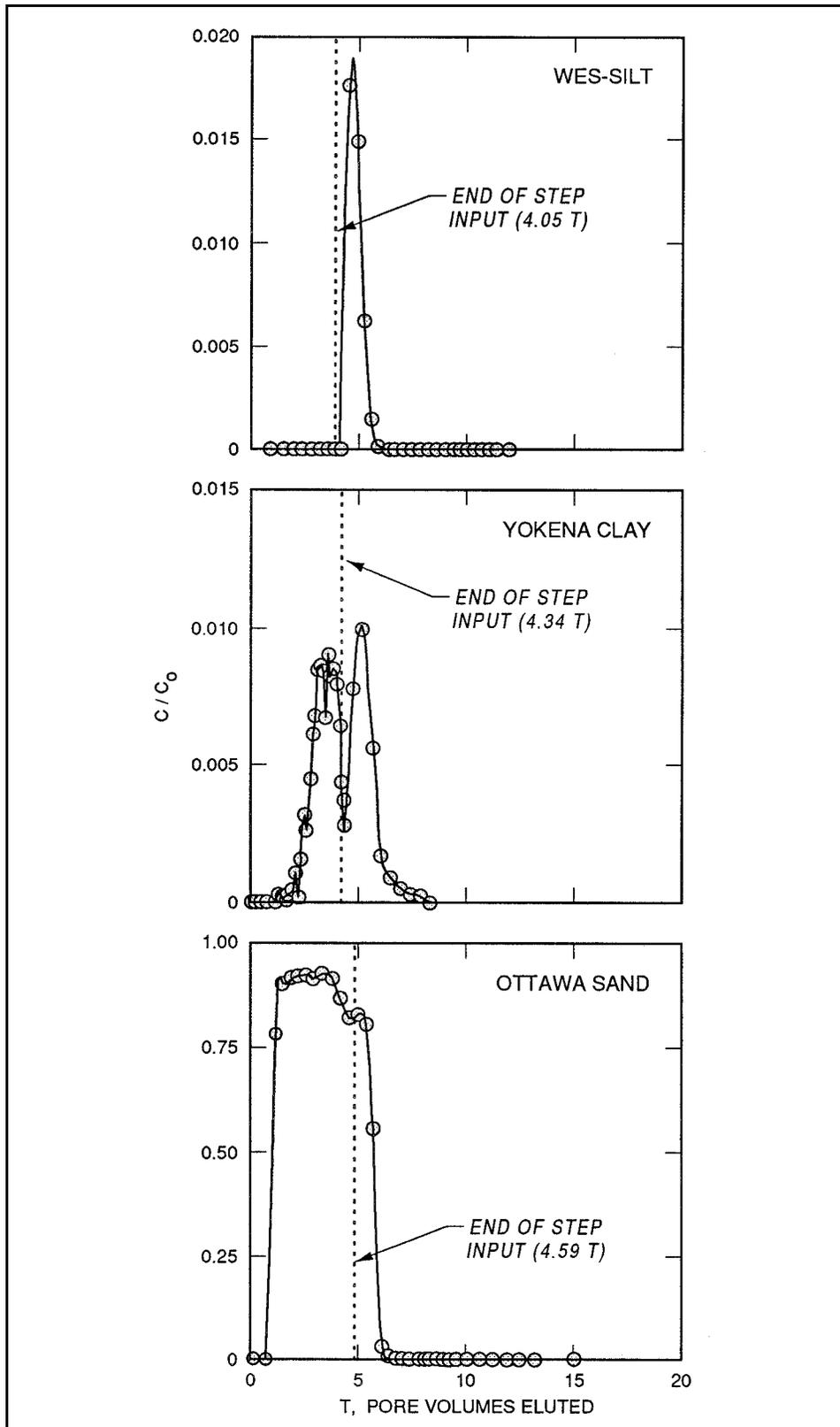


Figure 15. TNT column elution curves for WES-silt, Yokena clay, and Ottawa sand

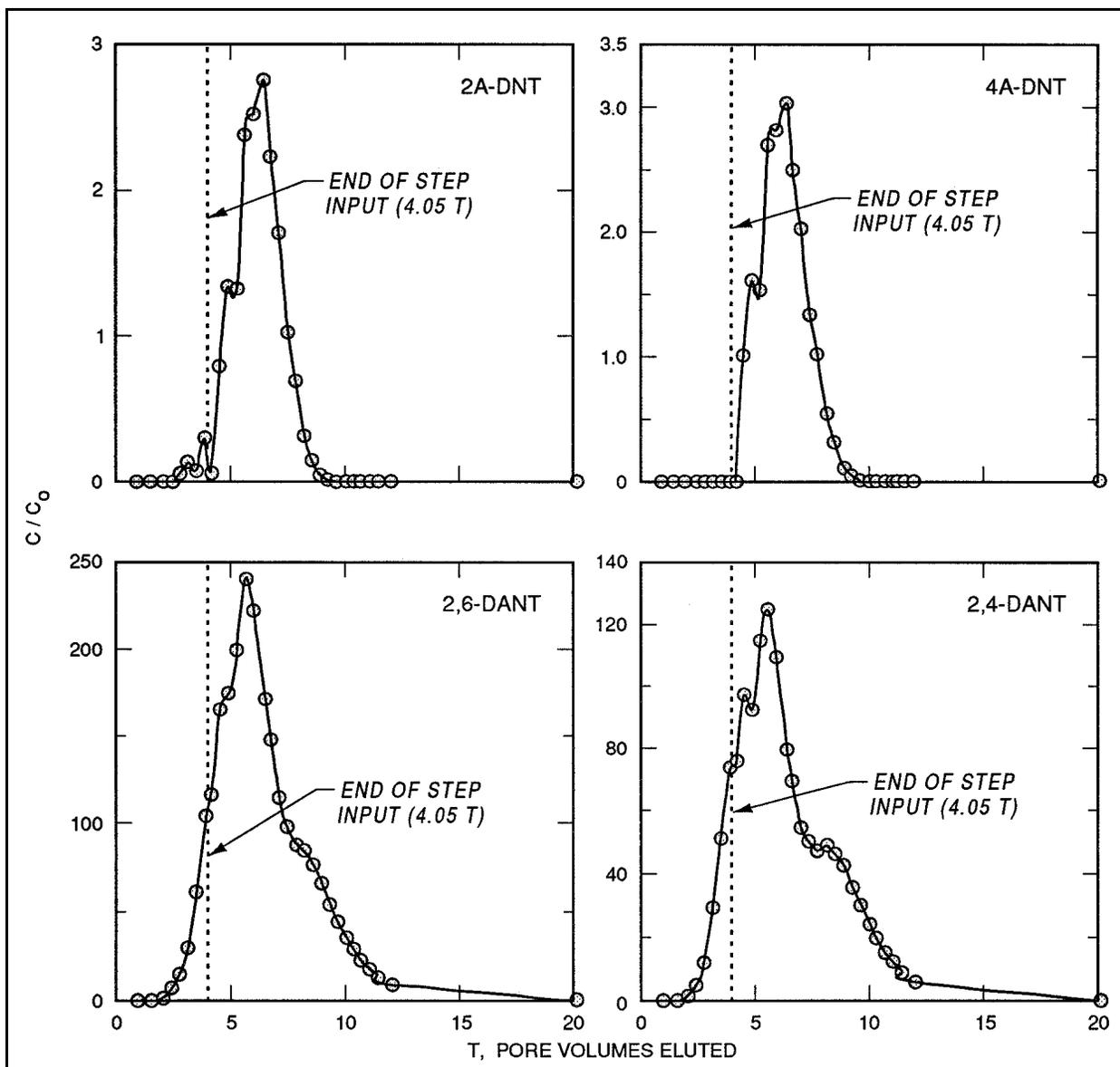


Figure 16. WES-silt elution curves for 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT

and 2,4-DANT concentrations in the PGW for Yokena clay were less than minimum detection limits (MDLs), actual 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT exit concentrations from the Yokena clay column are shown in Figure 17. The appearance of these products indicated TNT transformation during passage through the Yokena clay soil. Exit concentrations in the Ottawa sand column relative to concentrations in the PGW for 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT are shown in Figure 18. Unlike the WES-silt and Yokena clay, peak exit concentrations of 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT were similar to the PGW concentrations of these products, indicating minimal TNT transformation during passage through the Ottawa sand. The data

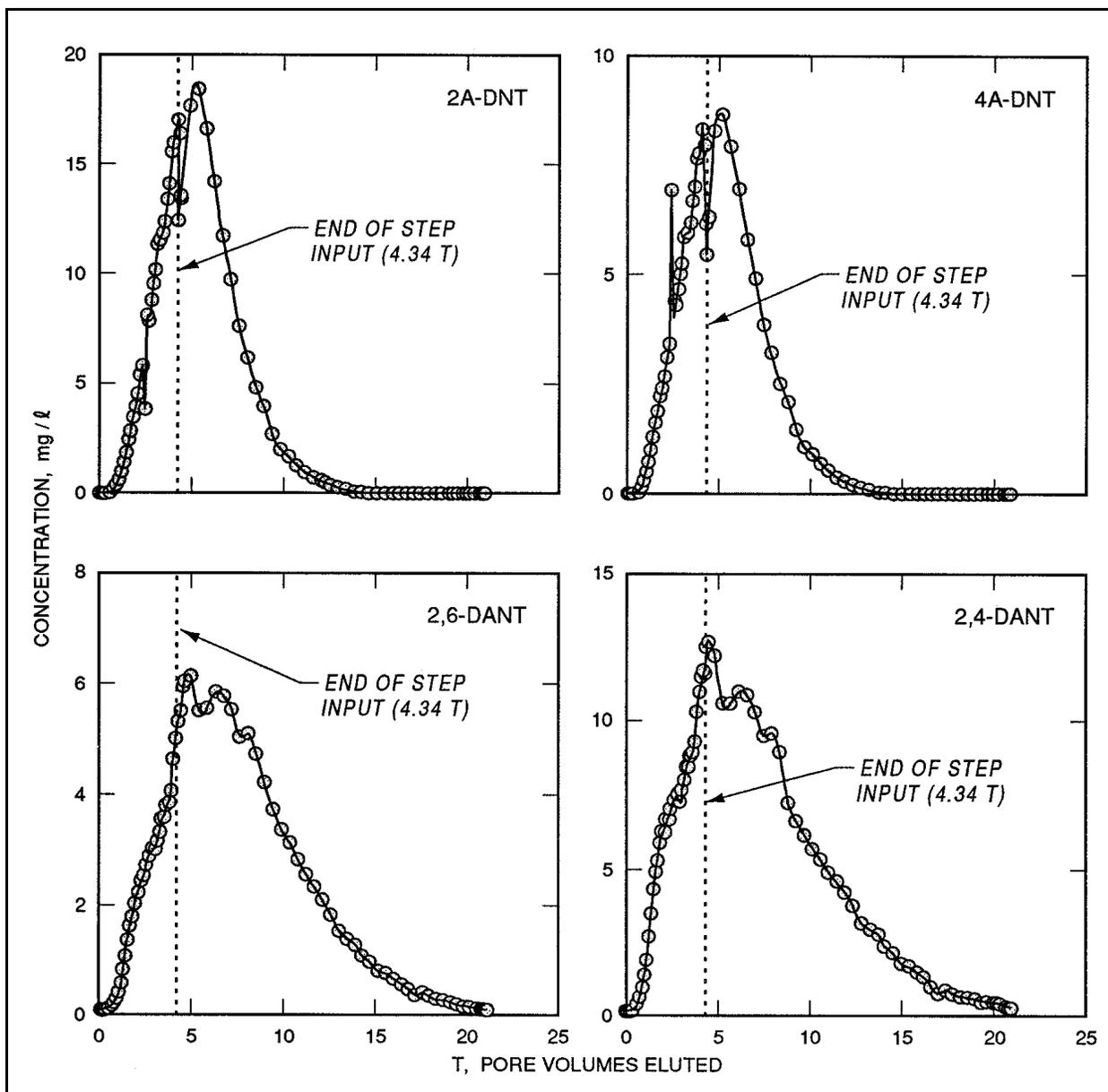


Figure 17. Yokena clay elution curves for 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT

in Figures 16, 17, and 18 suggest that the order of TNT transformation in the columns was WES-silt  $\approx$  Yokena clay  $\gg$  Ottawa sand.

