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2,4,6-Trinitrotoluene (TNT) Transformation/Sorption in Thin-Disk Soil Columns

by **Dan M. Townsend**

**North Carolina State University
Raleigh, NC 27650**

Tommy E. Myers

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

D. Dean Adrian

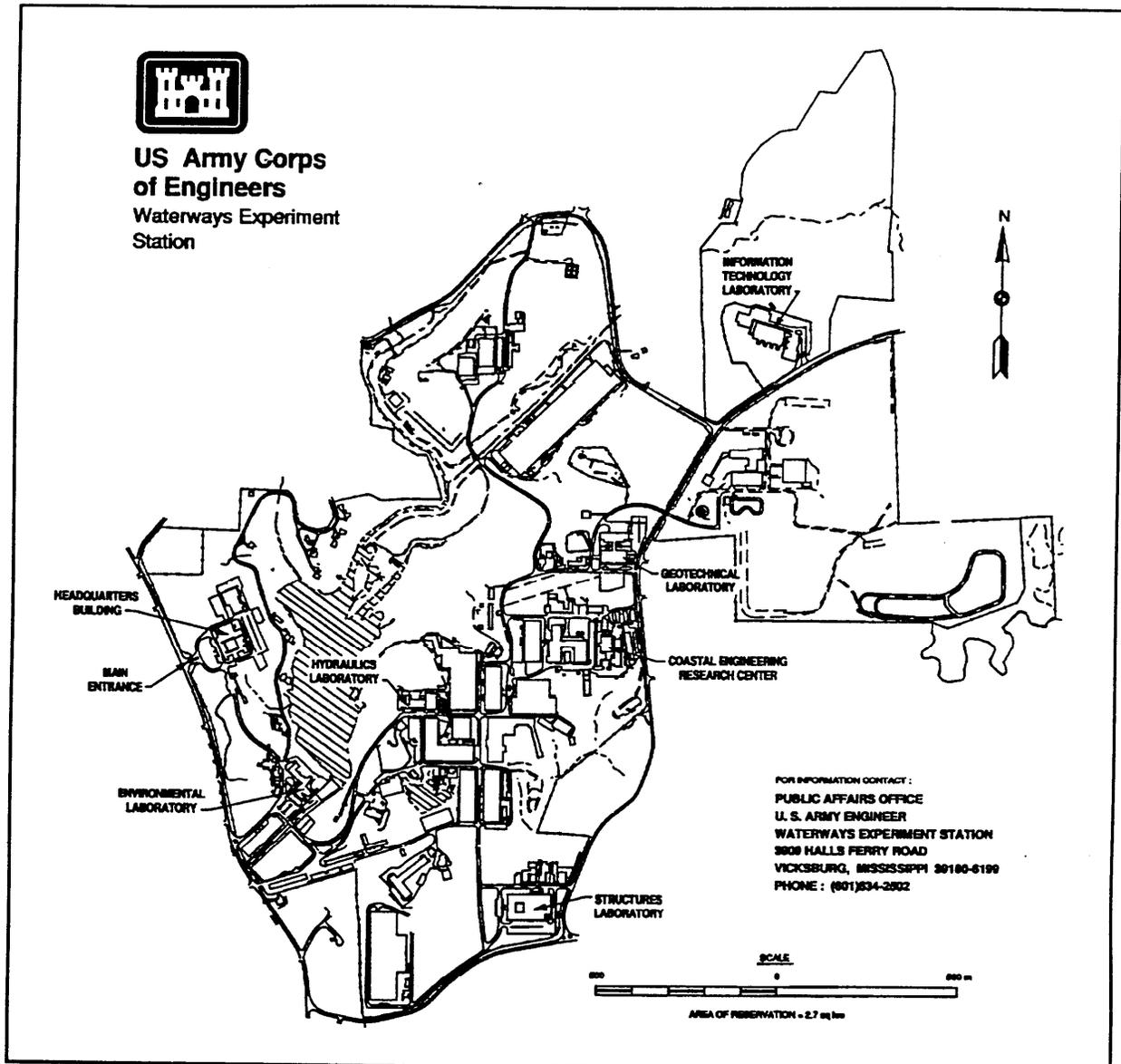
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Preface

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. Technical Monitors were Messrs. George O'Rourke and David Becker. The IRRP Program Manager was Dr. M. John Cullinane.

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

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

At the time of publication of this report, Dr. Robert W. Whalin was Technical Director of WES. Commander was COL Bruce K. Howard, EN.

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1 Introduction

Background

The fate and transport of explosives through porous media have become of greater concern recently, partly because of the increased number of military installation closings. Many of these installations were involved in the manufacture or packing of munitions, thus requiring various explosives to be produced, transported, stored, and disposed onsite. At many of these munitions plants, subsurface migration of explosives poses a potential threat to groundwater resources. Containment and remediation efforts are underway at many of these sites.

One of the most common explosive compounds found at military installations is 2,4,6-trinitrotoluene (TNT). The information available on subsurface TNT transformation and sorption is inadequate for accurate transport or remediation modeling. Because such models are used for planning containment and remediation measures, additional research concerning TNT sorption and transformation in soils is needed.

Process Overview

Many processes affect the fate and transport of TNT in soils and groundwater (McGrath, In Preparation). These processes include, but are not limited to, convection, hydrodynamic dispersion, biodegradation, abiotic transformations, soil sorption, facilitated transport by organic and inorganic colloids, dissolution, and diffusion.

Transformation

Transformation of TNT (Figure 1) has been well documented (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982b; Myers et al., In Preparation). Myers et al. (In Preparation) performed continuous-flow TNT experiments in soil columns that were 15.24 cm in length and found that the majority of the TNT introduced to the columns disappeared before reaching the column outlets. Much of this disappearance was attributed to transformation.

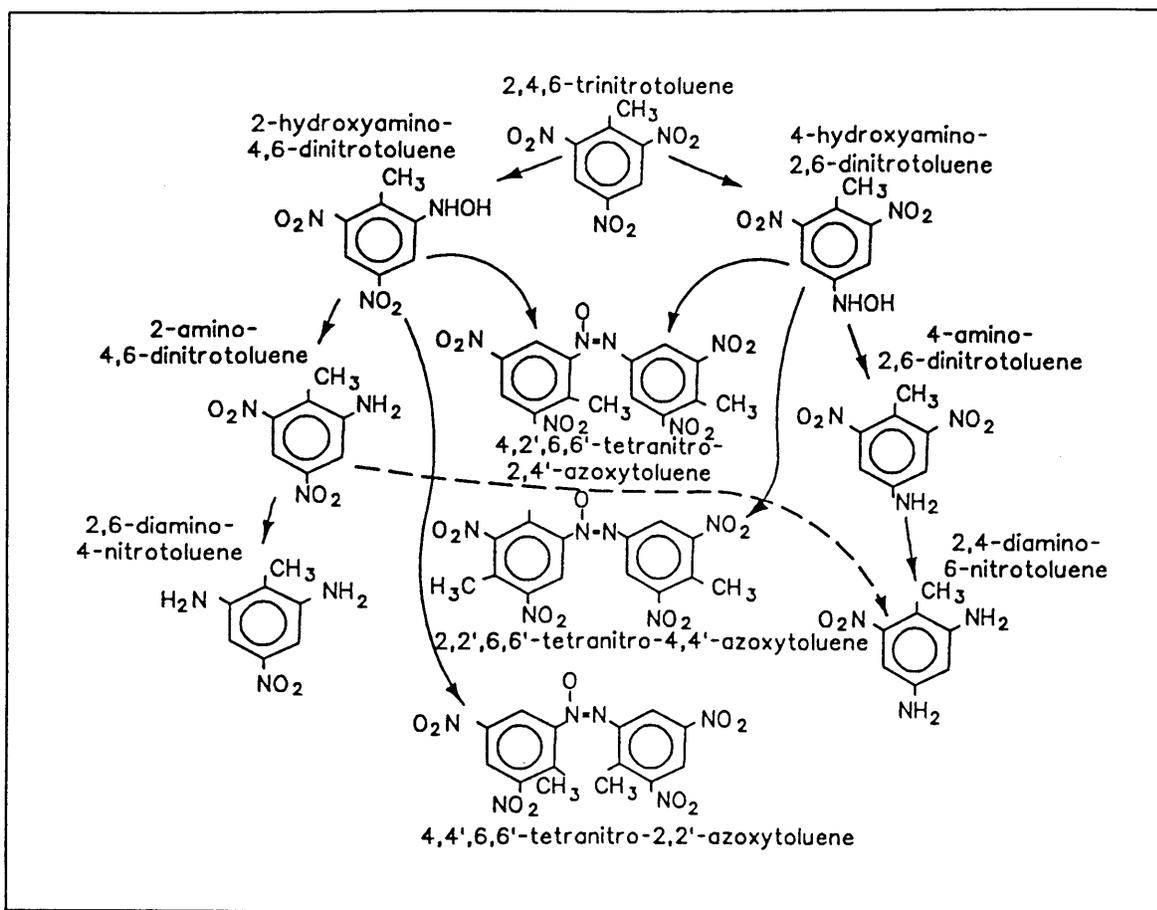


Figure 1. TNT transformation pathway diagram (from McGrath, In Preparation)

All of the products shown in Figure 1 are reduction products. Several researchers (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982b; Myers et al., In Preparation) have observed TNT transformations to the products 2-amino-dinitrotoluene (2A-DNT), 4-amino-dinitrotoluene (4A-DNT), 2,6-diamino-4-nitrotoluene (2,6-DANT), and 2,4-diamino-6-nitrotoluene (2,4-DANT). Less information is available on TNT transformation to azoxytoluenes. Kaplan and Kaplan (1982a) found that the 4A-DNT pathway is favored as opposed to the 2A-DNT pathway. TNT has been shown to undergo reductive transformation under both aerobic and anaerobic conditions (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982b; Pennington and Patrick 1990).

It is unclear whether TNT transformations are primarily biotic, abiotic, or a combination (McGrath, In Preparation). If the transformations occurring are primarily abiotic, then the key soil constituent(s) causing transformation may be exhausted if enough contaminant is introduced to the soil. On the other hand, abiotic soil constituents may be biologically regenerated. Ainsworth et al. (1993) speculate that iron porphyrins and quinones might act as electron

donors in the reduction of nitro groups and that the electron donors might be regenerated under reduced conditions.

Ainsworth et al. (1993) observed some TNT transformation in sterilized soils, though not as much as in unsterilized soils. The ability of both sterilized and unsterilized soils to transform TNT and the fact that TNT transforms under both aerobic and anaerobic conditions suggest that TNT-transformation reactions involve both biotic and abiotic components, with the significance of each component depending on specific conditions.

Sorption

Factors affecting sorption include the chemical characteristics of the inorganic and organic fractions of the porous medium, chemical characteristics of the solute, temperature, and pH (Tchobanoglous and Schroeder 1985). Pennington and Patrick (1990) performed TNT batch tests and found that, for the 16 soils used, TNT adsorption correlated well with extractable iron ($R = 0.89$) and cation exchange capacity ($R = 0.87$). Pennington and Patrick (1990) found that TNT adsorption correlated poorly with the fraction of organic carbon, extractable calcium, aluminum, and manganese, pH, and electrical conductivity.

Equilibrium sorption isotherms, which are determined from batch experiments, generally are used to estimate sorption parameters such as distribution coefficients (K_d). Many complicated isotherms have been proposed, but most sorption data tend to fit linear, Freundlich, or Langmuir isotherms (Tchobanoglous and Schroeder 1985).

A specific isotherm type has not been generally accepted for TNT sorption. Pennington and Patrick (1990) fit batch TNT data for 16 soils to each of the three previously mentioned isotherm types and found that the Langmuir isotherm best fit their data. For the soil column experiments of Ainsworth et al. (1993), the Freundlich sorption model provided the best fit for TNT data. Leggett (1985) suggested a dual component TNT sorption isotherm, fitting a Langmuir isotherm to low-TNT concentration data, and a linear isotherm to high-TNT concentration data. Selim and Iskandar (1994) found that TNT sorption for bentonite clay could be described equally well using linear, Freundlich, Langmuir, and dual component (Leggett 1985) models.

Some evidence of nonequilibrium TNT sorption has been observed (Ainsworth et al. 1993). In soil column experiments, Ainsworth et al. (1993) observed breakthrough curve asymmetry that appeared to be dependent on the type of soil being studied. Irreversible sorption is sometimes suggested to account for TNT losses that cannot be accounted for by transformation, though direct evidence of this is typically lacking (McGrath, In Preparation).

Reactor Models

Determining the most appropriate reactor model for a given experimental system is critical in the interpretation of the results. System hydraulics and hydrodynamic dispersion effects must be defined to resolve their effects from other transport processes and extract model parameters.

Four general categories of reactors exist: batch, complete-mix, plug flow, and advection-dispersion (Tchobanoglous and Schroeder 1985). Almost all systems can be modeled as one of these four, yet most real systems will not rigorously satisfy all of the assumptions associated with any one type of reactor. In some cases, two or more types of reactors may be needed to describe the total system.

Large length-to-diameter soil columns are often used in laboratory studies of contaminant transport in soils. These columns are usually modeled as advection-dispersion reactors. Advection-dispersion reactor models are complicated models that account for mixing along the column length.

Continuous flow experiments have been conducted using small length-to-diameter (thin-disk) soil columns (Skopp and McCallister 1986; Hinz 1992). One advantage that thin-disk columns have over traditional columns is that if the length of soil is small compared with the diameter, the column can be modeled as a complete-mix reactor. Therefore, hydrodynamic dispersion can be neglected, simplifying the equation governing solute transport. Furthermore, highly reactive contaminants such as TNT may transform into other products before eluting from a large length-to-diameter soil column. With thin disks, the contaminant residence time inside the reactor is shortened, increasing the chances of breakthrough. The shorter residence time also reduces the time needed to conduct breakthrough type studies, which may be important in some cases.