TNT and TNT transformation product concentrations remaining in the soil columns after the elution experiments were completed are shown in Figures 19, 20, and 21 for WES-silt, Yokena clay, and Ottawa sand, respectively. WES-silt TNT and TNT transformation product concentrations remaining in the soil were low. WES-silt TNT, 2A-DNT, and 4A-DNT concentrations were skewed toward the inlet, while WES-silt 2,6-DANT and 2,4-DANT concentrations were skewed toward the outlet. With the exception of 2,6-DANT, the Yokena clay soil

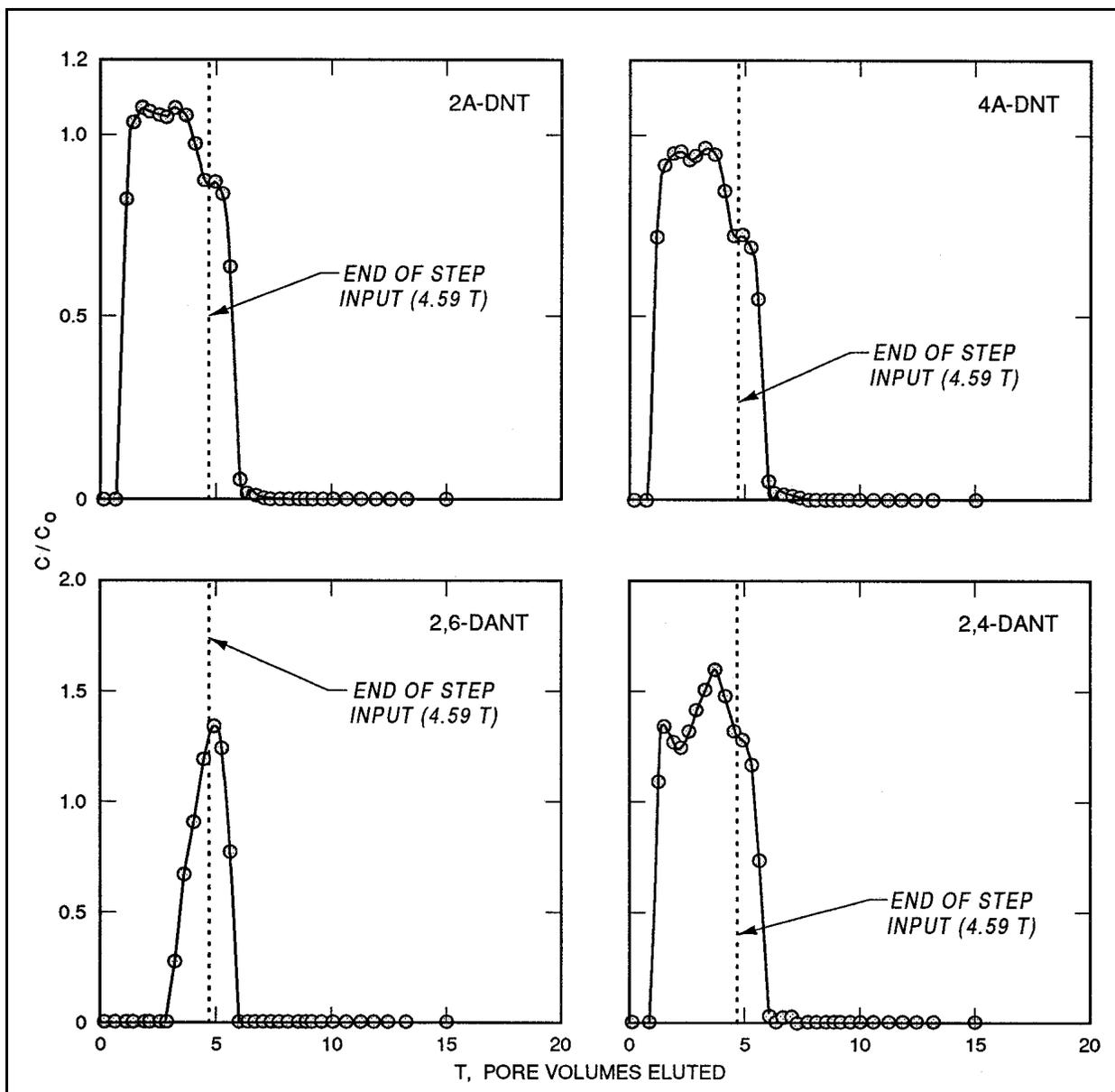


Figure 18. Ottawa sand elution curves for 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT

column residuals were slightly higher than the WES-silt soil column residuals. The Yokena clay TNT, 2A-DNT, and 4A-DNT residuals were skewed toward the inlet, while 2,4-DANT showed little skewness. No measurable TNT or diamino-nitrotoluene concentrations were detected in the Ottawa sand column after elution. Monoamino-nitrotoluene concentrations were detected in Ottawa sand at concentrations approximately an order of magnitude lower than the WES-silt monoamino-nitrotoluene solid phase concentrations.

Figure 22 shows TNT mass balances in molar equivalents for the soil column experiments. About 84 percent of the TNT introduced to the WES-silt

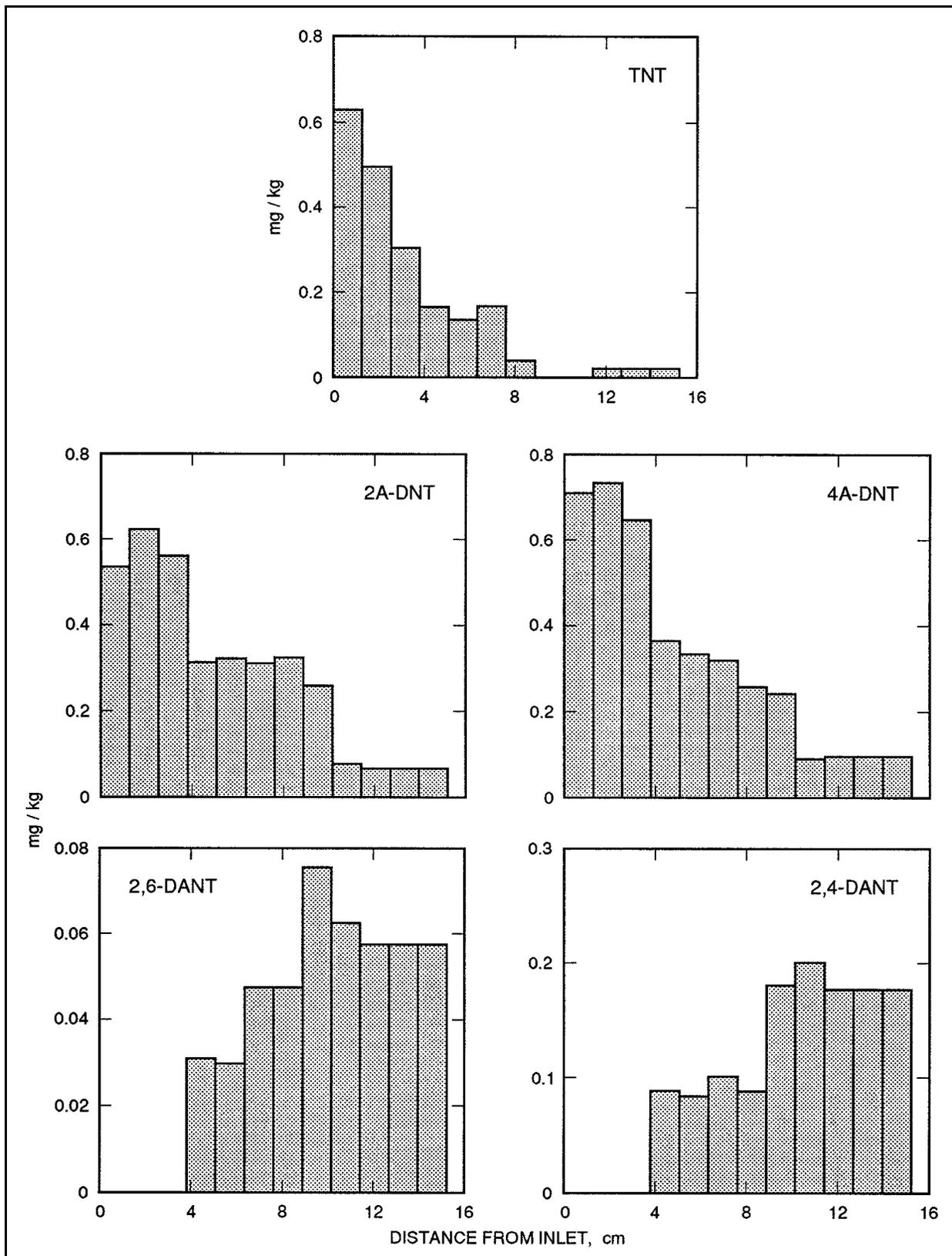


Figure 19. Residual explosives concentrations in WES-silt soil

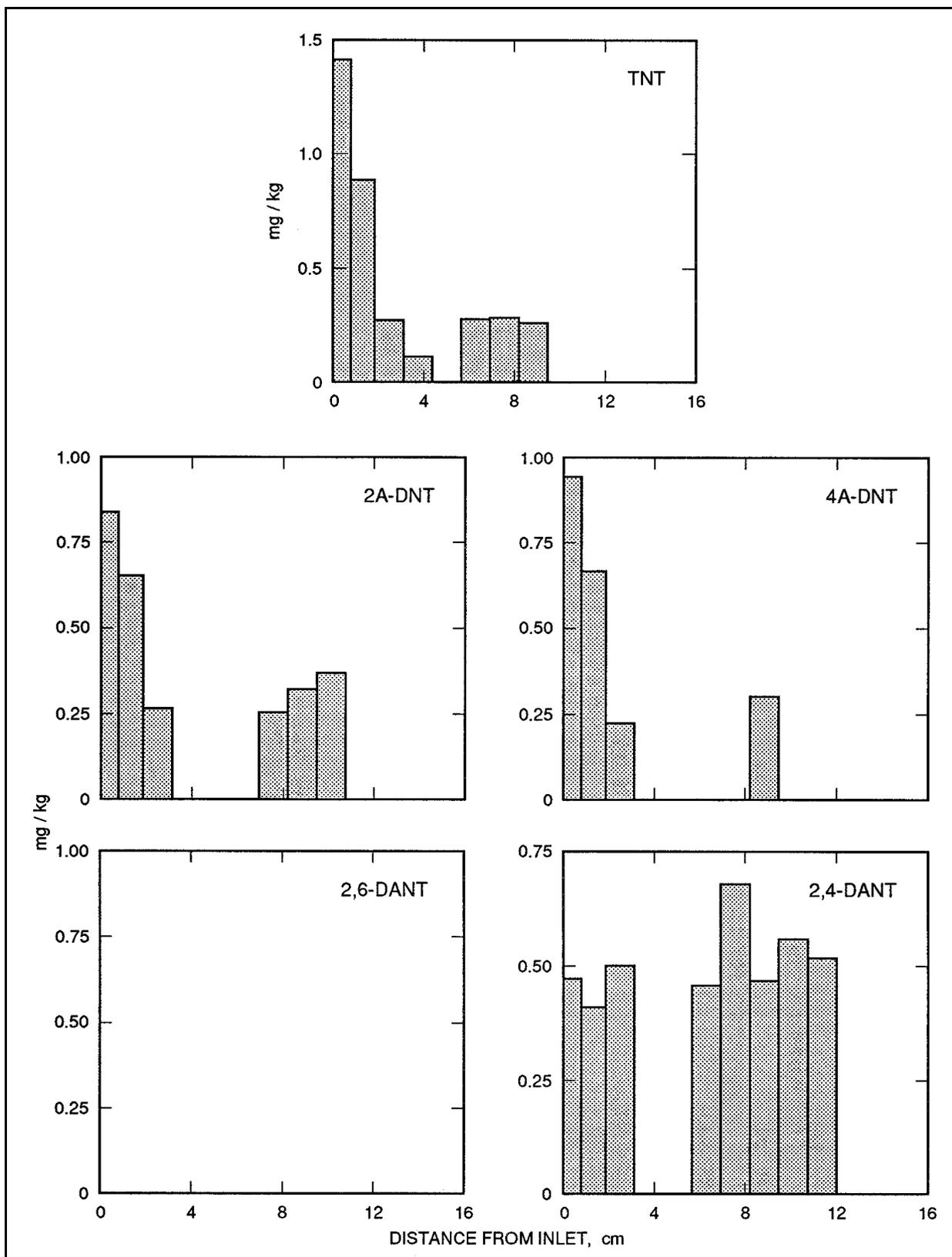


Figure 20. Residual explosives concentrations in Yokena clay soil

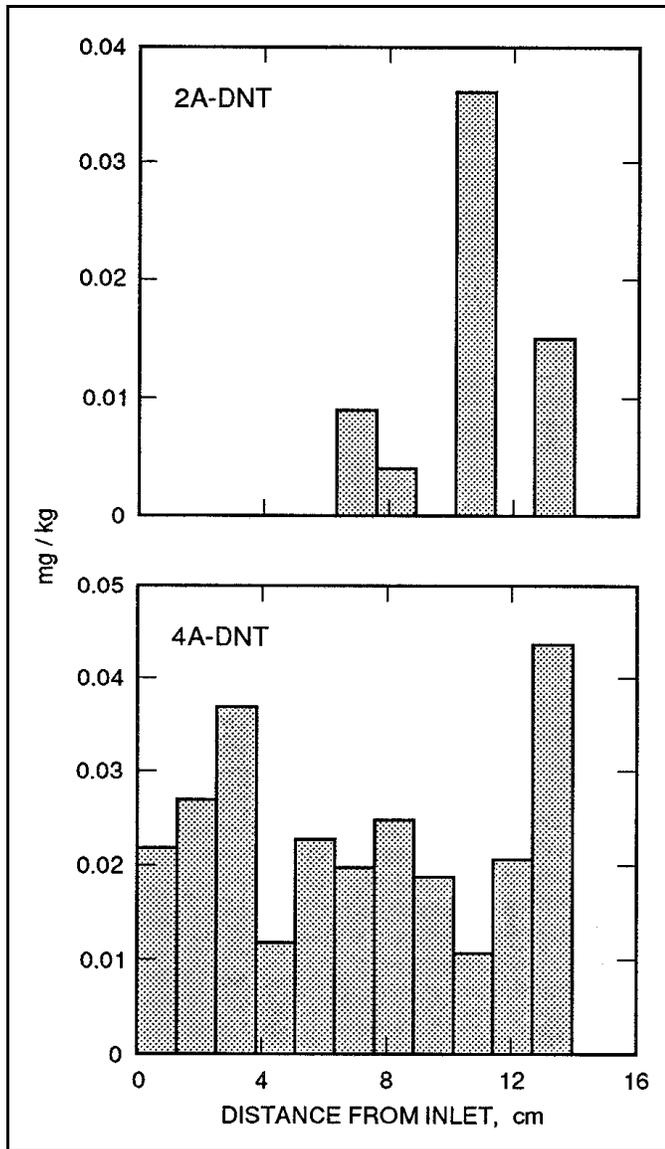


Figure 21. Residual explosives concentrations in Ottawa sand

soil column could be accounted for as TNT and TPs eluted or remained in the soil column. Most of this was in the form of TPs. The mass balance on 2A-DNT for the WES-silt soil showed a slight increase (2A-DNT eluted + 2A-DNT sorbed) over the amount of 2A-DNT introduced to the column. Thus, there was a net increase in 2A-DNT, and this increase is assumed to be reduced TNT. The mass balance on 4A-DNT for the WES-silt soil also showed a net increase (4A-DNT eluted + 4A-DNT sorbed) over the amount of 4A-DNT introduced to the column. TNT transformation to 2A-DNT accounted for 3.2 percent of the TNT introduced to the WES-silt soil column, and transformation to 4A-DNT accounted for 3.7 percent of the TNT introduced to the WES-silt soil. The TNT soil residual for WES-silt accounted for approximately 0.1 percent of the TNT introduced.

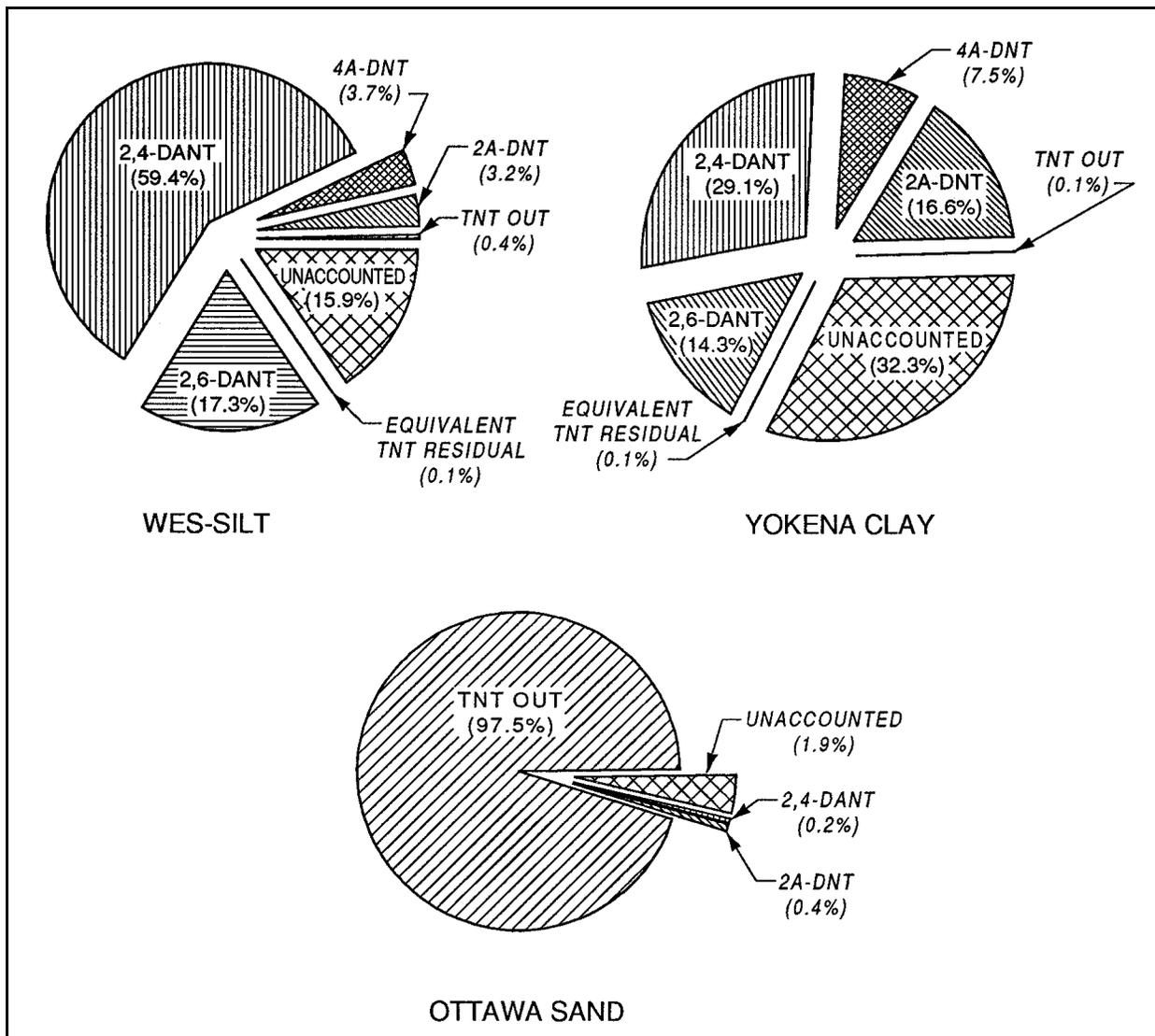


Figure 22. TNT mole balances for WES-silt, Yokena clay, and Ottawa sand

Most of the TNT mass accounted for was in the form of 2,4-DANT (59.4 percent) and 2,6-DANT (17.3 percent), TPs that were present in very small amounts in the PGW introduced to the soil column.

About 68 percent of the TNT introduced to the Yokena clay soil column could be accounted for, and most of this was in the form of TPs. The mass balance on 2A-DNT for the Yokena clay soil showed an increase (2A-DNT eluted + 2A-DNT sorbed) over the amount of 2A-DNT introduced to the column. This increase is assumed to be reduced TNT. The mass balance on 4A-DNT for the Yokena clay soil also showed a net increase (4A-DNT eluted + 4A-DNT sorbed) over the amount introduced to the column, and this increase is assumed to be reduced TNT. Transformation to 2A-DNT accounted for 16.6 percent of the TNT introduced to the Yokena clay soil, and transformation to 4A-DNT

accounted for 7.5 percent of the TNT introduced to the Yokena clay soil. Transformation to 2,4-DANT and 2,6-DANT accounted for 29.1 and 14.3 percent, respectively. The TNT soil residual for Yokena clay accounted for approximately 0.1 percent of the TNT introduced. Thus, most of the TNT mass accounted for in the Yokena clay soil was in the form of diamino-nitrotoluenes.

About 98 percent of the TNT introduced to the Ottawa sand column could be accounted for, and virtually all of this was in the form of TNT eluted (97.5 percent). The mass balance on 2A-DNT for the Ottawa sand showed a slight increase (2A-DNT eluted + 2A-DNT sorbed) over the amount of 2A-DNT introduced to the Ottawa sand. The mass balance on 4A-DNT for Ottawa sand indicated that 4A-DNT was possibly conservative during passage through the Ottawa sand. The mass balance on 2,6-DANT eluted from the Ottawa sand showed a slight decrease (2,6-DANT eluted + 2,6-DANT sorbed) over the amount of 2,6-DANT introduced to the column, although the peak 2,6-DANT concentration was slightly greater than the 2,6-DANT concentration in the PGW. As with the 2A-DNT, the 2,4-DANT showed an increase (2,4-DANT eluted + 2,4-DANT sorbed) over the amount of 2,4-DANT introduced to the column. Transformation to 2A-DNT accounted for 0.4 percent of the TNT introduced to the Ottawa sand, and transformation to 2,4-DANT accounted for 0.2 percent of the TNT introduced to the Ottawa sand. Residual TNT concentrations in the Ottawa sand were below the MDL. Thus, most of the TNT mass accounted for in the Ottawa sand was in the form of TNT eluted, showing that the TNT transformation rate was significantly slower in the Ottawa sand than in the WES-silt and Yokena clay.