Objectives

The objectives of this study were to obtain TNT breakthrough curves and estimate TNT transformation and sorption parameters.

Supporting objectives were as follows:

- To test the hypothesis that soils contain an exhaustible abiotic constituent responsible for TNT transformations.
- To determine the effects of holding times on TNT stability in column eluate samples.

2 Materials and Methods

Soils

Three soils were used in this study: silt from Vicksburg, MS (WES-silt), clay from Vicksburg, MS (Yokena clay), and sand (Ottawa sand) obtained from U.S. Silica Company, Ottawa, IL. Soil properties are shown in Table 1, and particle-size distributions are shown in Figures 2, 3, and 4.

Soil	pH	% TOC ¹	CEC ²	Particle Size		
				% Sand	% Silt	% Clay
WES-silt	5.3	0.567	12.4	2.5	90.0	7.5
Yokena clay	5.3	2.400	38.9	2.0	64.0	34.0
Ottawa sand	**	**	**	92.5	7.5	0

Note: ** = Not measured.
¹ Percent total organic carbon, dry weight basis.
² Cation exchange capacity (meq/100 g).

Thin Disks

Experiments were conducted in stainless steel columns (Figure 5) 0.32 cm in length, with a 4.45-cm inside diameter. Stainless steel porous plates (0.64 cm thick, 100 μ m nominal pore diameter, Mott Metallurgical, Farmington, CT) were placed on the inlet and outlet sides of the soil layer. These plates were used to distribute flow across the soil surface. Rubber O-rings (Mississippi Rubber Specialty Company, Vicksburg, MS) were used to seal the end caps. The end caps were connected to stainless steel inlet and outlet tubing.