## **RDX and HMX**

RDX and HMX elution from WES-silt, Yokena clay, and Ottawa sand (Figures 23 and 24, respectively) were similar to elution curves observed by many investigators who have conducted laboratory column experiments on other types of contaminants (Brusseau and Rao 1989). A rising limb due to convection of the step input loading is observed, followed by a declining limb due to convection of contaminant remaining in the columns after completion of the step input loading. The peak RDX exit concentrations relative to the RDX concentration in the PGW were reduced by factors of 1.2 and 1.3 for WES-silt and Yokena clay soils, respectively. The peak HMX exit concentration relative to the HMX concentration in the PGW was approximately 1.0 in the WES-silt column. The peak HMX exit concentration relative to the HMX concentration in the PGW was reduced by a factor of 1.8 for the Yokena clay soil. These reductions were one to two orders of magnitude lower than the TNT peak height reductions, indicating RDX and HMX transport are less affected by transformation than TNT transport. RDX and HMX exit concentrations reached the PGW concentrations in Ottawa sand. In both the WES-silt and Yokena clay columns, HMX required more pore volumes eluted to return to below MDL than did RDX. Both RDX and HMX required more pore volumes eluted to return to below

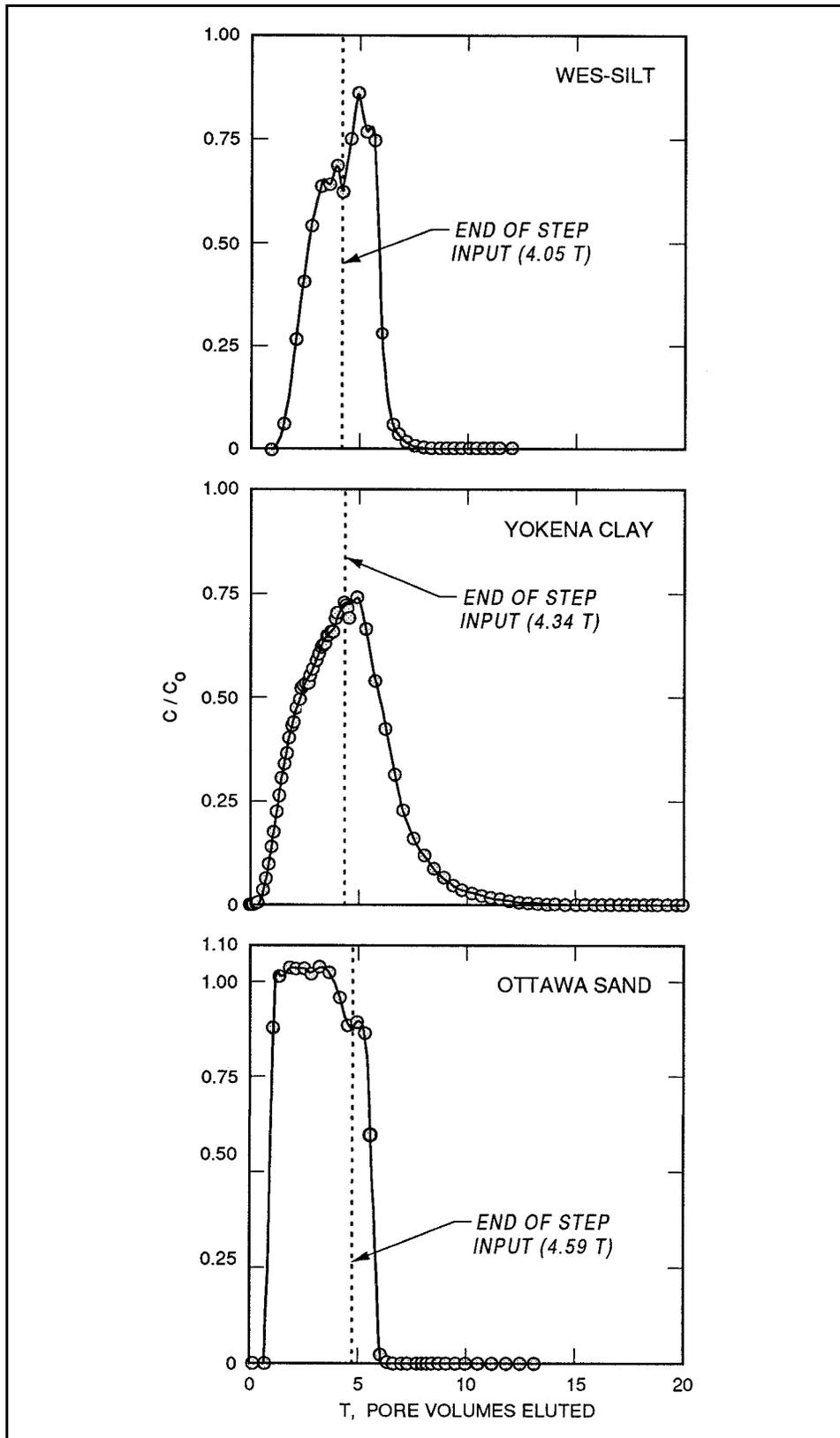


Figure 23. RDX elution curves for WES-silt, Yokena clay, and Ottawa sand

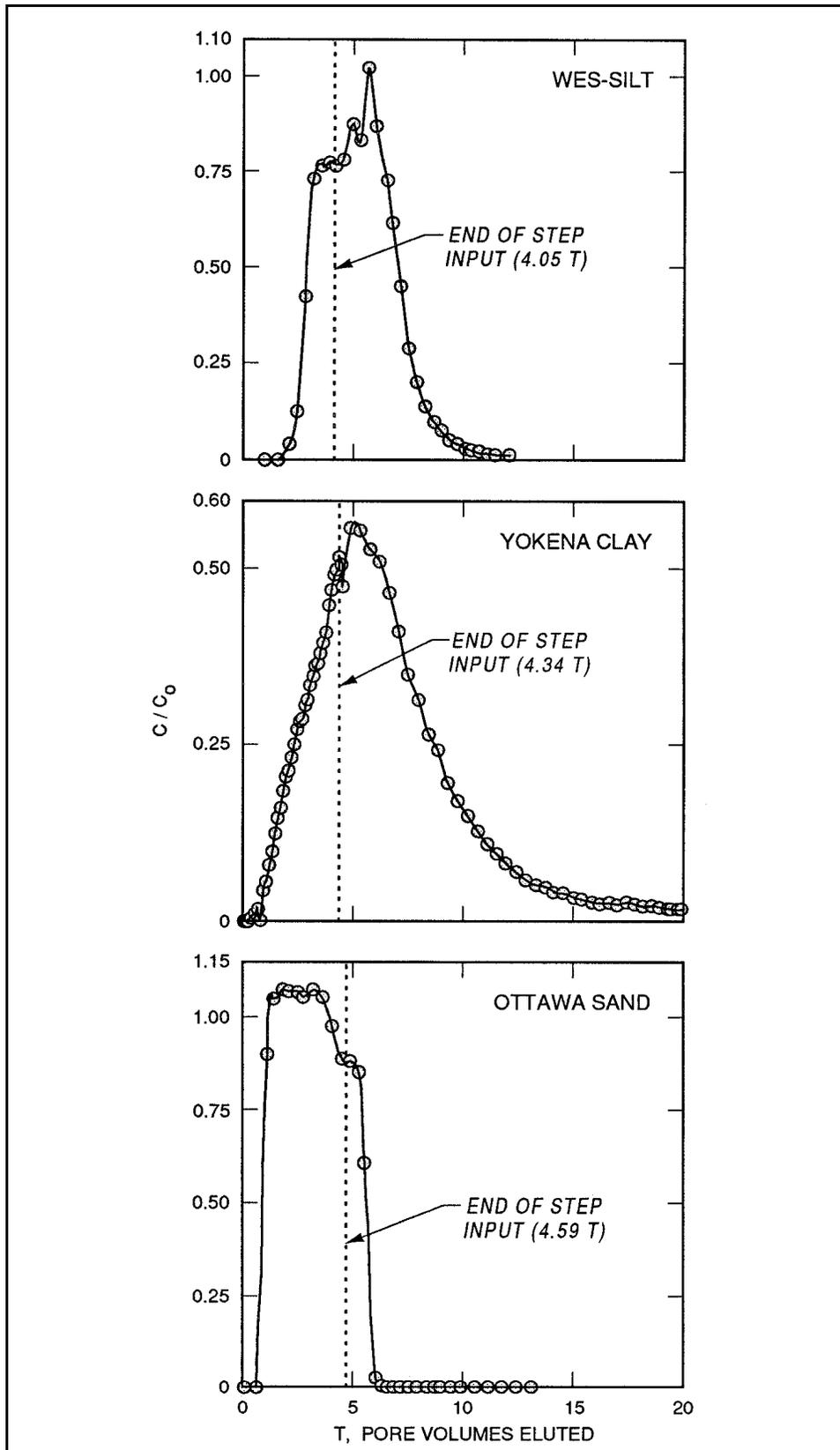


Figure 24. HMX elution curves for WES-silt, Yokena clay, and Ottawa sand

Soil	RDX Eluted	HMX Eluted	TNT	
			Eluted	Total
WES-silt	66.7	96.7	0.4	84.1
Yokena clay	80.0	80.5	0.1	67.7
Ottawa sand	107.5	109.3	97.5	98.1

MDL in the Yokena clay column than in the WES-silt column. Ottawa sand RDX and HMX breakthrough curves (BTCs) were nearly identical.

Mass balance analysis indicated that transformation was also important during the transport of RDX and HMX in the WES-silt and Yokena clay columns, although not as important as for TNT (Table 6). About 67, 80, and 108 percent of the RDX introduced to the WES-silt, Yokena clay, and Ottawa sand, respectively, were accounted for in the eluted water. About 97, 81, and 109 percent of the HMX introduced to the WES-silt, Yokena clay, and Ottawa sand, respectively, were accounted for in the eluted water. RDX and HMX in sectioned soil samples were below detection limits (2.2 and 1.0 mg/kg for RDX and HMX, respectively) in all samples.

Substantial disappearance of RDX during passage through the WES-silt and Yokena clay soils was observed. McCormick, Cornell, and Kaplan (1981) described an anaerobic scheme for biodegradation of RDX via successive reduction of nitro groups. Many of the intermediates in the McCormick, Cornell, and Kaplan (1981) scheme are short-lived. The final products include methanol and hydrazine. Since soil column eluates in the present study were not analyzed for methanol and hydrazine, the unaccounted for RDX in the soil column studies cannot be attributed conclusively to biological transformation. However, since RDX biodegrades under anaerobic conditions, at least a portion of the unaccounted for RDX was probably biologically transformed.

Approximately 97 percent of the HMX introduced to the WES-silt column was eluted, suggesting little or no transformation of HMX. However, in the Yokena clay column, only about 81 percent of the HMX introduced was eluted, indicating that HMX may also undergo reductive transformation under anaerobic conditions. However, very little information is available on HMX transformation pathways, intermediates, and end products (McGrath 1995). All of the HMX introduced to the Ottawa sand column was recovered in the effluent.

## Discussion

### TNT process descriptions

Aerobic and anaerobic batch testing showed an initial rapid disappearance of TNT from solution by adsorption. Adsorbed TNT tended to become unextractable, but at a slower rate than the initial adsorption rate. Thus, the batch results suggest a two-step disappearance process involving an initial rapid interphase transfer from solution phase to soil phase followed by disappearance from the soil phase. Column tests showed that the disappearance process(es) observed in the batch tests is significant. Under anaerobic, slow-flow conditions in the WES-silt and Yokena clay soil columns, more than 99 percent of the TNT introduced to the columns disappeared. Less than 1 percent of the TNT eluted or remained in the soil phase. In contrast to WES-silt and Yokena clay, over 97 percent of the TNT introduced to the Ottawa sand column was eluted.

TNT disappearance in batch and column tests varied with soil types investigated. The batch results suggest a dependence on grain size. The soil with the highest clay content (Yokena clay soil) showed the most disappearance in batch tests. This soil was also the highest in total organic carbon and lowest in soil pH (Table 2). Total organic carbon and pH of the other two soils were similar, but the TNT disappearance characteristics and grain sizes were different. The column results were consistent with the batch results indicating more TNT disappearance from the Yokena clay than from the WES-silt. In both soil columns, very little of the TNT introduced to the columns remained in the form of TNT. Compared with WES-silt and Yokena clay, Ottawa sand had relatively little TNT disappearance. Soil pH was the same for WES-silt and Yokena clay soils.

Selim, Xue, and Iskandar (1995) reported approximately 50-percent TNT disappearance in column studies with a Norwood soil that had a high pH, low CEC, low clay content, and low organic matter content. Comfort et al. (1995) also observed significant TNT disappearance in column studies with a Sharpsburg soil. The pH of the Sharpsburg soil was lower than the pH of the Norwood soil, while the CEC, clay content, and organic matter content of the Sharpsburg soil were approximately one order of magnitude higher than the values for these parameters in the Norwood soil. Differences in soil geochemistry may provide an explanation for the differences in explosives-soil reactivities, but the effects of soil geochemistry on TNT transformation are not well-known.

There was some transformation of TNT to 2A-DNT and 4A-DNT during batch testing, especially in anaerobic batch tests conducted at high initial TNT concentrations (100 mg/l). Formation of 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT during column testing was significant. Over 80 percent of the TNT introduced to the WES-silt soil column and over 60 percent of the TNT introduced to the Yokena clay soil column was eluted as one of these TPs, primarily 2,4-DANT and 2,6-DANT. Batch testing showed that one of the TPs, 4A-DNT, adsorbs and disappears much like TNT. There was also evidence of

competitive sorption between TNT and TPs, especially in batch tests conducted at the high initial TNT concentrations.

Batch testing showed that biotic conditions significantly enhanced TNT disappearance relative to disappearance under abiotic conditions. Under anaerobic conditions, enhanced biotic disappearance involved the pathways shown in Figure 2. This is evident from the appearance of 2A-DNT and 4A-DNT in the anaerobic batch tests (Figure 14) and the appearance of 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT in the column tests (Figures 16 and 17). Percent recovery data showed that adsorption plus transformation to 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT cannot account for all of the TNT introduced in batch and column tests. An additional loss mechanism is needed to fully explain the biotic losses in the anaerobic batch and column tests.

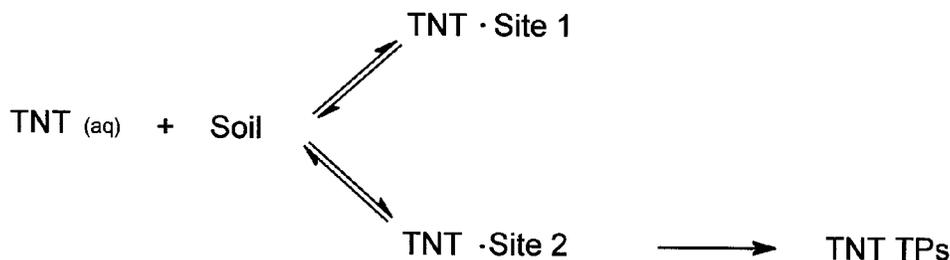
In the aerobic-biotic batch tests, accumulations of TNT TPs were either minimal or below the detection limits. Minimal accumulations of 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT are to be expected in aerobic tests since these TPs involve reductive not oxidative transformation of TNT. Micro-anaerobic regions around soil particles due to biological and chemical oxygen demands of soils could provide the reducing conditions needed for minimal accumulations of 2A-DNT and 4A-DNT. However, for the reductive pathways shown in Figure 1 to be important in the aerobic tests, significant amounts of reductive TPs should have been present. Aerobic biodegradation of TNT could have occurred, but TNB was not detected in the aerobic-biotic tests. Loss mechanisms other than biodegradation are needed to fully explain the biotic losses in the aerobic batch tests.

Batch testing showed TNT disappearance after the initial adsorption phase under abiotic as well as biotic conditions. Ainsworth et al. (1993) also observed TNT disappearance under abiotic conditions. The abiotic disappearance mechanism probably does not involve the pathways shown in Figure 1. Measurable accumulations of TNT TPs occurred only in the biotic tests and primarily in anaerobic tests. The absence of both reductive and oxidative TPs in the abiotic tests leaves the TNT mass balance in these tests unexplained. Some loss mechanism(s) other than abiotic transformation to the TPs analyzed in this study is needed to explain TNT disappearance under abiotic conditions.

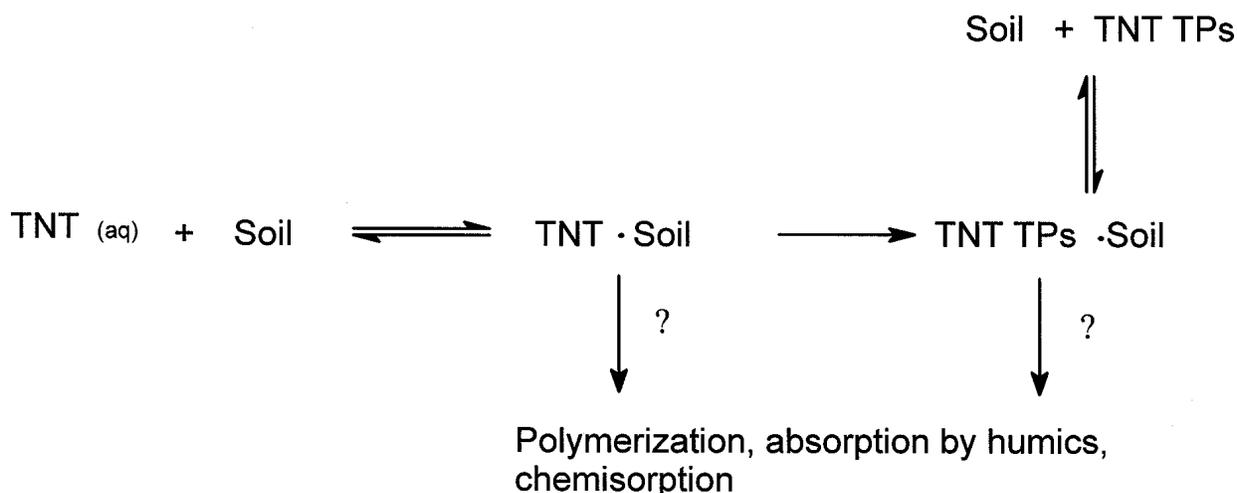
To explain TNT disappearance, Ainsworth et al. (1993) proposed the following process description:

Sorption followed by transformation is the basic process in the above model. Site 1 is a soil locale for reversible sorption. Site 2 is both a sorption and transformation locale. Sorption at Site 2 is reversible, but the transformations at Site 2 are irreversible.

The batch and column experiments in the present study are consistent with the Ainsworth et al. (1993) description. Rapid adsorption is described by reversible sorption. Biotic and abiotic disappearance is described as soil phase



transformation that is irreversible. However, trends for decreasing percent recovery, desorption of TPs, and competitive sorption in the present study suggest the following modifications of the Ainsworth et al. (1993) description:



Unlike the Ainsworth et al. (1993) model, the modified Ainsworth model has only one reversible sorption site for TNT. In reality, there may be many different reversible sorption sites due to natural soil chemical heterogeneities. The above model simply implies a composite reversible sorption result, regardless of the number of sites actually involved. In most studies, including the present study, sorption sites are not experimentally segregated. Multisite sorption models can provide better process descriptions, but require information on the sorptive properties of various sites. For the information available on TNT sorption, a two-site model provides little practical advantage over a one-site model.

The model proposed above identifies two irreversible transformation mechanisms for TNT. One involves the reductive pathways shown in Figure 1 and may be principally biotic. Since the general redox state and concomitant concentrations of reducing agents are driven by biological systems, it is possible that microbes are primarily providers of the necessary redox conditions for essentially abiotic reductive transformations to occur.

The reductive TPs formed under anaerobic conditions include 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT. Azoxytoluenes (Figure 2) may also be formed, but these compounds were not analyzed in the present study. Since the

reductive TPs desorb, reversible sorption of reductive TPs is included in the model. These TPs compete with TNT for sorption sites. This may be an important aspect in which the modified model differs from the original Ainsworth et al. (1993) model.

Percent recovery data showed that reductive TPs, even in anaerobic systems, do not account for all the TNT disappearance. In addition, abiotic results show unaccounted for losses. Thus, there must be some irreversible disappearance mechanism other than reductive transformation to the TPs measured in this study. It has been suggested that clay surface catalyzed polymerization of TNT and TNT TPs could be responsible for decreasing recoveries over time (Ainsworth et al. 1993). It is not known that TNT polymerizes or that in soils TNT polymerization would be completely irreversible. Kaplan and Kaplan (1982) postulated that TNT or TNT TPs become conjugated to humic material that are insoluble. Polymerization and conjugation with humics are mechanisms that potentially explain the percent recovery data. These processes are different forms of chemisorption. Chemisorption involves covalent bonding to soil surfaces (McGrath 1995).

Although results obtained in this study do not provide direct evidence of polymerization or conjugation, the results show that an unaccounted for disappearance occurs in the soil phase that mimics chemisorption. Similar results have been reported previously (Kaplan and Kaplan 1982; Pennington et al. 1992; Selim, Xue, and Iskandar 1995; Comfort et al. 1995; Price, Brannon, and Hayes 1995). Thus, the body of evidence suggests that TNT and/or TNT TPs irreversibly bind or chemisorb with soils to produce a residual that is no longer analytically identifiable as TNT and/or TNT TPs. Polymerization and conjugation hypotheses are consistent with these findings. The overall consequence of clay surface catalyzed polymerization or conjugation with humic material would be the same—abiotic chemisorption to the soil phase.

Ainsworth et al. (1993) suggested that the soil agents responsible for abiotic transformation are not regenerated; that is, soils have a finite capacity for TNT transformation. The finite capacity hypothesis was tested (Townsend, Myers, and Adrian 1995) in column experiments with WES-silt, Yokena clay, and Ottawa sand soils. Townsend, Myers, and Adrian (1995) found that after pumping over 150 and 200 pore volumes of TNT-contaminated feed solution through WES-silt and Yokena clay soils, respectively, TNT transformations were still occurring. Their data suggest that TNT transformations are biotic, biologically mediated, or that an abiotic soil constituent responsible for TNT transformations is constantly being renewed. Further, their data showed no evidence of irreversible sorption. Price, Brannon, and Hayes (1995) suggest that reductive TNT transformations involve ferrous-ferric iron cycling that would be inexhaustible under highly reduced conditions.

Other explanations involving complicated interactions with soil are also possible for low percent recoveries. These include intraparticle pore phenomena (diffusion, sorption, and transformation) and complete mineralization. Over the relatively short testing times in this study, diffusion-limited intraparticle pore

phenomena could not account for the TNT losses observed. Complete mineralization is also not likely. The radiolabeled TNT studies of Price, Brannon, and Hayes (1995) showed minimal TNT mineralization ( $\leq 2.7$  percent). The literature thus far contains little evidence of TNT mineralization, but there is evidence of TAT formation when the oxidation-reduction potential is sufficiently low (Rieger and Knackmuss 1995).