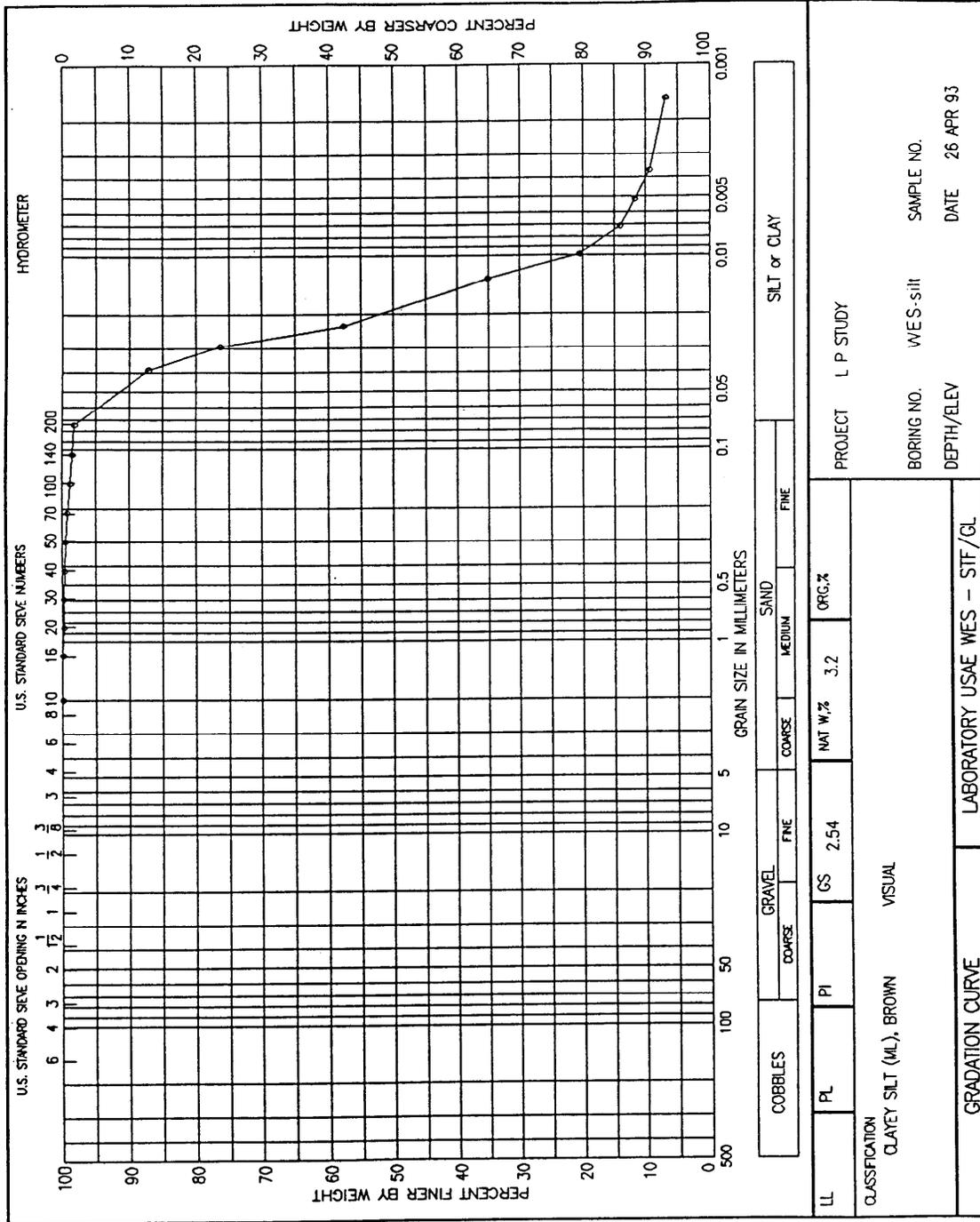


Figure 2. WES-silt particle-size distribution

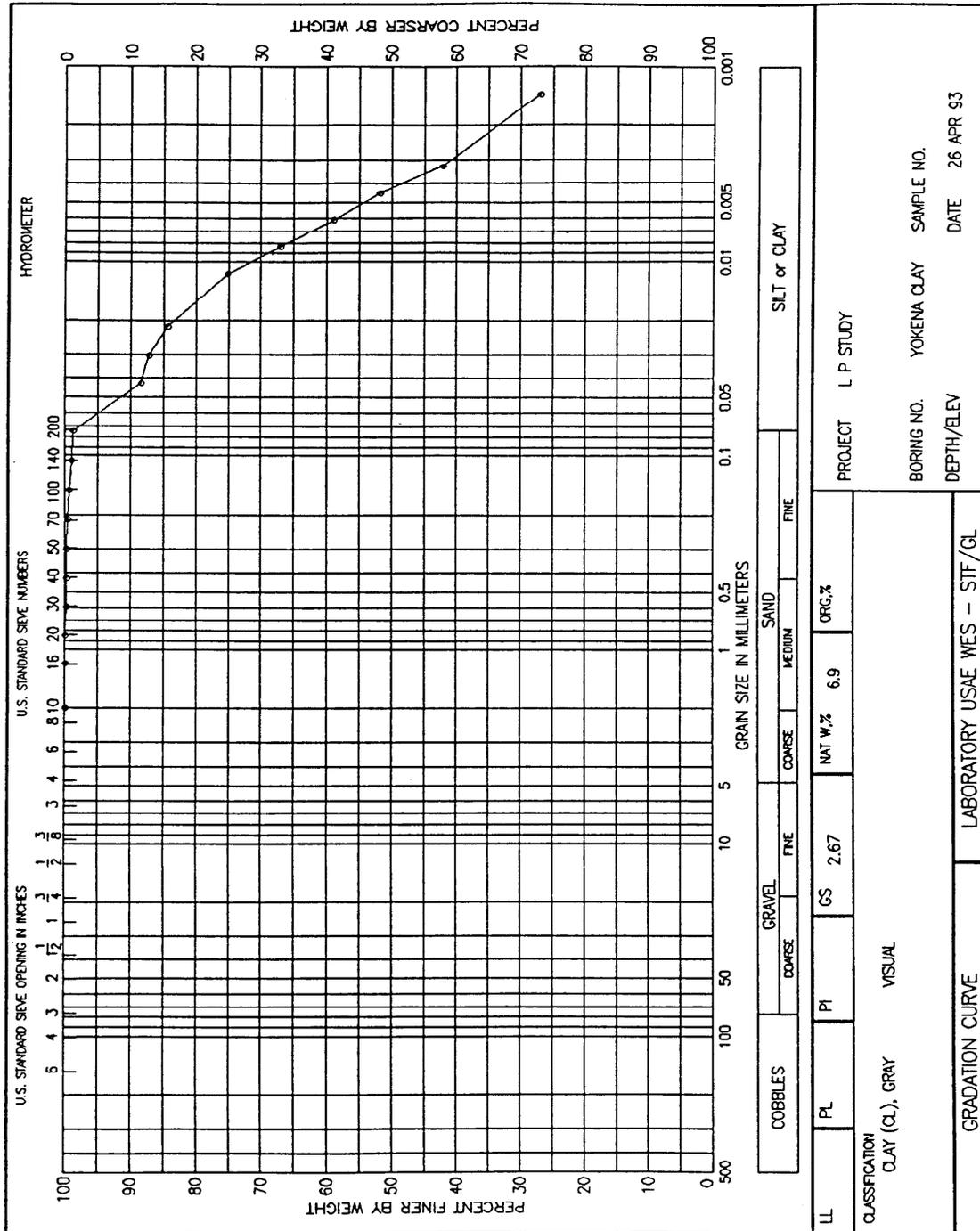


Figure 3. Yokena clay particle-size distribution

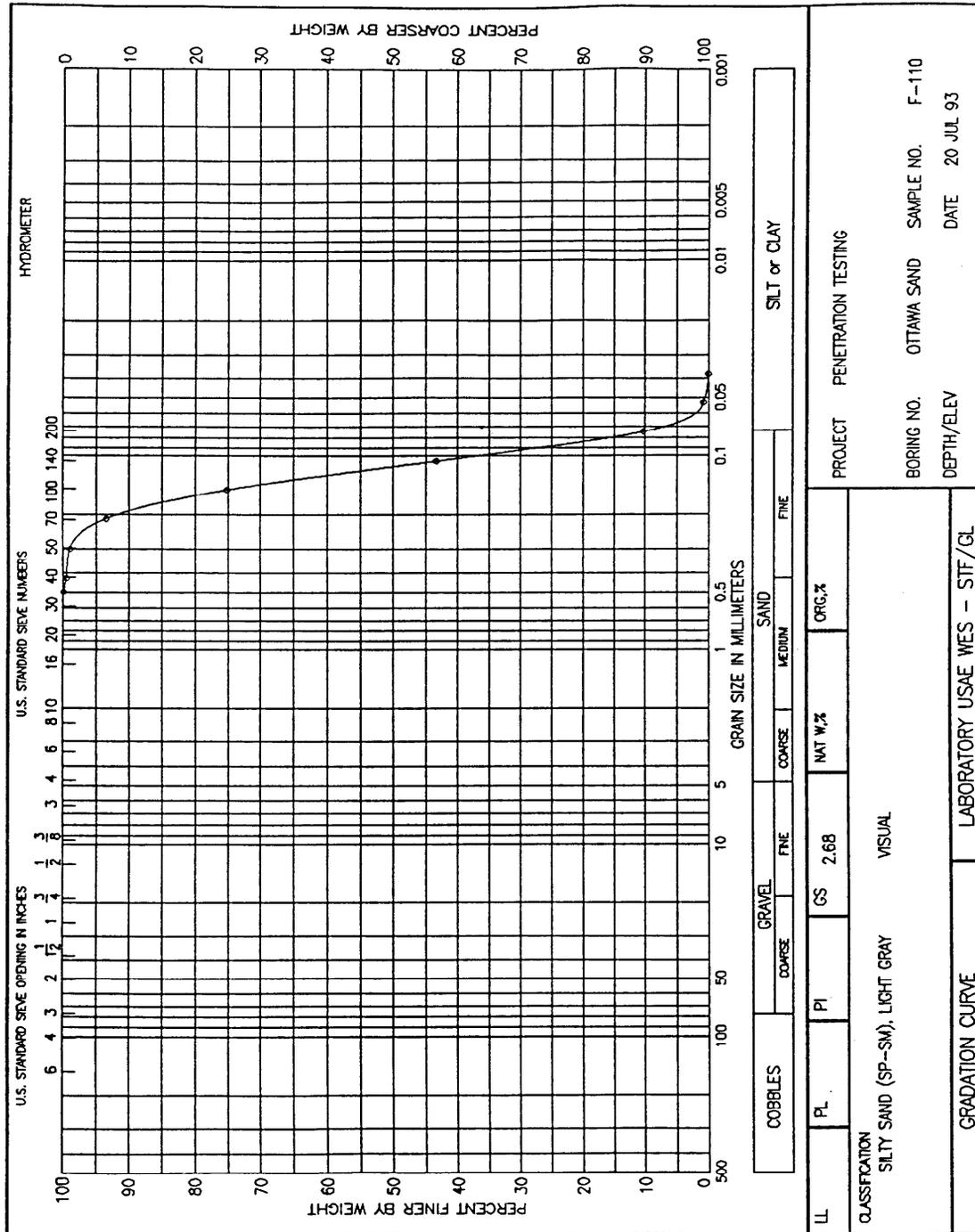


Figure 4. Ottawa sand particle-size distribution

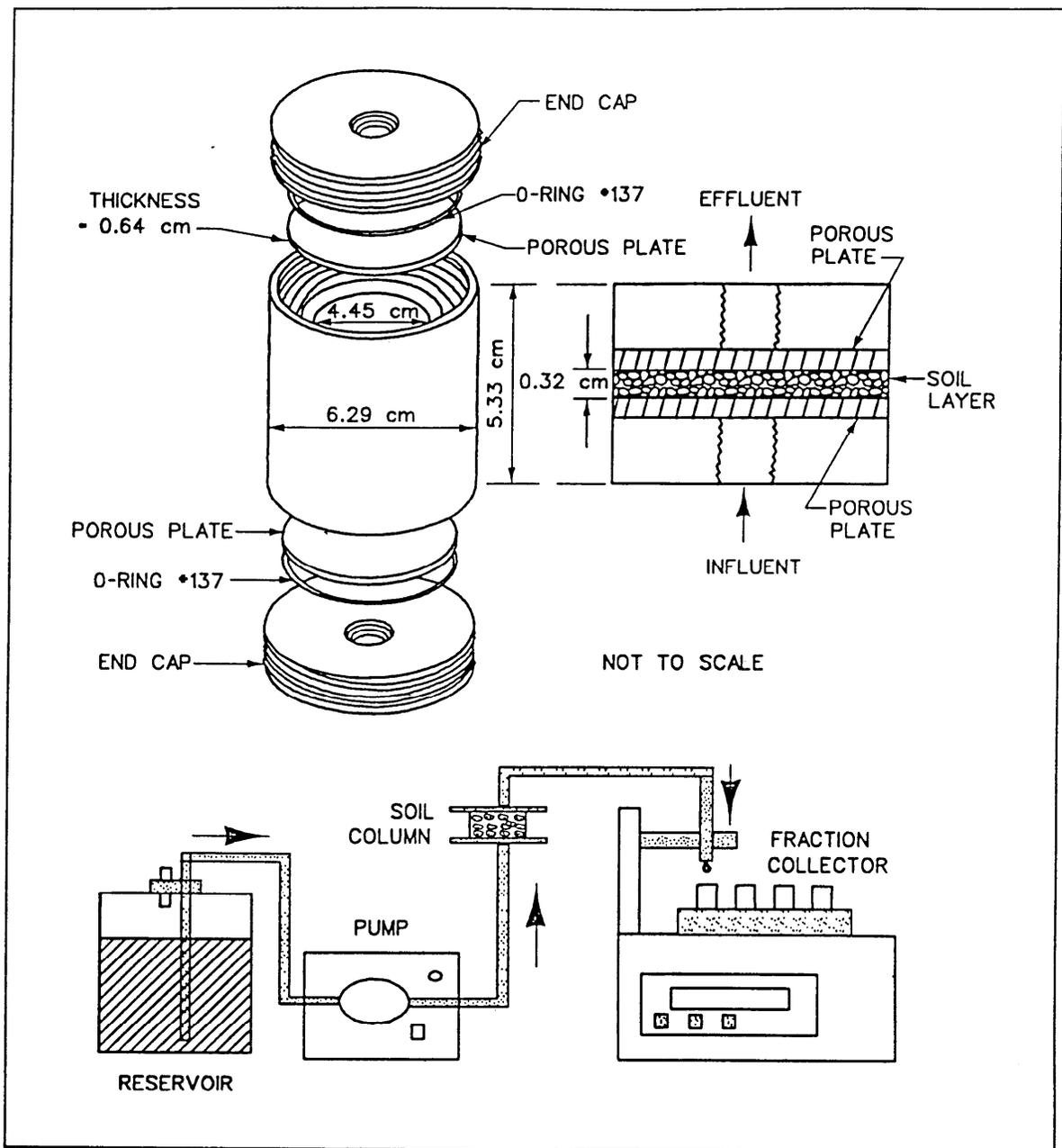


Figure 5. Thin-disk schematic and experimental apparatus

Disk Loading

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

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

WES-silt

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

Yokena clay

As with the WES-silt, the mass of Yokena clay needed to give a 0.32-cm soil layer was estimated using specific gravity, water content, and an assumed porosity (0.65). This was calculated to be 4.88 g. On the first loading attempt, an 8:1 water to soil ratio was used, and the slurry was transferred to the column using the same procedure as with the WES-silt soil. The slurry was allowed to gravity drain, which took approximately 75 min. Upon inspection, it was noted that the clay apparently had swelled, making the soil layer thicker than the desired 0.32 cm. The same procedure was followed in a second loading attempt. The water took longer to drain, but the results were similar to the first loading attempt. Loading was also attempted using a slight vacuum to remove water. This procedure produced an uneven surface on the soil layer.

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

transferred to the column as before. A smooth, even layer was obtained using the 10:1 water to Yokena clay, 4 hr of stirring, and gravity drainage.

Ottawa sand

As with the previous soils, the mass of Ottawa sand needed to produce a 0.32-cm layer was calculated using its specific gravity, water content, and an assumed porosity (0.30). The mass needed was calculated (9.25 g), a slurry was made, and the slurry was transferred to the column. With this procedure, the sand settled too fast, resulting in an uneven layer.

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

Contaminated Feed Solution Preparation

Contaminated feed solution was prepared using field-contaminated soil from the Naval Surface Warfare Center in Crane, IN. The soil (labeled Crane Sifter-Conveyor) contained a TNT concentration of approximately 1,500 mg/kg (Pennington et al. 1995). Two batches were prepared during the project.

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

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

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

Thin-Disk Column Tests

Breakthrough curves

DDI water was pumped (upflow mode) through three soil columns (WES-silt, Yokena clay, and Ottawa sand) using constant-volume metering pumps (Model QG6-2-SSY, Fluid Metering Inc., Oyster Bay, NY) until target flows were obtained (approximately 1.8 to 2.3 ml/hr). When these flows were achieved, the pumps were stopped, and DDI water was replaced with contaminated feed solution. The pumps were restarted with the contaminated feed solution. Column operating parameters and average feed solution concentrations are shown in Tables 2 and 3.

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

¹ Average pore water velocity.
² Bulk density.
³ Porosity.
⁴ Specific gravity.

Parameter ¹	WES-Silt	Yokena Clay	Ottawa Sand
TNT	63.2	63.2	58.8
HMX	2.47	2.47	2.18
RDX	33.6	33.6	30.9
TNB	0.27	0.27	0.184
DNB	<0.02	<0.02	<0.02
TETRYL	<0.05	<0.05	<0.05
4A-DNT	0.145	0.145	0.110
2A-DNT	2.23	2.23	1.97
2,6-DNT	<0.020	<0.020	<0.020
2,4-DNT	0.028	0.028	0.026
AZOXY	<0.100	<0.100	<0.100
3,5-DNA	0.054	0.054	0.051
2,6-DANT	<0.100	<0.100	<0.100
2,4-DANT	<0.200	<0.200	<0.200

¹ See Appendix B for full chemical names.

Contaminated feed solution was pumped through the WES-silt and Yokena clay columns for step inputs of 160 and 211 pore volumes, respectively (284 and 329 hr, respectively). Contaminated feed solution was pumped through the Ottawa sand column for a step input of 51 pore volumes (48 hr).

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

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

Pause in flow

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

Blank column

In addition to the previous soil column experiments, an empty column (blank) experiment was performed. DDI water was pumped through the blank column until a target flow was achieved (1.9 ml/hr). When this flow was achieved, DDI water was replaced with contaminated feed solution, which was pumped through the blank column for a step input of 11 pore volumes (28 hr). The blank column experiment was ended after addition of the step input.

Sampling procedure

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

Holding-Time Study

Since some samples were not preserved immediately after being collected, a study was conducted to assess the impacts of delayed preservation on TNT concentrations in the samples. Fifteen contaminated feed solution samples

were diluted 1:10 with DDI water. These samples were placed in 20-ml amber vials, capped, labeled, and placed on a bench top in the laboratory. Three of the samples were preserved by pipetting 5 ml of sample into another amber vial and adding an equal volume of acetonitrile. The remaining samples were allowed to sit on the bench top. Three more vials were preserved every 6 hr. The final suite was preserved at an elapsed time of 24 hr.

Chemical Analysis

Samples were analyzed for 2,4,6-trinitrotoluene (TNT), 1,3-dinitrobenzene (DNB), methyl-2,4,6-trinitrophenylnitramine (TETRYL), 1,3,5-trinitrobenzene (TNB), 4-amino-2,6-dinitrotoluene (4A-DNT), 2-amino-4,6-dinitrotoluene (2A-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), and 3,5-dinitroaniline (3,5-DNA) on two independent high performance liquid chromatography (HPLC) systems using the dual column confirmation method developed by Jenkins, Miyares, and Walsh (1988). The first system consisted of a 600E system controller, a 712 Wisp Auto Injector, and a 486 Tunable Absorbance Detector (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-18 (Supelco 25 cm by 4.6 mm) column eluted with 1:1 methanol/water at 1.2 ml/min. The second HPLC system consisted of an HPLC Module I (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-CN (Supelco 25 cm by 4.6 mm) column eluted with 1:1 methanol/water at 1.2 ml/min.

Samples were analyzed for 2,6-diamino-4-nitrotoluene (2,6-DANT) and 2,4-diamino-6-nitrotoluene (2,4-DANT) using the above method except that the columns were eluted with 4:6 methanol/water instead of 1:1. There was some difficulty in resolving 2,6-DANT and 2,4-DANT using this method.

Samples were analyzed for a composite of 4,2',6,6'-tetranitro-2,4'-azoxytoluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 4,4',6,6'-tetranitro-2,2'-azoxytoluene using the above method except that the columns were eluted with 5.4:4.6 acetonitrile/water at 1.5 ml/min instead of 1:1 methanol/water at 1.2 ml/min.

Chloride Tracer

A sodium chloride solution (500-mg/l as chloride) was pumped through the blank column until chloride concentrations reached the initial concentration. Because sample volumes were smaller than what is needed for analysis with a dip-type chloride ion probe, chloride concentrations were indirectly measured using an in-line conductivity electrode (Mfr. #018010, Orion Research, Inc., Boston, MA) that was attached at the end of the outlet tubing. Conductivity readings were taken using a conductivity meter (Model 35, Yellow Springs Instrument Co., Inc., Yellow Springs, OH). The conductivity curve was used to estimate the effective hydraulic residence time of the apparatus.

3 Results and Discussion

TNT Breakthrough Curves (BTCs)

The normalized WES-silt TNT BTC (Figure 6) showed that TNT concentrations reached steady-state after about 40 pore volumes were eluted. Steady-state concentrations were about 95 percent of the initial concentration, indicating the presence of a disappearance process. The shape of the curve was approximately symmetrical, indicating reversible sorption.

The Yokena clay TNT BTC (Figure 6) also showed evidence of a disappearance process. TNT concentrations reached steady-state after approximately 60 pore volumes were eluted and were about 97 percent of the initial concentration. The Yokena clay TNT breakthrough curve was also approximately symmetrical.

The Ottawa sand TNT BTC (Figure 6) showed a smaller amount of disappearance than the WES-silt and Yokena clay BTCs, which is indicated by a normalized steady-state concentration of about 0.99. The concentration was very near steady-state after about 50 pore volumes were eluted, and the available data suggest TNT effluent concentrations would have approached steady-state at the input concentration had the step input been longer. As with the WES-silt and Yokena clay BTCs, the Ottawa sand TNT BTC was approximately symmetrical.

All three TNT BTCs showed consistent trends with minimal scattering of data. The WES-silt and Yokena clay effluent TNT concentrations did not reach steady-state at the input concentration, indicative that some type of disappearance mechanism is operative (e.g., transformation and irreversible sorption).

Figure 7 shows hypothetical BTCs for reversible sorption with no transformation, reversible sorption with exhaustible transformation, and reversible sorption with nonexhaustible transformation. At steady-state, effluent concentration does not change with respect to time, which implies that the rate of adsorption equals the rate of desorption. If the steady-state effluent concentration is below the influent concentration, the difference is indicative of some type of disappearance process. While transformation is occurring, effluent

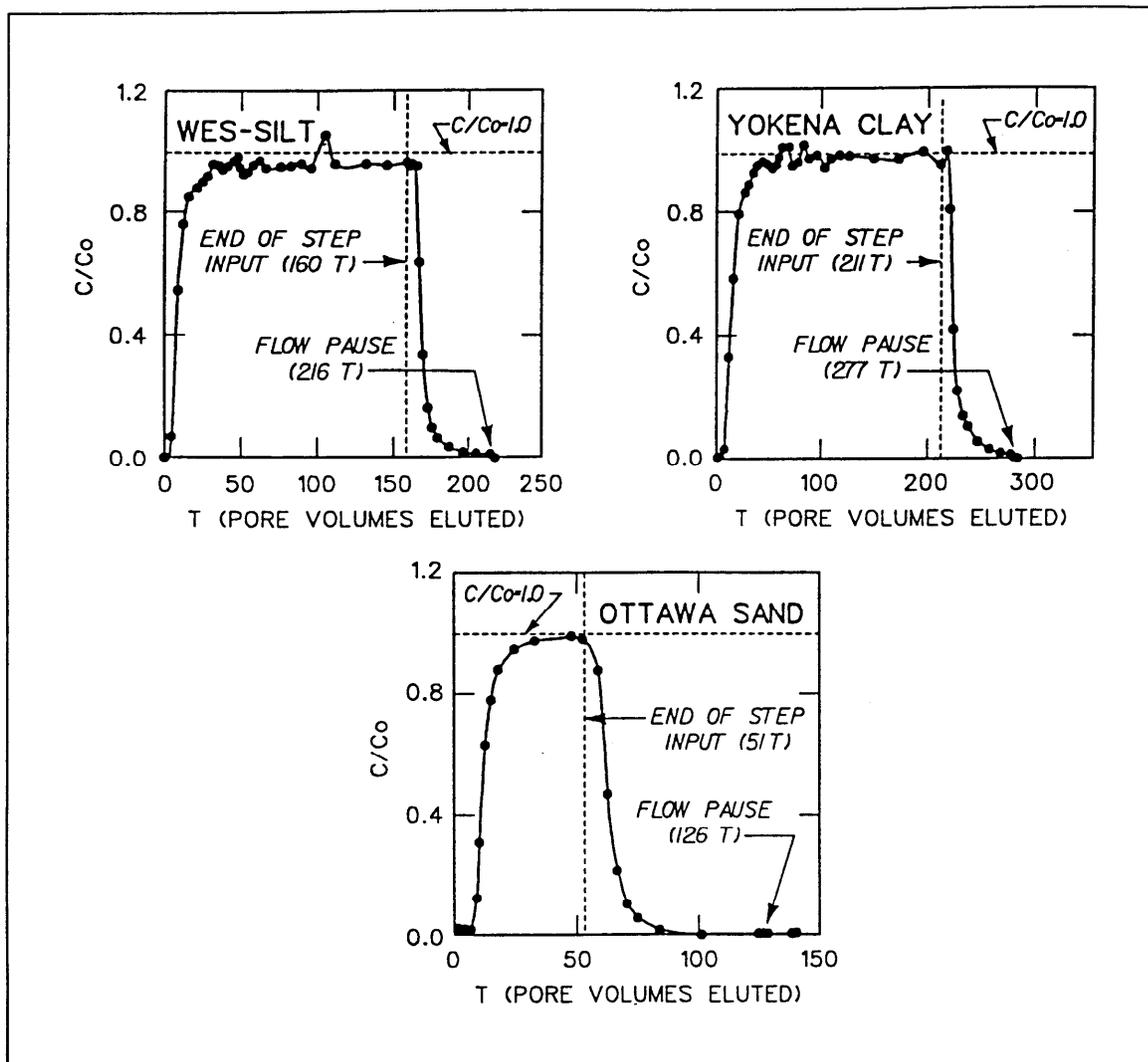


Figure 6. Normalized TNT breakthrough curves

concentrations cannot reach the influent concentration. If the soil component(s) responsible for transformation (e.g., terminal electron donor) is exhausted, the TNT concentration should show a delayed return to the influent concentration. The WES-silt and Yokena clay TNT BTCs did not show evidence of an exhaustible transformation process. The Ottawa sand TNT BTC approached steady-state at the influent concentration.