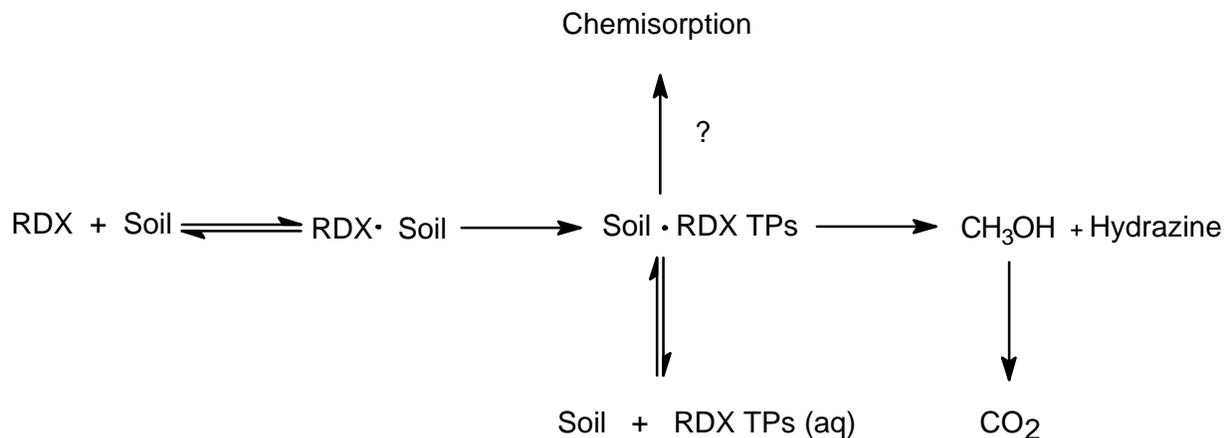
### **RDX and HMX process descriptions**

Batch and column testing showed that RDX undergoes reversible sorption. Column testing showed that HMX also undergoes reversible sorption. However, percent recoveries for RDX and HMX showed that a significant portion of the RDX disappeared in both the WES-silt and Yokena clay soil columns, and a significant portion of HMX disappeared in the Yokena clay soil column. These data suggest transformation or some irreversible loss mechanism as previously discussed for TNT.

The work of McCormick, Cornell, and Kaplan (1981) suggests that anaerobic biodegradation accounts for some, perhaps all, of the RDX disappearance in the column tests. McCormick, Cornell, and Kaplan (1981) showed sequential buildup and disappearance of mononitroso, dinitroso, and trinitroso analogs of RDX, concurrent with RDX disappearance. The RDX nitroso analogs then undergo further reduction; after several steps, methanol and hydrazine are produced. Since RDX TPs were not analyzed in the present study, the relative significance of anaerobic reduction of RDX is not known.

Irreversible sorption of RDX and RDX TPs may be possible, but there is little data at the present time to support this explanation for the column percent recovery data. Radiolabel work conducted by McCormick, Cornell, and Kaplan (1981) showed most of the radiolabel in the solution phase. This indicates that RDX was transformed to soluble compounds, e.g., methanol and hydrazine. Unlike TNT, there is little evidence in the literature of an abiotic disappearance mechanism for RDX involving conjugation with humics or polymerization.

The aerobic batch data showed no long-term disappearance of RDX. McCormick, Cornell, and Kaplan (1981) showed that aerobic biological degradation of RDX does not occur. Thus, the available information suggests anaerobic-biotic transformation as the primary disappearance mechanism for RDX. Based on the available information, a tentative process description for RDX is as follows:



The above process description will likely require modification or refinement as additional studies on RDX process description are conducted.

Since HMX is similar to RDX, HMX anaerobic biodegradation may also be important. However, the paucity of information on HMX does not permit a detailed process description. The available information suggests that the process description for HMX can be assumed to be essentially the same as the process description for RDX. This is a tentative conjecture that may require substantial revision as more information on RDX and HMX becomes available.

### Transport modeling considerations

Percent recoveries from batch and column experiments for TNT, RDX, and HMX show that disappearance is an important process to be accounted for in TNT, RDX, and HMX transport modeling. Sorption takes place; however, without disappearance terms in a transport model, critical model results will be substantially in error. Critical model results that will be impacted if disappearance is not accounted for include contaminant concentrations in time and space, plume advancement trends, and soil or aquifer material residual concentrations.

Soil column mass balances on TNT, RDX, and HMX (Figure 22 and Table 6) demonstrated the relative significance of disappearance for the three compounds. The order of significance is TNT >>> RDX  $\approx$  HMX. Unaccounted for transformations and other potential disappearance processes were greater in the Yokena clay soil than in the WES-silt and Ottawa sand soils.

The transport of contaminants in porous media is usually analyzed by means of an advection-dispersion equation with reaction (van Genuchten and Alves 1982; Parker and van Genuchten 1984). Transport of a single reactive species during steady, one-dimensional flow in a column containing a homogeneous, saturated porous medium can be described by

$$\left( \frac{\rho_b}{n} \frac{\partial q}{\partial t} + \frac{\partial C}{\partial t} \right) = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu_w C - \mu_s \frac{\rho_b q}{n} \quad (3)$$

where

$\rho_b$  = porous medium bulk density, kg-solids/ $\ell$

$n$  = porosity,  $\text{cm}^3/\text{cm}^3$

$q$  = contaminant solid-phase concentration, mg-contaminant/kg-solids

$t$  = time, sec

$C$  = contaminant solution-phase concentration, mg-contaminant/ $\ell$

$D$  = dispersion coefficient reflecting the combined effects of diffusion and hydrodynamic dispersion on transport,  $\text{cm}^2/\text{sec}$

$x$  = distance from column inlet, cm

$v$  = average pore water velocity, cm/sec

$\mu_w$  = solution phase first order disappearance constant,  $\text{sec}^{-1}$

$\mu_s$  = solid phase first order disappearance constant,  $\text{sec}^{-1}$

The terms on the right-hand side of Equation 3 involving disappearance constants,  $\mu_w$  and  $\mu_s$ , model disappearance reactions in solution and soil phases as first-order processes. First-order disappearance is just one of many ways to structure disappearance kinetics for explosives (McGrath 1995). The batch data obtained in this study are not sufficient to precisely define disappearance mechanisms or kinetics because of the rapidity with which disappearance occurred. The simple empirical approach provided by the first-order assumption was therefore selected to represent transformation kinetics in the soil column experiments.

The term on the right-hand side of Equation 3 involving the second derivative with respect to distance models dispersion and diffusion, and the term involving the first derivative with respect to distance models convection.

The term on the left-hand side of Equation 3 involving  $q$  represents interphase transfer of chemical from solution to solid phase. The representation in Equation 3 is a generic structure, basically equivalent to a definition. Solution of Equation 3 requires an expression relating solid phase concentration to solution concentration. Several expressions are available for this purpose. Interphase transfer could be mathematically structured to model sorption (equilibrium, nonequilibrium, reversible, irreversible), ion-exchange, precipitation, dissolution, etc. (McGrath 1995). The instantaneous, linear

sorption formulation is very common in contaminant transport modeling and is consistent with the rapid initial sorption observed in batch tests. In this study, only the linear isotherm model is considered. The general structure of this model is

$$q = K_d C \quad (4)$$

where  $K_d$  is an equilibrium distribution constant ( $\ell/\text{kg}$ ). Substitution from Equation 4 for  $q$  into Equation 3 yields

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu C \quad (5)$$

where

$$R = 1 + \rho_b K_d / n, \text{ retardation factor, dimensionless}$$

$$\mu = \mu_w + \mu_s \rho_b K_d / n, \text{ overall first-order disappearance constant, sec}^{-1}$$

Several types of boundary conditions are applicable to the soil column experiments conducted in this study (van Genuchten and Alves 1982). De Smedt and Wierenga (1979) have shown that the effluent concentration from a column can be calculated without substantial error using the solution for a semi-infinite column and concentration type boundary condition at the inlet. Thus, the following initial and boundary conditions are considered:

$$C(x,0) = 0$$

$$C(0,t) = \begin{cases} C_o & : 0 < t < t_o \\ 0 & : t > t_o \end{cases}$$

$$\frac{\partial C}{\partial x}(\infty,t) = 0$$

where

$$C_o = \text{single chemical concentration in the water used for the step input loading, mg}/\ell$$

$$t_o = \text{time at which the step input loading ceases}$$

The analytical solution for this problem over the two time domains is (van Genuchten and Alves 1982)

for  $0 < t < t_o$

$$C(x,t) = C_o B(x,t) \quad (6)$$

and for  $t > t_o$

$$C(x,t) = C_o B(x,t) - C_o B(x,t-t_o) \quad (7)$$

where

$$B(x,t) = \frac{1}{2} \exp\left(\frac{(v-m)x}{2D}\right) \operatorname{erfc}\left[\frac{Rx - mt}{\sqrt{4DRt}}\right] + \frac{1}{2} \exp\left(\frac{(v+m)x}{2D}\right) \operatorname{erfc}\left[\frac{Rx + mt}{\sqrt{4DRt}}\right] \quad (8)$$

and

$$m = v \sqrt{1 + \frac{4\mu D}{v^2}} \quad (9)$$

Observed and fitted breakthrough curves for TNT, RDX, and HMX are shown in Figures 25, 26, and 27, respectively. Retardation factors,  $R$ , and first-order decay constants,  $\mu$ , were obtained by trial and error and are indicated with the graphs of the observed and fitted results. Average pore water velocities,  $v$  (Table 3), were obtained from column operating records. Dispersion coefficients,  $D$  (Table 3), were obtained from chloride tracer studies previously discussed. The theoretical curves are for  $x = L$ , where  $L$  = column length, and were plotted as a function of pore volumes eluted (dimensionless time) using the dimensionless variable,  $T$ , where  $T$  is given by

$$T = \frac{v t}{L} \quad (10)$$

With the exception of WES-silt TNT, the observed data and fitted results from the analytical solution compare reasonably well. The majority of WES-silt TNT elution data was below the minimum detection limit for TNT, making the WES-silt observed TNT more difficult to fit with the theoretical solution. The Yokena clay HMX elution curve showed distinct tailing that the theoretical model could not fit. The Yokena clay RDX elution curve also showed some tailing although much less than the Yokena clay HMX. Otherwise, the analytical solution captured the major features of the observed elution curves.

Physical nonequilibrium and nonequilibrium sorption effects are often used to explain tailing and spreading in laboratory soil column experiments. The observation that nonequilibrium adsorption can cause increased tailing and spreading has been identified by several investigators (Brusseu and Rao 1989). In many experiments, pore water velocities are too high for the local equilibrium

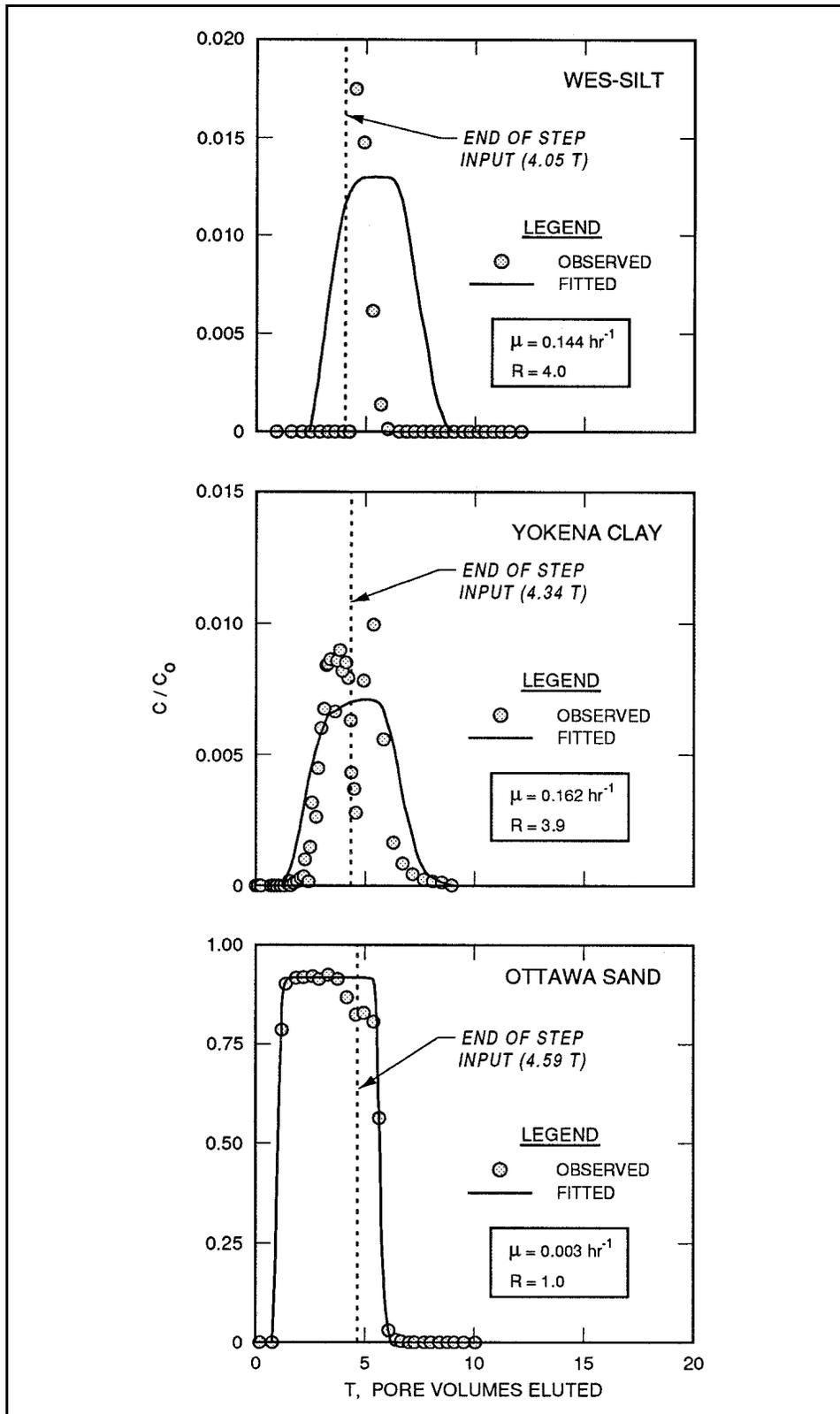


Figure 25. Observed and fitted TNT breakthrough curves for WES-silt, Yokena clay, and Ottawa sand

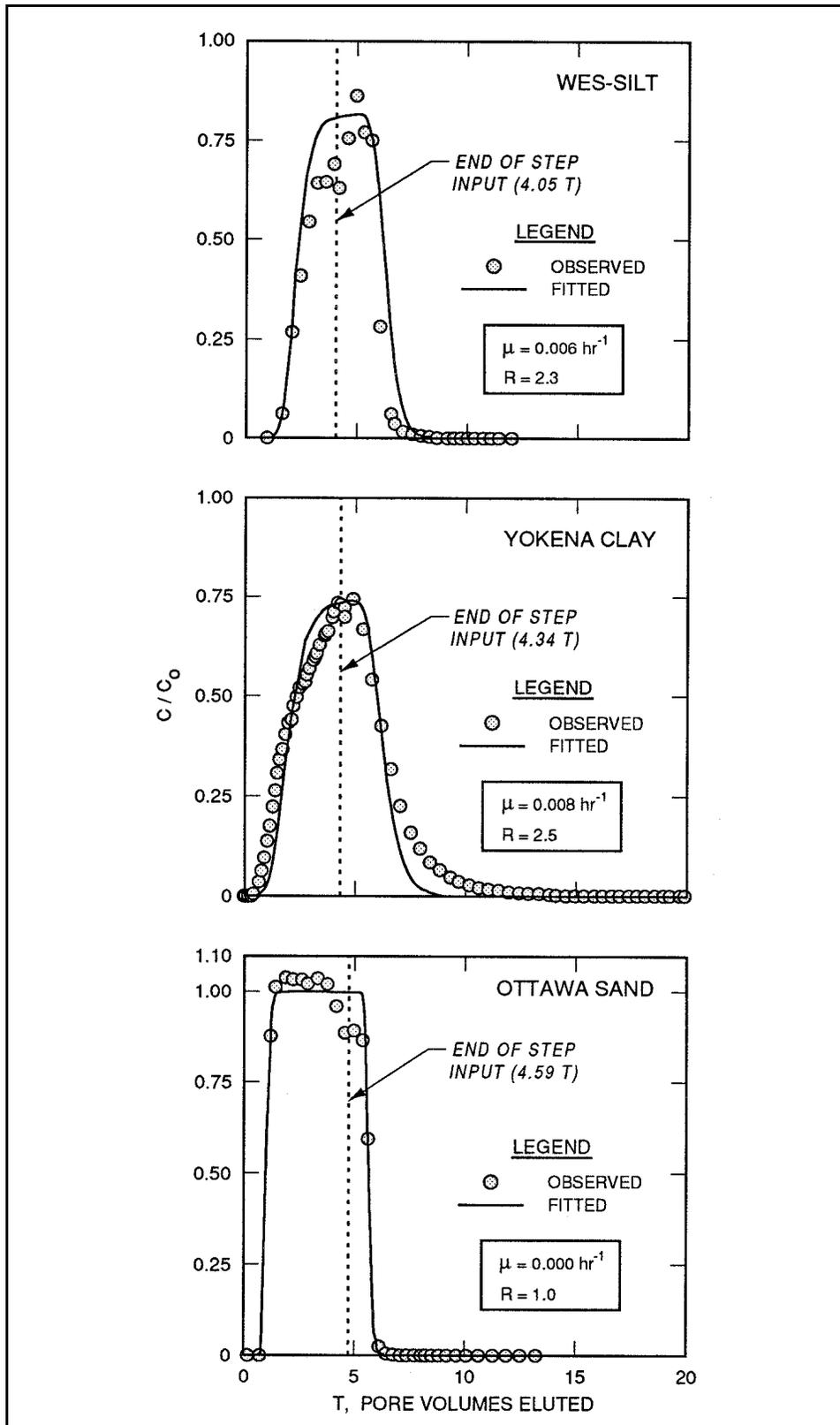


Figure 26. Observed and fitted RDX breakthrough curves for WES-silt, Yokena clay, and Ottawa sand

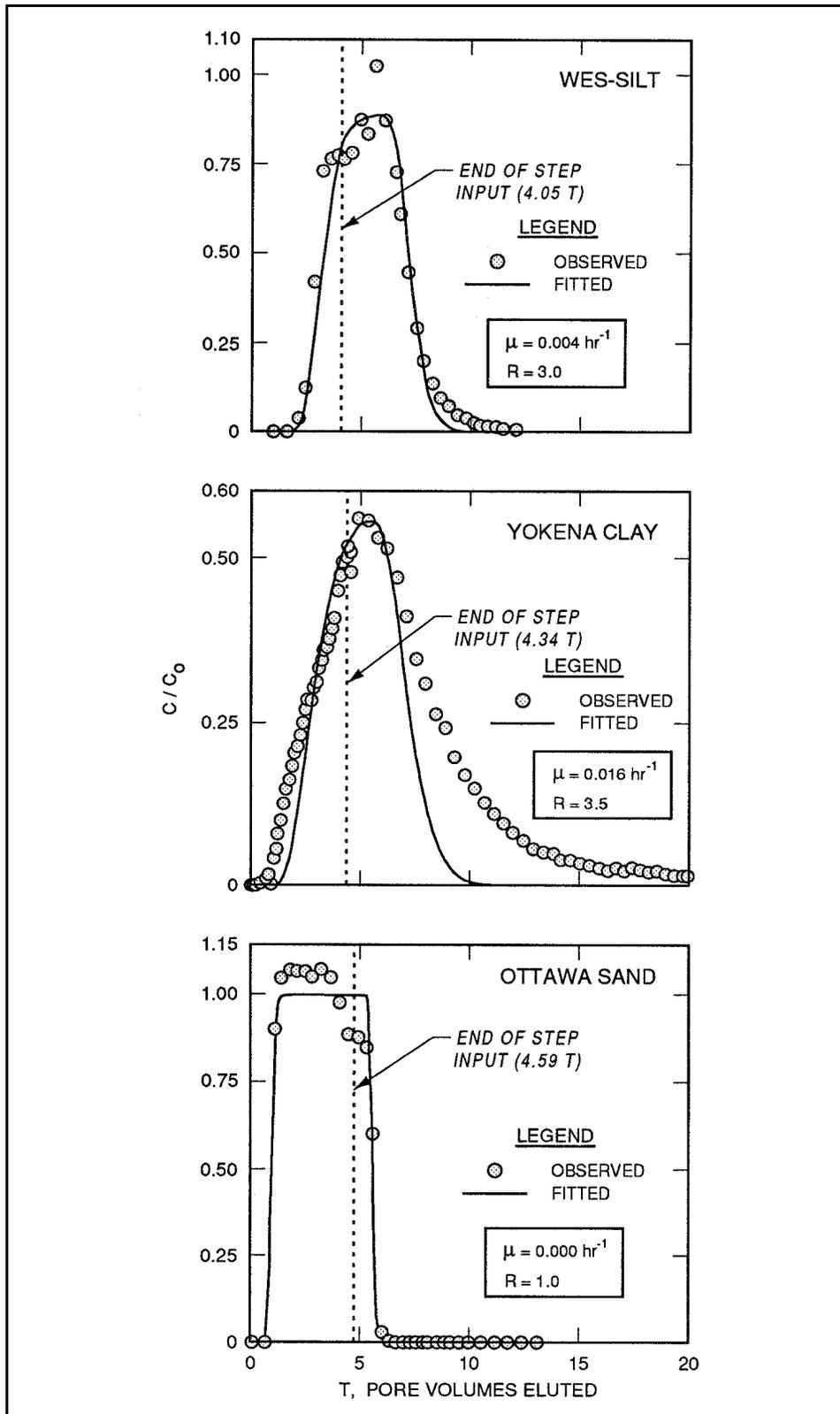


Figure 27. Observed and fitted HMX breakthrough curves for WES-silt, Yokena clay, and Ottawa sand

assumption to be valid. However, Ainsworth et al. (1993) applied the local equilibrium assumption to column experiments in which average pore water velocities were as high as 0.01 cm/sec and found good fit between observed and predicted TNT elution curves. Bahr and Rubin (1987) developed a method for using Peclet and Damkohler numbers for determining the applicability of the local equilibrium assumption. Application of their method showed Peclet numbers of about 30 and Damkohler I number of about 98 for RDX. These values are just outside the range of applicability of the local equilibrium assumption. Thus, some of the discrepancies between observed and theoretical results may be due to sorption nonequilibrium.

Physical nonequilibrium effects arise due to mass transfer limitations in intraparticle pores, dead-end channels, and other immobile water regions. Numerous mathematical descriptions of physical nonequilibrium are available (McGrath 1995). Most of these descriptions are mathematically formulated to account for diffusive mass transfer in films, intraparticle pores, or immobile water as well as hydrodynamic dispersion. Diffusive mass transfer limitations are usually indistinguishable from sorption nonequilibrium. Thus, some of the discrepancies between observed and theoretical results may be due to physical nonequilibrium effects.