TNT Transformation Product BTCs

TNT and TNT transformation products were measured in column effluents. In each of the columns, effluent concentrations of certain transformation products exceeded their influent concentrations, indicating that TNT was transformed during passage through the soils (Figures 8, 9, and 10).

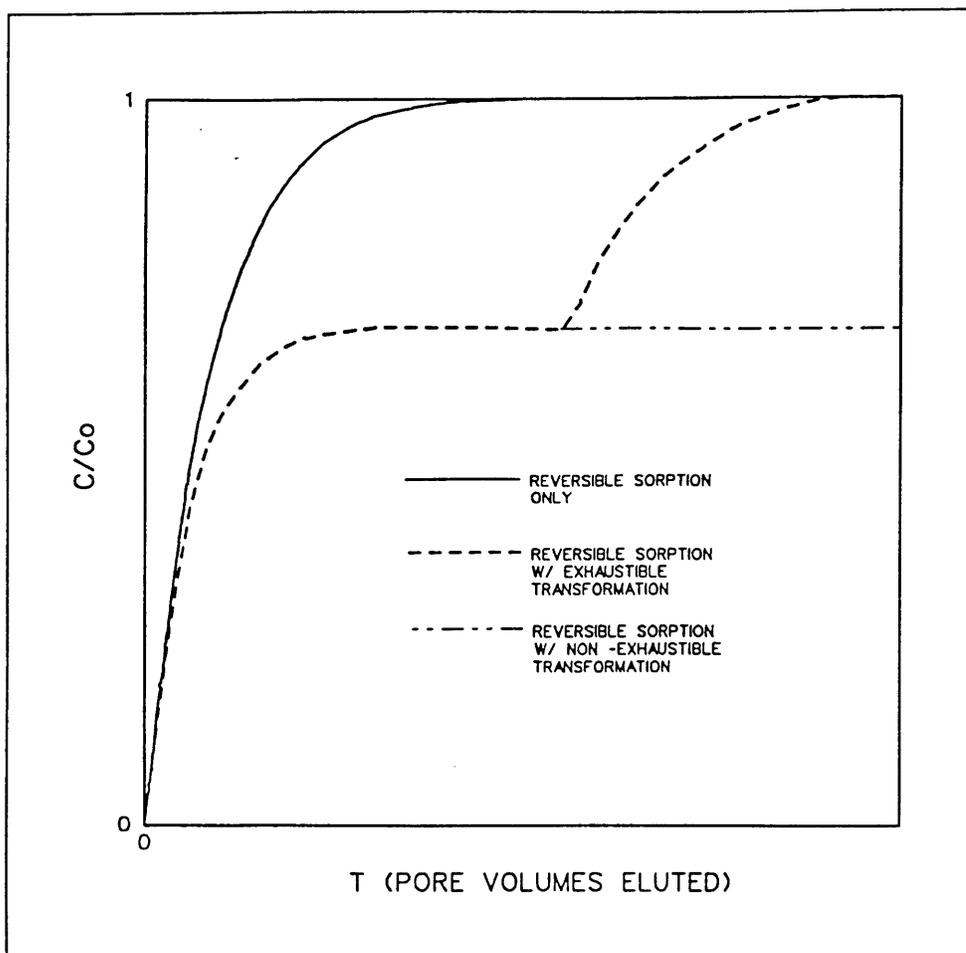


Figure 7. Normalized hypothetical breakthrough curves for complete mix

WES-silt

The WES-silt showed more TNT disappearance than the Yokena clay and Ottawa sand. Most of this disappearance is accounted for by the accumulation of 4A-DNT (Figure 8). This constituent reached steady-state at a normalized concentration of about 12, indicating that 4A-DNT was being generated from TNT. The fact that 4A-DNT reached steady-state is indicative that 4A-DNT was being transformed to another product.

The 2A-DNT concentration also increased to a level above the influent concentration and reached steady-state (Figure 8). The 2A-DNT steady-state concentration is only about 1.2 on the normalized scale, rather than the 12 observed from the 4A-DNT BTC. These data suggest that the 4A-DNT pathway was favored.

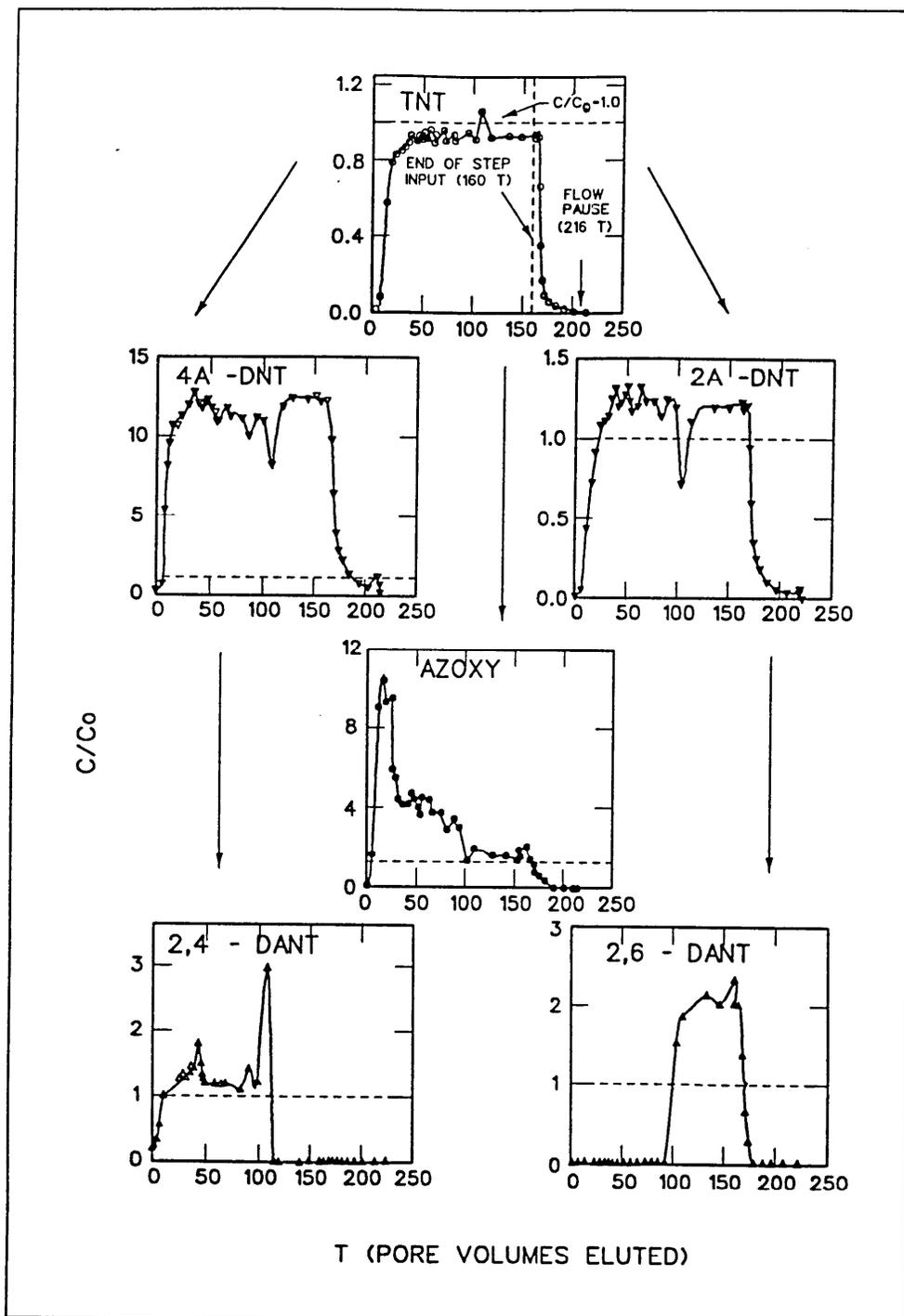


Figure 8. Normalized WES-silt transformation product breakthrough curves

As shown on the TNT transformation pathway diagram (Figure 1), the subsequent product of 4A-DNT is 2,4-DANT, and the subsequent products of 2A-DNT are 2,6-DANT and 2,4-DANT. The 2,4-DANT and 2,6-DANT influent concentrations were below the minimum detection limits (MDLs) for these compounds (0.200 mg/l for 2,4-DANT and 0.100 mg/l for 2,6-DANT). For

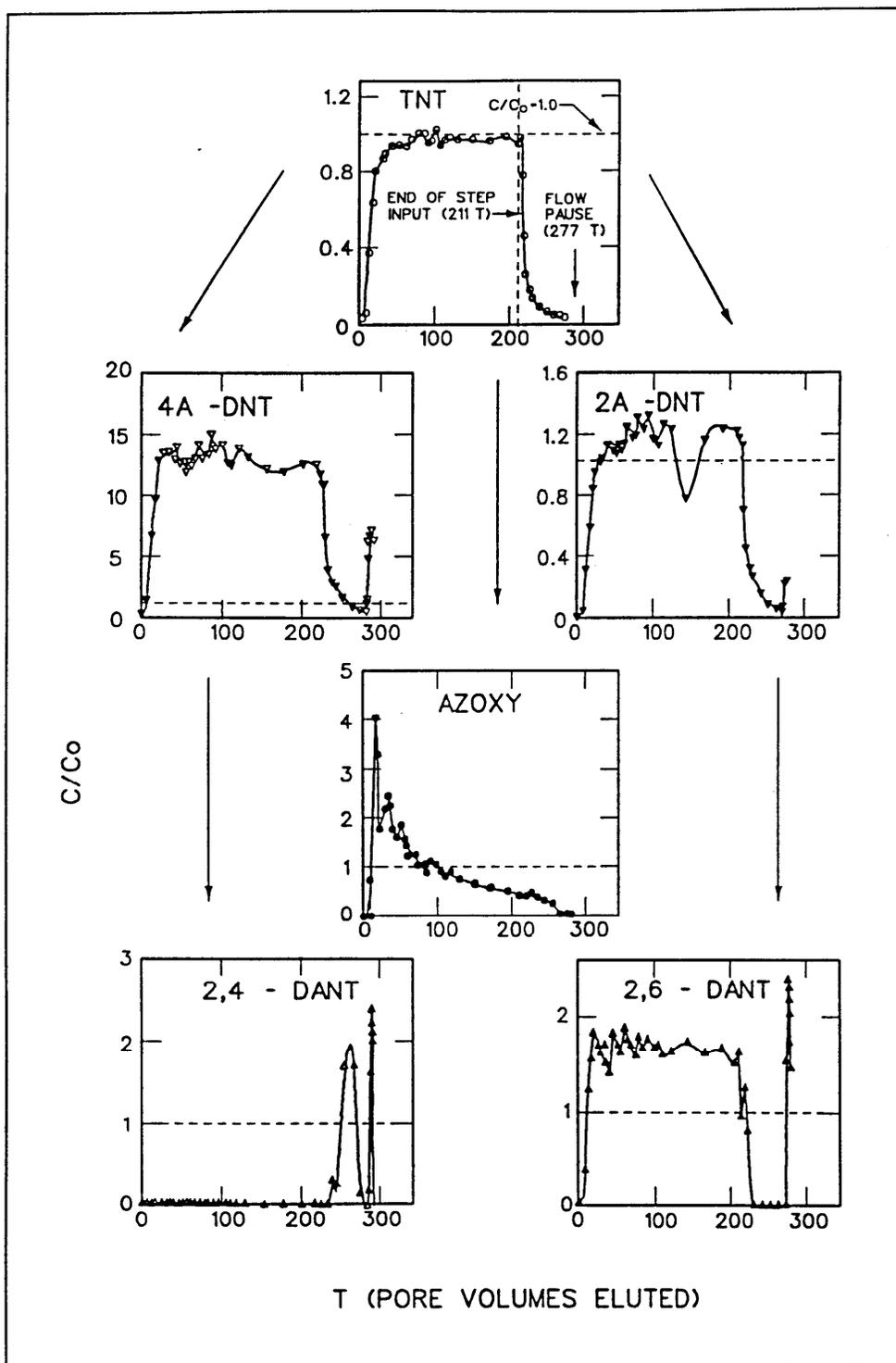


Figure 9. Normalized Yokena clay transformation product breakthrough curves

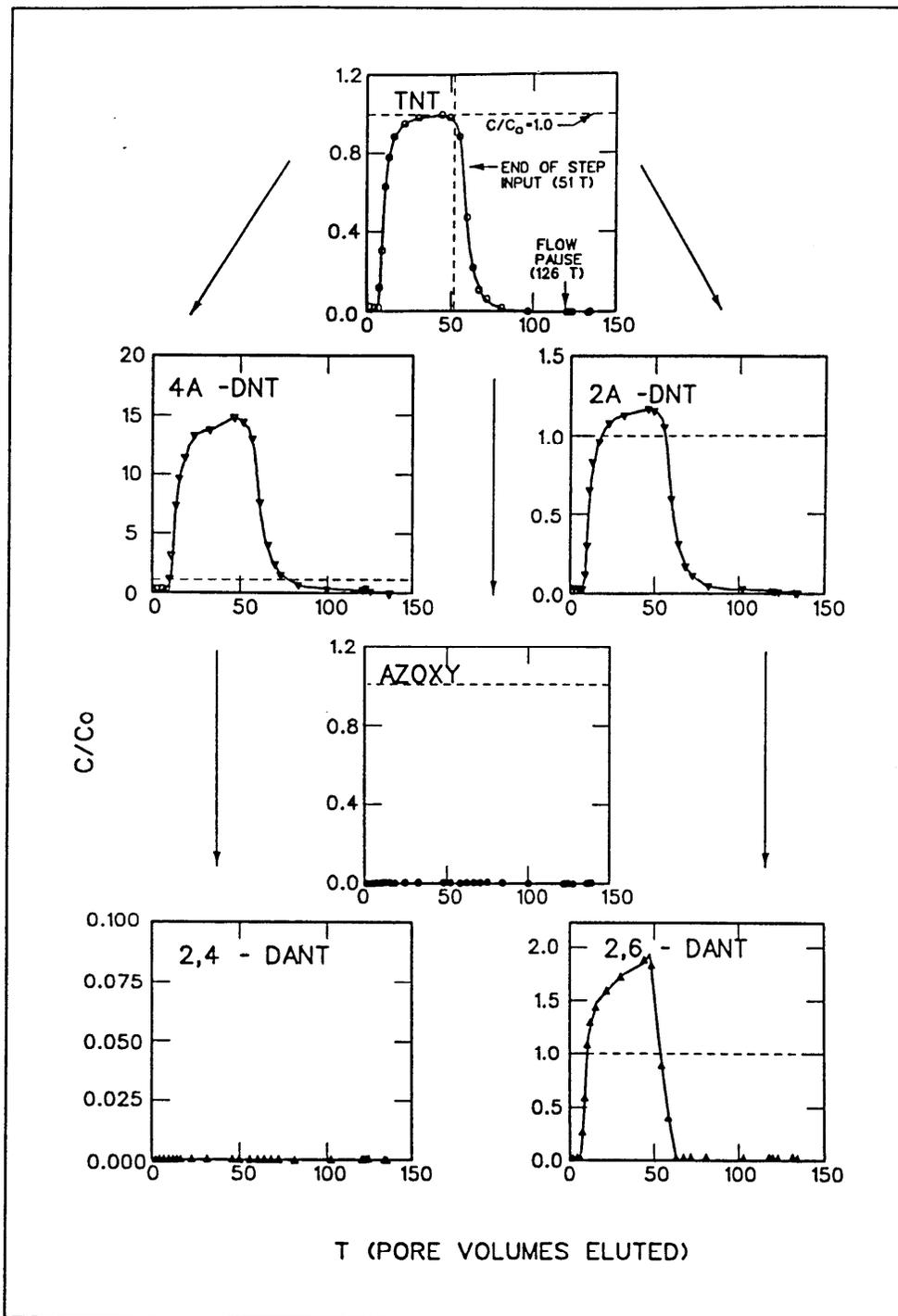


Figure 10. Normalized Ottawa sand transformation product breakthrough curves

the purpose of plotting these BTCs, the influent concentrations of 2,4-DANT and 2,6-DANT were assumed to be one-half of the MDLs for these compounds. The 2,4-DANT and 2,6-DANT BTCs are somewhat erratic (Figure 8), which probably reflects the difficulty of separating these two compounds by

HPLC analysis. Since, for all three soils, some points on the 2,4-DANT and 2,6-DANT BTCs may actually be combinations of both of these products, interpretation of the 2,4-DANT and 2,6-DANT BTCs is not possible.

Other possible TNT transformation products include azoxytoluenes (Figure 1). The composite azoxytoluene (AZOXY) BTC (Figure 8) showed an initial sharp rise to a normalized concentration of about 10. The peak occurred at about 15 pore volumes. After peaking, the AZOXY concentration decreased throughout the remainder of the experiment. The AZOXY influent concentration was below the MDL (0.100 mg/l). For the purpose of plotting the AZOXY BTC, the influent concentration was assumed to be one-half of the AZOXY MDL.

Other TNT manufacturing impurities and/or possible transformation products included in the chemical analysis were 2,6-DNT, 2,4-DNT, 3,5-DNA, and TNB. None of these compounds were found to be significant TNT transformation products for any of the column tests. A summary of the effluent data for these compounds is presented in Table 4.

Table 4 Effluent Concentrations for Selected Transformation Products (mg/l)									
Parameter	WES-Silt			Yokena Clay			Ottawa Sand		
	Min ¹	Max ²	Mean ³	Min	Max	Mean	Min	Max	Mean
2,6-DNT	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2,4-DNT	<MDL	0.035	<MDL	<MDL	0.032	<MDL	<MDL	0.022	<MDL
3,5-DNA	<MDL	0.064	0.038	<MDL	0.061	0.035	<MDL	0.049	<MDL
TNB	<MDL	0.333	0.156	<MDL	0.300	0.115	<MDL	0.166	0.053
AZOXY	**			**			<MDL	<MDL	<MDL

Note: Minimum detection limits (MDLs): 2,6-DNT = 0.02 mg/l; 2,4-DNT = 0.02 mg/l; 3,5-DNA = 0.02 mg/l; TNB = 0.02 mg/l; AZOXY = 0.10 mg/l.
 ** Data is presented in Figures 8 and 9.
¹ Minimum observed effluent concentration.
² Maximum observed effluent concentration.
³ Mean observed effluent concentration.

Yokena clay

Although the Yokena clay soil showed less TNT disappearance than the WES-silt soil, the transformation products showed similar behavior (Figure 9). The 4A-DNT reached a normalized steady-state concentration of approximately 12. The Yokena clay 2A-DNT reached steady-state at a normalized concentration of about 1.2. The Yokena clay 2,4-DANT and 2,6-DANT BTCs probably

indicate the difficulty in separating these two compounds by HPLC analysis, as previously discussed.

The Yokena clay AZOXY BTC showed an initial sharp rise to a normalized concentration of about 4, followed by a decrease throughout the remainder of the experiment. The peak occurred at approximately 15 pore volumes.

Ottawa sand

Most of the transformed TNT in the Ottawa sand column was in the form of 4A-DNT (Figure 10). The 4A-DNT BTC approached steady-state and peaked at a normalized concentration of about 15. The Ottawa sand 2A-DNT approached steady-state near the influent concentration, indicating that 2A-DNT was not a significant TNT transformation product in the Ottawa sand column. The Ottawa sand 2,4-DANT and 2,6-DANT BTCs are probably reflective of HPLC separation difficulty. The Ottawa sand AZOXY concentrations were less than the MDL throughout the experiment (Table 4).

Summary

The transformation product BTCs clearly show that TNT transformations were occurring in each of the three soils. The relative order of magnitude was silt > clay > sand. For each soil, 4A-DNT was the main transformation product. The trends in Figures 8, 9, and 10 are consistent with a nonexhaustible transformation process and are generally consistent with the TNT transformation pathway (Figure 1).

Pause in Flow

During washout, flow to each column was stopped, and the columns were sealed for 8 weeks. After this pause in flow, washout was restarted. For each soil, TNT concentrations were slightly above the minimum detection limit immediately before flow was stopped. Immediately after restarting flow, TNT concentrations were slightly below concentrations before the flow pause (Figures 11, 12, and 13).

The stopped-flow technique produced different results for the TNT transformation products than for the TNT (Figures 11, 12, and 13). Effluent 2A-DNT and 4A-DNT concentrations increased after the flow pause in all three soils.

Hinz (1992) used a similar stopped-flow technique when studying the sorption/desorption of zinc and observed a concentration increase from nearly zero to 55 percent of the initial concentration during the pause in flow. The concentration increase observed by Hinz (1992) was attributed to diffusion out of pores (physical nonequilibrium). In the present study, TNT concentrations