Another type of nonequilibrium phenomenon that may be important but is rarely considered is coupled physical-chemical nonequilibrium effects due to variations in pore water velocities. These effects cannot be captured with the hydrodynamic dispersion concept or concepts involving dispersion and diffusive mass transfer in films, intraparticle pores, and other immobile water regions. Variations in travel time for individual parcels of water result in different manifestations of sorption and chemical reaction kinetics. For reactive solutes, variations in pore water velocities imply a potential for significant excursions away from mean pore water quality. Thus, the averaging of water velocities built into dispersion coefficients is a major problem for modeling reactive contaminants because averaging loses the effects that extreme excursions away from the mean pore water velocity have on transport of reactive solutes. The problem is analogous to the Reynolds stress terms that arise in the analysis of turbulent momentum flux (Bird, Stewart, and Lightfoot 1960). At present, no generally accepted methods for accounting for coupled physical-chemical nonequilibrium effects are available short of modeling each pore.

The fitted retardation coefficients for TNT were low (1 to 4), and retardation coefficients were higher for WES-silt and Yokena clay than for Ottawa sand. Differences between explosives transport in WES-silt and Yokena clay soils were minor except for HMX. Mass balance indicated that virtually all of the HMX introduced to the WES-silt soil column was accounted for. About 80 percent of the HMX introduced to the Yokena clay soil column was accounted for.

The fitted first-order disappearance constants,  $\mu$ , were in the range of 0 to 0.016 hr<sup>-1</sup> for RDX and HMX in WES-silt, Yokena clay, and Ottawa sand. For

WES-silt soil, the TNT first-order disappearance constant,  $0.144 \text{ hr}^{-1}$  was approximately 30 times higher than the values for RDX and HMX, and in Yokena clay soil, the TNT disappearance constant,  $0.162 \text{ hr}^{-1}$  was approximately 20 and 10 times higher than the values for RDX and HMX, respectively. For Ottawa sand, RDX and HMX did not disappear. The WES-silt and Yokena clay TNT disappearance constants were about 6 to 12 times higher than ones reported for the same soils by Townsend, Myers, and Adrian (1995), while the Ottawa sand TNT disappearance constant was about 2 times lower than the value reported by Townsend, Myers, and Adrian (1995) for Ottawa sand. The differences in WES-silt and Yokena clay TNT disappearance constants between this experiment and the Townsend, Myers, and Adrian (1995) experiment can possibly be explained by differences in oxidation-reduction potentials. Townsend, Myers, and Adrian (1995) performed experiments in columns that were 0.32 cm long. The soil columns used in the present study were 15.24 cm long. Although oxidation-reduction potentials were not measured in either study, the longer columns used in the study here were probably more anaerobic than the short columns used by Townsend, Myers, and Adrian (1995). The fitted WES-silt and Yokena clay first-order disappearance constants for RDX and HMX were on the order of 10 times higher than first-order decay constants for herbicides and pesticides in soils (Rao and Davidson 1980). The disappearance constants are high for unacclimated soils and suggest that abiotic reactions may be partially or primarily responsible for TNT, RDX, and HMX disappearance.

The fitted theoretical curves shown in Figures 25, 26, and 27 do not necessarily mean that the governing equation (Equation 2) is correct. McGrath (1995) reviewed several complex processes potentially affecting explosives transport. The retardation factor, first-order disappearance constant, and dispersion coefficient in the governing equation include few of the processes discussed by McGrath (1995). Thus, agreement between observed and theoretical soil column results obtained in this study only imply that the structure of the governing equation with regard to sinks has the capability to approximate governing processes. Also, caution should be exercised in applying the parameter values obtained in this study. Since the experiments were designed as adsorption-dominated experiments, the retardation coefficients ( $R$ ) and the overall first-order disappearance constants ( $\mu$ ) may be applicable at the advancing edge of a plume entering soils with properties similar to WES-silt, Yokena clay, and Ottawa sand. Retardation coefficients and first-order decay constants for leaching of explosives from source areas (highly contaminated soils and aquifer materials) could be substantially different. Key processes could also be different. For highly contaminated soils, dissolution/precipitation may be the dominant interphase transfer process until the soil is substantially cleaned. In addition, transformation reactions may not be important if they are primarily abiotic and the soil constituents involved in transformation reactions have been exhausted.

Observed and predicted elution curves for 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT were not developed because the theoretical model (Equation 2) is too simple to properly simulate generation of transformation products. To model TNT and the four transformation products simultaneously, a system of five partial

differential equations is needed. A five component model could be developed, but parameter identification using soil column effluent data alone would be difficult. Development of such a model and the needed parameter identification algorithm was beyond the scope of this study.

# 4 Conclusions and Recommendations

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## Conclusions

Reductive transformation was established in this study as a key process affecting subsurface transport of TNT, RDX, and HMX. In batch sorption testing, soil column elution studies, and field-scale modeling, transformations must be accounted for. Although abiotic transformations may be an important process in TNT reduction, this study corroborates other work indicating biological systems play an important role in TNT and RDX transformation. Distinguishing between those processes involving direct biological transformation and those involving chemical reactions that depend on conditions provided by biological activity would be useful.

Previous work indicating soil sorption of explosives was confirmed. Transformation, however, is more important than sorption in the soils studied. Soil sorption of explosives is rapid, occurring on a time scale of a few minutes. Steady-state TNT concentrations in batch are not possible as long as transformation continues.

Although the batch and column data in this study are not sufficient to conduct correlation analysis, the data suggest that organic carbon, CEC, and pH are weak indicators of soil TNT transformation properties.

Many details of TNT, RDX, and HMX sorption and transformation remain unknown and puzzling. The relative significance of nonlinear sorption, competitive sorption, and abiotic versus biotic reduction is not well understood. Knowledge, even of the reducing agents for abiotic reduction, is insufficient.

Application of a one-dimensional, time-varying advection-dispersion equation with first-order decay and instantaneous sorption was encouraging. The major features of an advancing plume of TNT, RDX, and HMX can be approximated by modeling convection and hydrodynamic dispersion and assuming instantaneous sorption and first-order decay. Simplifying yet realistic assumptions can be made such that multidimensional, time-varying transport

models suitable for assessment of site cleanup alternatives can be developed. However, irreversible TNT disappearance and mass balance remain as important issues that have not been resolved. In light of process information gaps, models to simulate field-scale subsurface transport of explosives should be used with caution, and unrealistic expectations of models should be avoided.

## Recommendations

Future research should be directed toward gaps in understanding TNT, RDX, and HMX transport in the subsurface environment. The coupling of transformation, interphase transfer, and porous media fluid mechanics should be systematically investigated so that the respective roles of physical, chemical, and biological processes and their interrelationships can be adequately modeled. The following specific knowledge and technology gaps should be priority areas of work:

- Information on the relative significance of abiotic and biotic reduction of TNT, RDX, and HMX, the nature of abiotic reducing agents, and optimal redox conditions for reductive transformations is critical. Research is needed to determine if microbes are active in situ reducers of explosives or primarily providers of the necessary redox conditions for essentially nonbiological reductive transformations to occur. It would be useful to distinguish between those processes involving direct biological transformation from those involving chemical reactions that depend on conditions provided by biological activity.
- Laboratory experiments and field studies should include analysis of as complete an array of explosive transformation products as possible. Without direct measurements of transformation products, transformation cannot be distinguished from irreversible sorption.
- Batch experiments are needed to evaluate the sorption and transformation properties of 2,4-diamino-6-nitrotoluene and 2,6-diamino-4-nitrotoluene. Information on the stability of these compounds in soils is needed to model transport of TNT and TNT transformation products.
- Soil column experiments conducted over a range of average pore water velocities are needed in order to obtain information on film effects and mass transfer limitations.
- Laboratory leaching studies are needed to identify key interphase transfer processes and to evaluate the significance of transformation reactions in highly contaminated soils. This information is needed to develop process descriptors for areas that are sources of contamination.

To complement the above specific recommendations, some general guidance on process research and its role in developing transport models for explosives is

provided. An understanding of processes and factors affecting processes and the capability to develop and apply mathematical models are important to remedial design activities. However, in few if any cleanup efforts will it be necessary or prudent to model the minutia of physicochemical and biological phenomena occurring in such complex media as soils. Description and simulation of the minutia of chemical behavior may be mathematical overkill in the face of site physical, chemical, and biological heterogeneities. Process research should focus on identifying and characterizing governing phenomena and rate-limiting processes.

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# Appendix A

## Key to Acronyms

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### Acronyms

BTC	breakthrough curve
CEC	cation exchange capacity
DOA	Department of Army
DOD	Department of Defense
HMX	Her Majesty's eXplosive; oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high performance liquid chromatography
LS	Liquid Scintillation
MDL	minimum detection limit
NSWC	Naval Surface Warfare Center
PGW	laboratory synthesized polluted groundwater
PTFE	Polytetrafluoroethylene
RDX	Royal Demolition eXplosive; 2,3,5-trinitro-1,3,5-triazine
TAT	triaminotoluene
TNB	trinitrobenzene
TNT	2,4,6-trinitrotoluene

TOC	total organic carbon
TPs	TNT transformation products
2A-DNT	2-amino-4,6-dinitrotoluene
4A-DNT	4-amino-2,6-dinitrotoluene
2,4-DANT	2,4-diamino-6-nitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
USEPA	U.S. Environmental Protection Agency
WES	U.S. Army Engineer Waterways Experiment Station

# Appendix B

## Key to Symbols

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### Letters

$C$  = contaminant solutions-phase concentration, mg-contaminant/ $\ell$

$C(x,t)$  = chloride concentration at  $x$  and  $t$ , mg/ $\ell$

$C_o$  = initial chloride concentration, mg/ $\ell$

$D$  = dispersion coefficient,  $\text{cm}^2/\text{sec}$

$K_d$  = equilibrium distribution coefficient,  $\ell/\text{kg}$

$L$  = column length, cm

$n$  = porosity,  $\text{cm}^3/\text{cm}^3$

$q$  = contaminant solid-phase concentration, mg-contaminant/kg-solids

$R$  = retardation factor, dimensionless

$T$  = dimensionless time (pore volumes eluted)

$t$  = time, sec

$v$  = average pore water velocity, cm/sec

$x$  = length (distance from column inlet), cm

## Greek

$\rho_b$  = porous medium bulk density, kg-solids/ $\ell$

$\mu$  = overall first-order disappearance constant,  $\text{sec}^{-1}$

$\mu_s$  = solid phase first order disappearance constant,  $\text{sec}^{-1}$

$\mu_w$  = solution phase first order disappearance constant,  $\text{sec}^{-1}$

# REPORT DOCUMENTATION PAGE

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<b>14. SUBJECT TERMS</b> HMX RDX Reductive transformation		Soil sorption TNT	<b>15. NUMBER OF PAGES</b> 77
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Soil sorption of explosives was rapid, occurring on a time scale of a few minutes. Sorbed TNT and RDX concentrations tended to disappear from the soil phase, especially in the biotic batch tests. TNT disappearance in the batch and column tests could not be fully accounted for as transformation to 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,4-diamino-6-nitrotoluene (2,4-DANT), and 2,6-diamino-4-nitrotoluene (2,6-DANT). Thus, an additional mechanism(s) and/or an additional transformation product(s) are needed to fully explain the disappearance process for TNT in soils. Results from this study indicate that the order of magnitude of sorption is TNT > HMX > RDX and that the order of magnitude of disappearance is TNT >>> RDX = HMX.