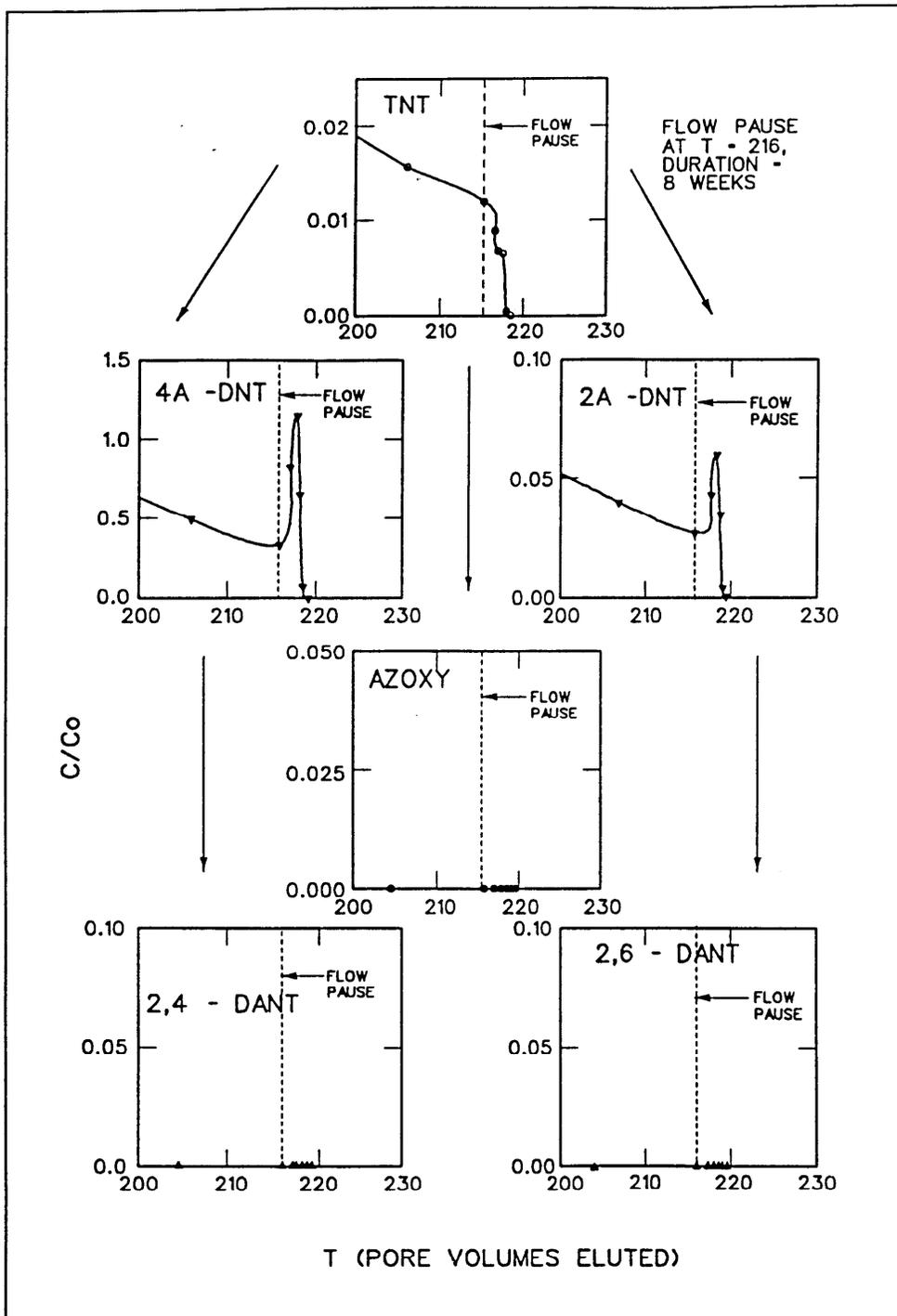


Figure 11. Normalized WES-silt breakthrough curves describing flow pause

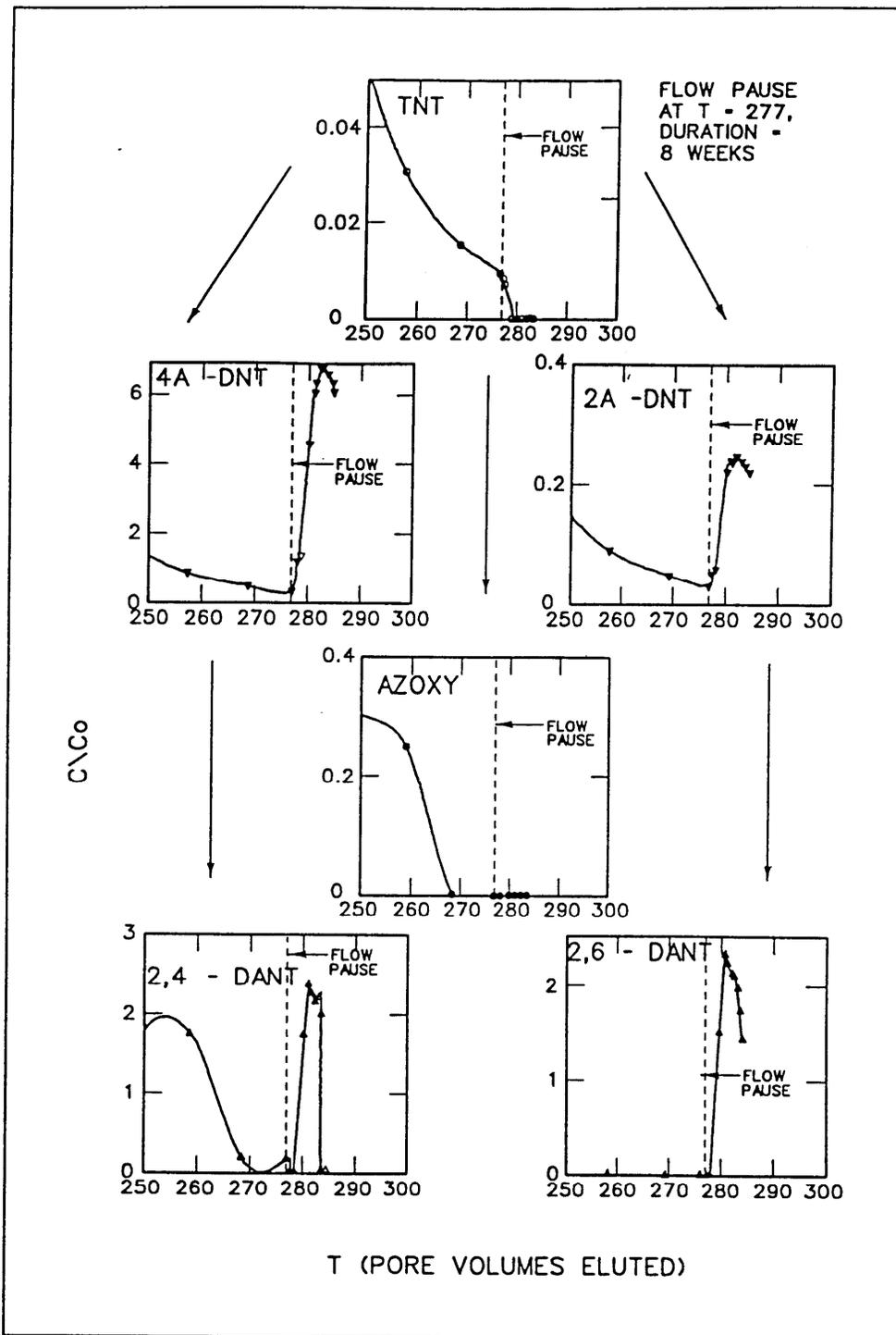


Figure 12. Normalized Yokena clay breakthrough curves describing flow pause

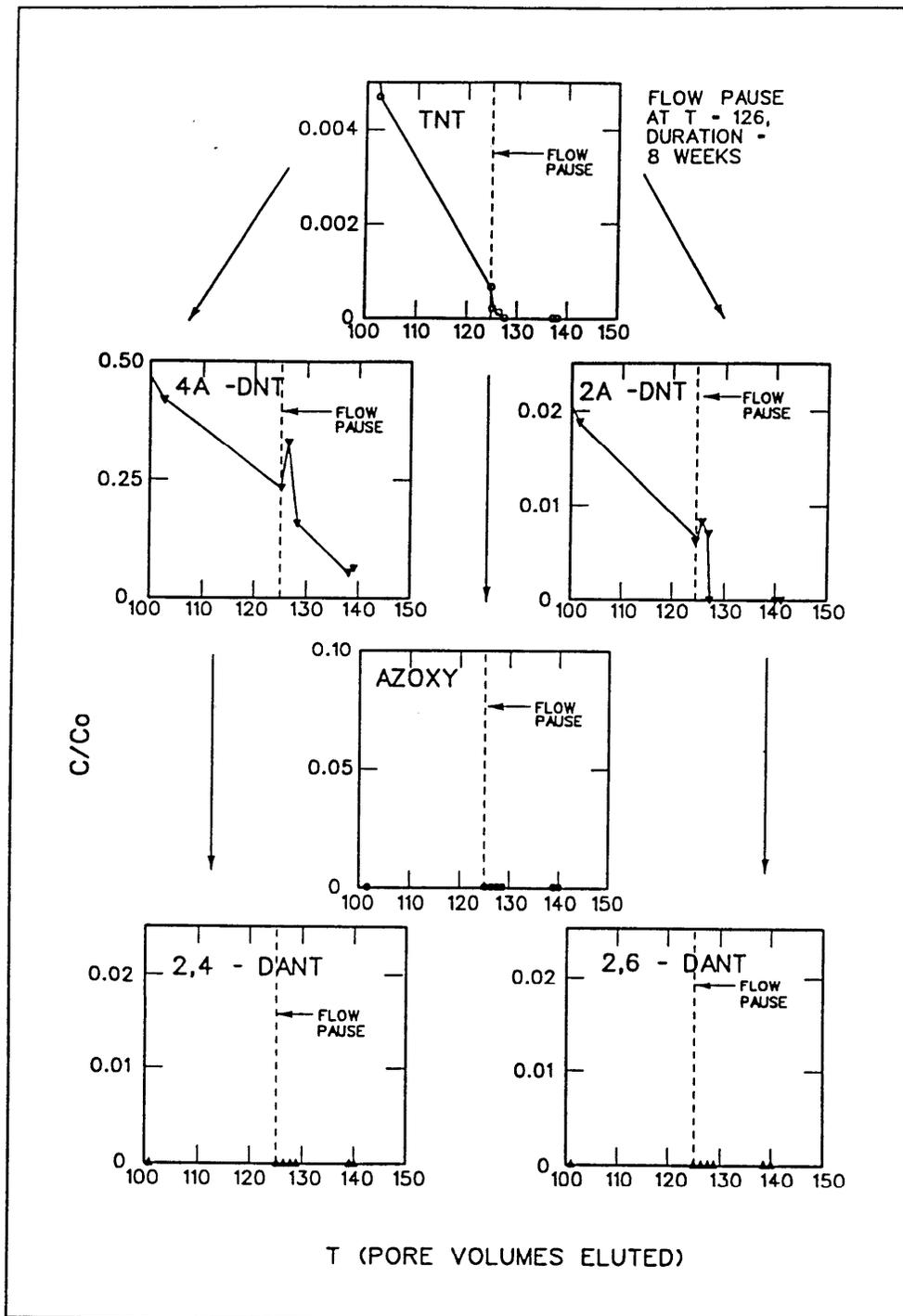


Figure 13. Normalized Ottawa sand breakthrough curves describing flow pause

decreased during the flow pause because TNT continued to transform to the products 4A-DNT and 2A-DNT, as indicated by the increase in the concentrations of these products.

Mole Balance

Eluted TNT transformation products were converted to TNT equivalents on a molar basis. Excellent mole balances were observed for all three soil columns. An account could be given for virtually all of the TNT that was pumped into the soil column (Figure 14). Greater than 90 percent of the TNT input to each column was eluted as TNT. The remainder of the input mass was either eluted as TNT transformation products or remained in the soil.

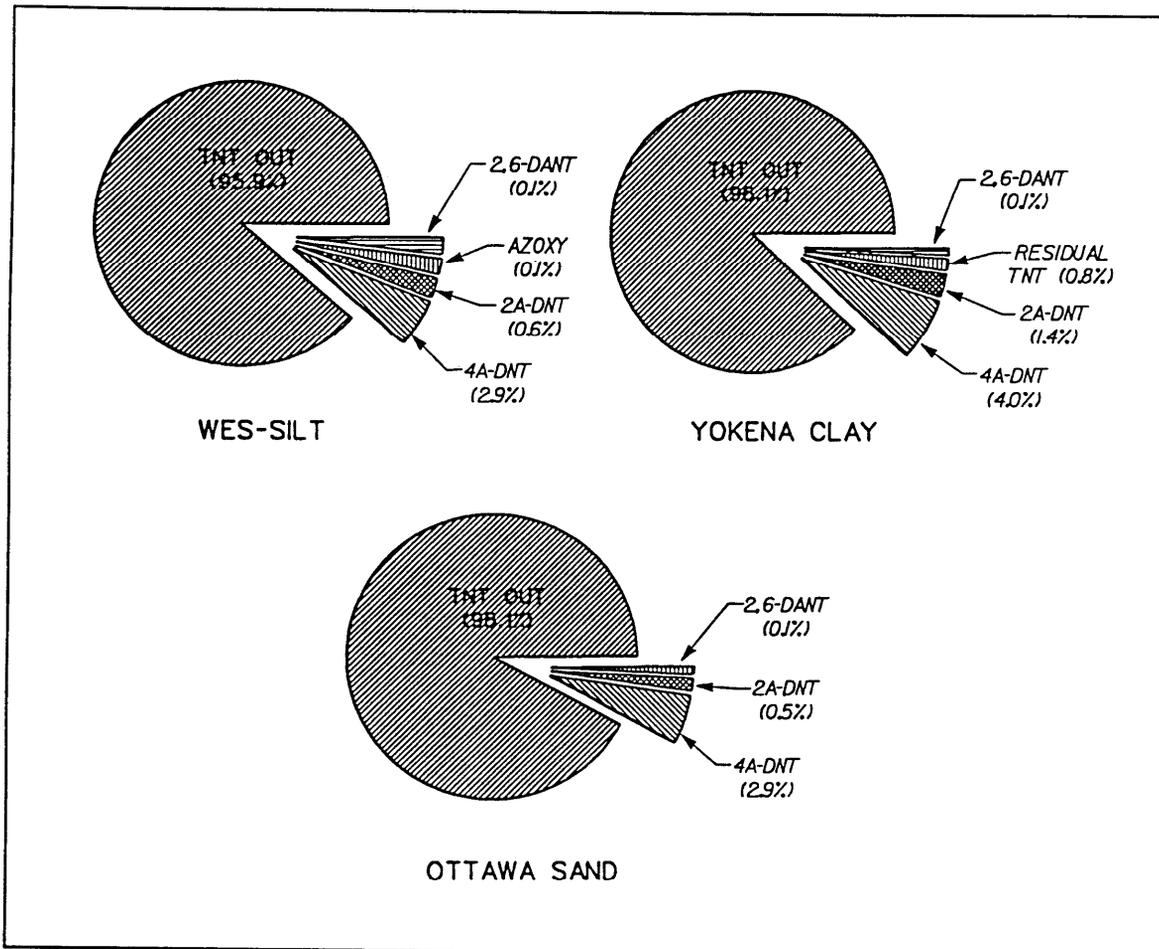


Figure 14. TNT mole balance

WES-silt

In the WES-silt soil column, 95.9 percent of the TNT entering the column was eluted as TNT. No residual TNT was measured in the soil after the experiments were completed, suggesting that the TNT sorption was governed by a reversible process and/or the sorbed TNT had been transformed into other products. The majority of the remaining input TNT could be accounted for as 4A-DNT (2.9 percent). The production of 2A-DNT accounted for 0.6 percent of the input TNT. Other transformation products (2,6-DANT and AZOXY) together account for 0.2 percent of the input TNT. An account was given for a total of 99.6 percent of the input TNT (Figure 14).

Yokena clay

In the Yokena clay soil column, 98.1 percent of TNT mass input was eluted as TNT. As with the WES-silt column, the majority of remaining TNT input was eluted as 4A-DNT (4.0 percent). Transformations to 2A-DNT and 2,6-DANT accounted for 1.4 and 0.1 percent of the input TNT, respectively. A small amount of the TNT (0.8 percent) was measured in the Yokena clay soil after the washout period. The residual TNT in the Yokena clay column is indicative of an irreversible sorption process. Overall, an account was given for 104.4 percent of the Yokena clay input TNT (Figure 14).

Ottawa sand

The Ottawa sand soil column effluent trends were similar to the WES-silt and Yokena clay columns, but less transformation occurred. In the Ottawa sand column, 98.1 percent of input TNT was eluted as TNT. As before, most of the remaining TNT was accounted for as eluted 4A-DNT (2.9 percent). Other transformation products (2A-DNT and 2,6-DANT) accounted for 0.6 percent of the input TNT. Overall, an account was given for 101.6 percent of the input TNT (Figure 14).

Blank column

A mass balance indicated that approximately 90 percent of the TNT introduced to the blank column could be accounted for as effluent TNT and TNT remaining in the column. Only 2 percent of the TNT introduced to the blank column could be accounted for as generated transformation products, all of which was in the form of 4A-DNT. Contaminated feed solution was not washed out of the blank column, unlike the other columns, and the mass balance on the blank column was based on nine analyzed effluent samples. Therefore, experimental error is probably responsible for the poor TNT mass balance relative to the other columns.

Transformation Product Distribution

The TNT to 4A-DNT reduction reaction clearly dominated under the experimental conditions investigated. Of the total TNT transformation products produced in the columns, between 73.9 and 83.0 percent was in the form of 4A-DNT (Figure 15). The 2A-DNT made up between 15.3 and 25.0 percent. These results are consistent with those reported by Kaplan and Kaplan (1982a). Kaplan and Kaplan (1982a) found similar ratios of 4A-DNT to 2A-DNT. In the study conducted here, 2,6-DANT made up between 1.1 and 2.6 percent, and the azoxytoluene composite made up between zero and 3.0 percent. However, as stated earlier, the 2,6-DANT BTCs may actually be combinations of 2,6-DANT and 2,4-DANT.

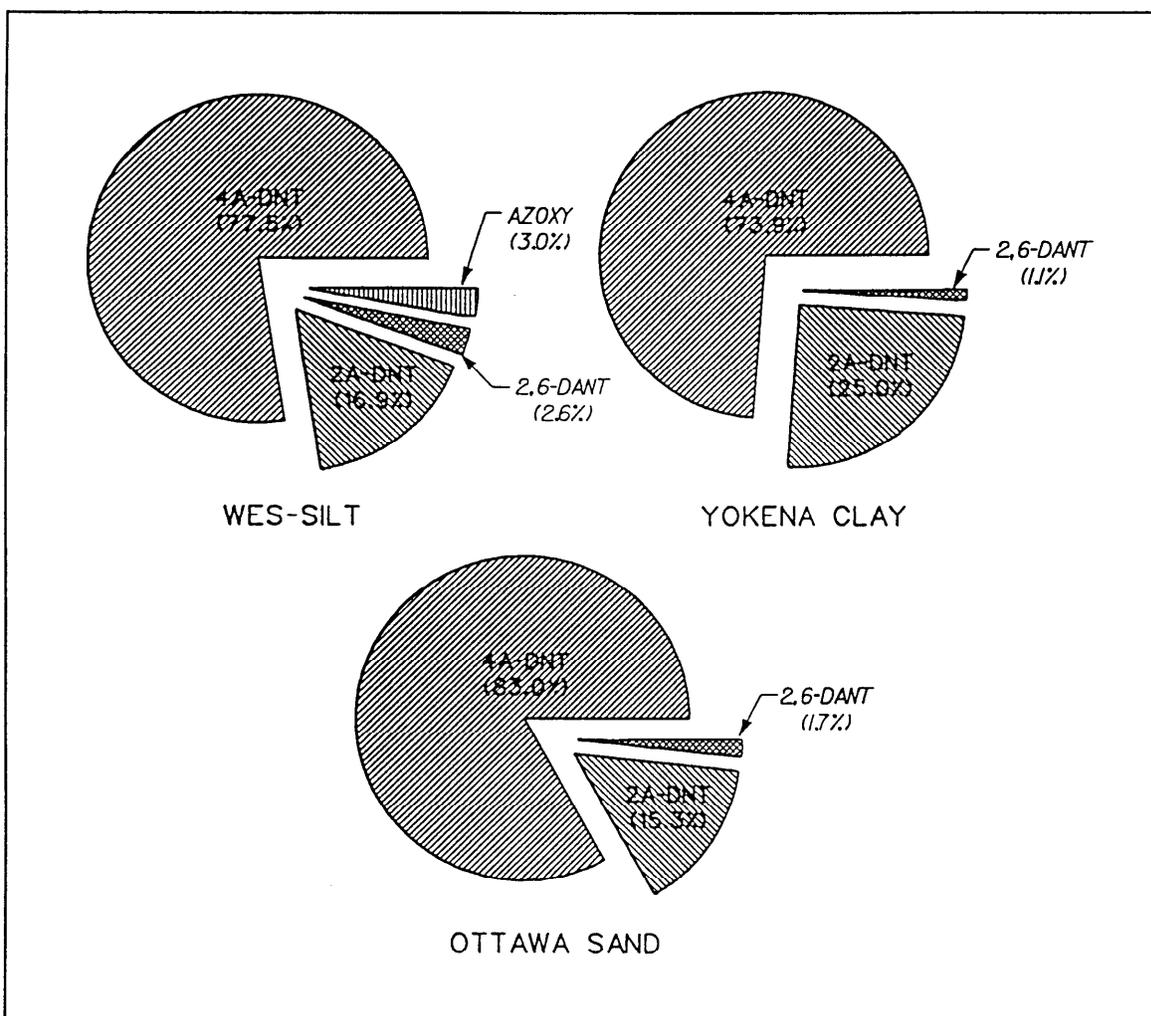


Figure 15. Distribution of total transformation products produced

The breakthrough curves suggest that TNT is transformed into 2A-DNT at a slower rate than TNT is to 4A-DNT. A significantly lower percentage of 2A-DNT was produced relative to 4A-DNT (Figure 16). Compared with 4A-DNT and 2A-DNT, the azoxytoluene composite transformations were insignificant.

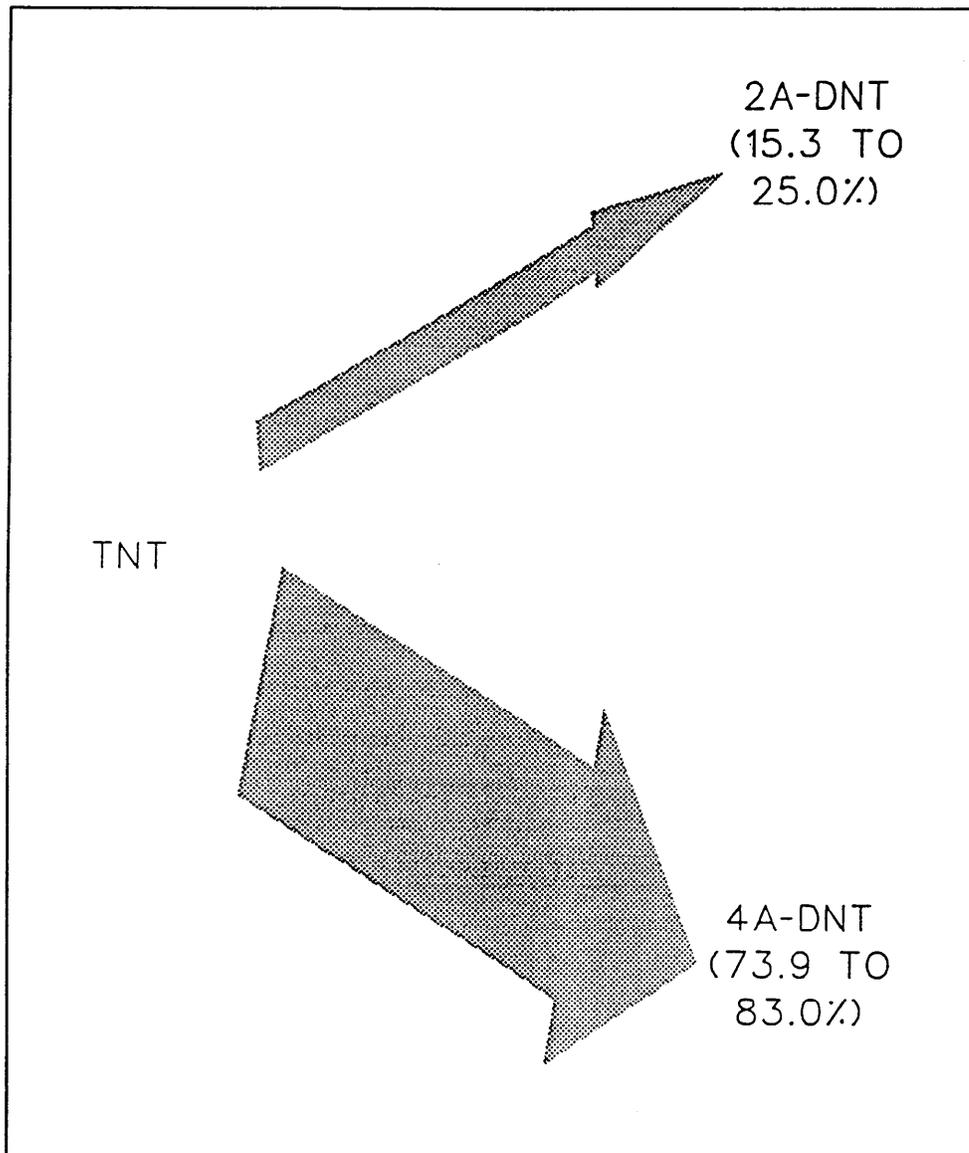


Figure 16. Relative significance of 2A-DNT and 4A-DNT

Effects of Holding Times

Chemical analysis of the holding time samples showed that TNT samples held in amber glass vials under ordinary room temperature and light were stable over a 24-hr period (Table 5). A two-sided t-test (Miller and Freund

Table 5 Holding Time Study Concentrations				
Sample	Elapsed Time, hr	TNT, mg/ℓ	4A-DNT, mg/ℓ	TNB, mg/ℓ
A1	0	66.2	2.18	<MDL ¹
A2	0	65.9	2.19	<MDL
A3	0	65.6	2.15	<MDL
B1	6	65.6	2.17	<MDL
B2	6	65.8	2.13	<MDL
B3	6	65.8	2.15	<MDL
C1	12	66.0	2.15	<MDL
C2	12	66.1	2.15	<MDL
C3	12	66.1	2.15	<MDL
D1	18	66.2	2.15	<MDL
D2	18	66.4	2.14	0.45
D3	18	66.3	2.16	<MDL
E1	24	66.2	2.13	<MDL
E2	24	66.0	2.16	<MDL
E3	24	66.3	2.18	0.45

¹ Minimum detection limit (0.020 mg/ℓ).

1977) indicated that differences in concentrations over the 24-hr period were not statistically significant ($\alpha = 0.01$). This was true for both TNT and 4A-DNT. After 18 to 24 hr, trace quantities of TNB were observed. TNB is a photolysis product of TNT (McGrath, In Preparation). Therefore, TNT undergoes photolysis at room temperature even if the samples are protected by amber glass. However, over a 24-hr period, photolysis is slight and did not statistically change the concentration of the TNT.

Complete-Mix Analytical Model

A complete-mix model was developed for the thin-disk breakthrough curves in order to elucidate the TNT transport process. The model used here is similar to one derived by Skopp and McCallister (1986). In a complete-mix model, hydrodynamic dispersion is neglected. The concentration inside the cell is assumed to be equal to the concentration exiting the cell.

A linear equilibrium sorption model was adopted for this study. This sorption model is attractive because of its mathematical simplicity and because

nonlinear sorption is not needed to fit the data obtained in this study. A first-order reaction expression was assumed for these experiments since a specific rate law for TNT degradation has not been established.

From conservation of mass (Equation 1) and a linear sorption isotherm (Equation 2), Equation 3 is derived for the initial condition where $C(0) = 0$ (see Appendix C for a complete derivation).

$$QC_o - QC - \mu nVC = nV \frac{dC}{dt} + \rho V \frac{dS}{dt} \quad (1)$$

$$S = K_d C \quad (2)$$

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - e \left(- \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right) \right] \quad (3)$$

where

C = effluent solute concentration, mg/l

C_o = influent solute concentration, mg/l

θ_H = hydraulic residence time, hr

μ = transformation rate constant, hr⁻¹

n = porosity

ρ = bulk density, kg/l

K_d = distribution coefficient, l/kg

Equation 3 is the basic equation describing reactive, sorptive contaminant transport through a complete-mix soil system. This equation has several practical limitations. For instance, difficulties arise in taking measurements directly at the soil layer boundary. In general, columns have an inlet and an outlet associated with them, which are usually not part of the main model. Therefore, the solute must first travel through the inlet portion of the column before coming into contact with the soil layer and, upon leaving the soil layer, must travel through an outlet before being collected for analysis. In traditional columns, the inlet and outlet travel time is usually much smaller than the residence time in the soil and is often neglected. With thin-disk columns, the inlet and outlet residence times are significant and therefore must be considered.

In order to determine the total inlet-outlet (inlet plus outlet) residence time (t_o), a chloride tracer study was performed on a blank column. It was assumed that both the inlet and outlet could be modeled as plug flow and that sorption and degradation were not occurring in the inlet or outlet. Therefore, the inlet-outlet residence time (t_o) was measured with the tracer study, and the model was modified to account for this travel time.

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

where

t_o = inlet-outlet residence time, hr

Equation 4 describes solute travel through the complete thin-disk apparatus during the step input of the feed solution.

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

$$C = C_{t_1} e^{\left(\left[\frac{1}{\theta_H} + \mu n \right] \left[\frac{1}{n + \rho K_d} \right] (t - t_1) \right)} \quad (5)$$

where

C_{t_1} = effluent concentration at time t_1

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

It is sometimes useful to represent contaminant transport through porous media as a function of the number of pore volumes eluted instead of a function of time. In order to do this, the following relationship is used:

$$T = \frac{ut}{L} \quad (6)$$

where

T = pore volumes eluted

L = column length, cm

u = average pore water velocity, cm/s

Parameter Estimation

Equations 4 and 5 were used to fit the TNT breakthrough curves. Good fits were obtained for each column (Figure 17) by visual inspection. First-order TNT transformation rate constants (μ) and TNT linear equilibrium distribution coefficients (K_d) for each soil were estimated from the best-fitting model parameters (Table 6).

WES-silt

The WES-silt TNT breakthrough curve was described well by the analytical model (Figure 17). Slight discrepancies between the data and the model occurred at the beginning of breakthrough and near the end of washout. The model predicted earlier breakthrough and a shorter washout tail.

A transformation rate constant (μ) of 0.025 hr^{-1} was estimated for the WES-silt TNT breakthrough curve. This rate is fast compared with most contaminants in groundwater. Howard et al. (1991) estimate a transformation rate constant of 0.001 hr^{-1} for TNT in unacclimated anaerobic groundwater. Their estimate is based on scientific judgment rather than experimental results. Myers et al. (In Preparation) estimate a TNT transformation rate constant for WES-silt that is approximately an order of magnitude larger than the value reported here.

The estimated WES-silt TNT distribution coefficient (K_d) was 4.5 l/kg . However, the data in this study do not provide sufficient evidence that TNT sorption is actually governed by linear equilibrium sorption. It may be that K_d is only an adjustable parameter that can be used to obtain a better curve fit.

Yokena clay

The Yokena clay TNT curve fit (Figure 17) was similar to the WES-silt curve fit. Again, the model predicted slightly earlier breakthrough and a shorter tail than the observed data. However, the majority of the data was described very well.

A transformation rate constant of 0.013 hr^{-1} was estimated for the Yokena clay TNT. This is roughly one-half of the value estimated for the WES-silt

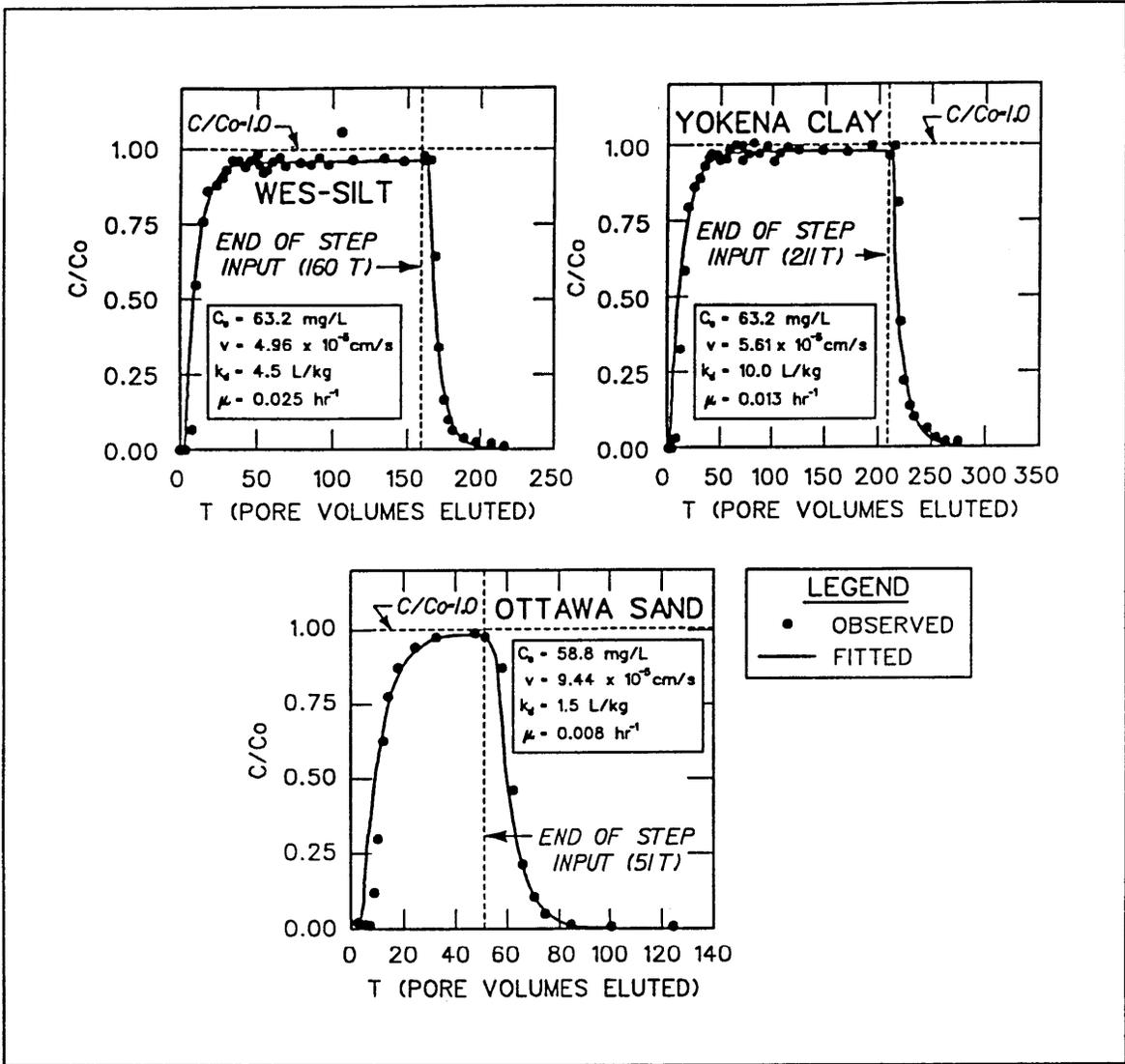


Figure 17. Normalized observed and fitted TNT breakthrough curves

Table 6 Fitted Transformation and Sorption Parameters for TNT		
Column	μ^1 , hr ⁻¹	K_d^2 , l/kg
WES-silt	0.025	4.5
Yokena clay	0.013	10.0
Ottawa sand	0.008	1.5

¹ First-order transformation rate constant.
² Linear equilibrium distribution coefficient.

soil. The Yokena clay was higher than the WES-silt in both cation exchange capacity (CEC) and percent total organic carbon (TOC). For Yokena clay, Myers et al. (In Preparation) report a first-order transformation rate constant that is an order of magnitude higher than the value reported here. The difference in first-order constants between the two experiments is possibly due to differences in redox conditions. Although redox conditions were not monitored in either experiment, the soil columns used by Myers et al. (In Preparation) were probably more anaerobic than the thin disks used in this study since the hydraulic residence times in the Myers et al. (In Preparation) columns were greater than in the thin disks.

The estimated Yokena clay TNT distribution coefficient was 10 l/kg . This value was higher than the one for the WES-silt soil, which would be expected since the Yokena clay is higher in TOC and CEC than the WES-silt soil.

Ottawa sand

The Ottawa sand TNT curve fit (Figure 17) is similar to the previous column fits in that there is some discrepancy between model and observed data at the beginning of breakthrough. However, the model fit the other portions of the data well, even near the end of washout.

The estimated transformation rate constant for the Ottawa sand breakthrough curve was 0.008 hr^{-1} . This value is lower than that for the WES-silt and Yokena clay soils, as would be expected since the Ottawa sand is over 99-percent quartz. Myers et al. (In Preparation) estimate a TNT transformation rate constant for Ottawa sand that is approximately half of the value reported here.

The estimated Ottawa sand TNT distribution coefficient was low ($1.5 \text{ } l/kg$).

4 Conclusions and Recommendations

Conclusions

Although highly simplified, the complete-mix model in conjunction with thin-disk elution curves provides a physically based theoretical/empirical framework for investigating TNT transformation/sorption simultaneously. The thin-disk soil columns provided well-behaved TNT breakthrough curves that could be simulated closely using a complete-mix model with first-order decay and linear equilibrium sorption. Excellent mole balances were obtained (100 ± 5 percent), making interpretation of transformation data reliable.

TNT transformation was observed in all three soils. TNT transformation products were primarily reduction products resulting from transformation of nitro groups to amino groups. Transformation of TNT to 4A-DNT was favored over transformation of TNT to 2A-DNT.

The WES-silt and Yokena clay soils did not show evidence of an exhaustible soil constituent responsible for TNT transformation. The TNT breakthrough curves for these soils suggest that transformations were primarily biotic, biologically mediated, or that an abiotic soil constituent responsible for TNT transformations was constantly renewed.

Agreement between observed and model breakthrough curves suggests that simple formulations of sorption and reaction in transport models for TNT will capture the main effects of these processes, even at high solution concentrations for the conditions and soils investigated. Compared with sorption, transformation is a very significant process affecting TNT transport in soils.

TNT samples left unpreserved in amber glass vials at normal room temperature and light show no statistically significant change in TNT concentration over a 24-hr period. Photolysis could present a problem if TNT samples are not preserved within 24 hr of collection.

Recommendations

Many questions regarding TNT transport in soils remain to be answered. The following aspects of TNT transport in the subsurface need to be addressed:

- The influence of redox conditions on TNT transformation rates and pathways needs to be studied systematically before TNT migration through soils can be fully understood.
- An improved understanding of the environmental controls (e.g., Eh, pH, soil composition, and microbial activity) on TNT reaction rates is needed to explain why TNT rapidly transforms in virgin laboratory soil columns, yet remains in the soil profile at many sites.
- More work is needed to determine the specific soil parameters important in TNT reduction.

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Appendix A

Feed Solution Concentrations

Table A1														
Day	TNT	HMX	RDX	TNB	DNB	TETRYL	AZOXY	4A-DNT	2A-DNT	2,6-DNT	2,4-DNT	3,5-DNA	2,6-DANT	2,4-DANT
WES-Silt and Yokena Clay Feed Solution Concentrations, mg/l														
0	64.4	2.50	33.7	0.258	<0.020	<0.050	<0.100	0.154	2.26	<0.020	0.024	0.053	<0.100	<0.200
5	64.6	2.49	33.9	0.265	<0.020	<0.050	<0.100	0.197	2.27	<0.020	0.028	0.050	<0.100	<0.200
7	62.9	2.45	33.3	0.234	<0.020	<0.050	<0.100	0.068	2.19	<0.020	0.031	0.053	<0.100	<0.200
10	62.6	2.47	33.5	0.250	<0.020	<0.050	<0.100	0.157	2.21	<0.020	0.028	0.056	<0.100	<0.200
15	62.6	2.46	34.0	0.296	<0.020	<0.050	<0.100	0.166	2.22	<0.020	0.028	0.055	<0.100	<0.200
17	62.0	2.45	33.4	0.429	<0.020	<0.050	<0.100	0.101	2.25	<0.020	0.030	0.052	<0.100	<0.200
18	60.8	2.40	32.8	0.349	<0.020	<0.050	<0.100	0.162	2.20	<0.020	0.029	0.053	<0.100	<0.200
Ottawa Sand Feed Solution Concentrations, mg/l														
0	59.3	2.20	31.2	0.180	<0.020	<0.050	<0.100	0.129	1.98	<0.020	0.026	0.053	<0.100	<0.200
3	58.3	2.17	30.5	0.185	<0.020	<0.050	<0.100	0.065	1.95	<0.020	0.025	0.049	<0.100	<0.200
5	58.0	2.16	30.6	0.194	<0.020	<0.050	<0.100	0.144	1.97	<0.020	0.025	0.049	<0.100	<0.200

Appendix B

Chemical Abbreviations

TNT	2,4,6-trinitrotoluene
RDX	2,3,5-trinitro-1,3,5-triazine
HMX	oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
DNB	1,3-dinitrobenzene
TNB	1,3,5-trinitrobenzene
4A-DNT	4-amino-2,6-dinitrotoluene
2A-DNT	2-amino-4,6-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
2,4-DNT	2,4-dinitrotoluene
3,5-DNA	3,5-dinitroaniline
2,6-DANT	2,6-diamino-4-nitrotoluene
2,4-DANT	2,4-diamino-6-nitrotoluene
AZOXY	composite of 4,2',6,6'-tetranitro-2,4'-azoxytoluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 4,4',6,6'- tetranitro-2,2'-azoxytoluene
TETRYL	methyl-2,4,6-trinitrophenylnitramine

Appendix C

Thin-Disk Model Derivation

Assuming first-order degradation, the conservation of mass in a complete-mix reactor can be written for a reactive contaminant traveling through saturated porous media with the initial condition that $C(0) = 0$:

$$QC_o - QC - \mu nVC = nV \frac{dC}{dt} + \rho V \frac{dS}{dt} \quad (C1)$$

where

Q = flow rate, cm^3/hr

C_o = influent TNT solution concentration, mg/ℓ

C = effluent TNT solution concentration, mg/ℓ

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

n = porosity, dimensionless

V = disk volume, cm^3

ρ = bulk density, mg/ℓ

S = TNT sorbed concentration, mg/kg

t = time, hr

A linear sorption isotherm is assumed:

$$S = K_d C \quad (C2)$$

where

K_d = distribution coefficient, l/kg

Substituting for S :

$$nV \frac{dC}{dt} + \rho VK_d \frac{dC}{dt} = QC_o - QC - \mu nVC$$

Dividing by V and using the relationship, $\theta_H = V/Q$:

$$(n + \rho K_d) \frac{dC}{dt} = \frac{C_o}{\theta_H} - \frac{C}{\theta_H} - \mu nC$$

where

θ_H = hydraulic residence time, hr

Factoring out C and rearranging:

$$\frac{dC}{dt} (n + \rho K_d) + \left(\frac{1}{\theta_H} + \mu n \right) C = \frac{C_o}{\theta_H}$$

Dividing by $(n + \rho K_d)$:

$$\frac{dC}{dt} + \left(\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} \right) C = \frac{C_o}{\theta_H (n + \rho K_d)}$$

Solve the differential equation using an integrating factor (I.F.):

$$I.F. = \exp \left[\int \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} dt \right] = \exp \left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right]$$

$$C \exp \left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right] = \int_0^t \left[\frac{C_o}{\theta_H (n + \rho K_d)} \exp \left(\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right) dt \right]$$

Solving the integral:

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

The equation for solute transport becomes:

$$C = \left(\frac{C_o}{1 + \theta_H \mu n} \right) \left[1 - \exp \left(- \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right) \right] \quad (C3)$$

Adjust the equation to account for the plug flow inlet and outlet:

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - \exp \left(- \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} (t - t_o) \right) \right] \quad (C4)$$

where

t_o = inlet-outlet residence time, hr

Equation C4 is the model equation for TNT transport through a thin disk for a step input condition at the inlet. After the step input, the model is modified for the condition of $C = 0$ at the inlet as follows:

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[\exp \left(- \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} (t - t_1) \right) - \exp \left(- \frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} t \right) \right] \quad (C5)$$

where

t_1 = time of step input plus t_o , hr

The following relationship is used to convert time to pore volumes eluted in Equations C4 and C5:

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

where

T = pore volumes eluted

L = disk length, cm

u = average pore water velocity, cm/hr

REPORT DOCUMENTATION PAGE

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13 ABSTRACT (Maximum 200 words) Remediation and containment efforts are underway for 2,4,6-trinitrotoluene (TNT) contamination in the subsurface at many Army installations. Contaminant transport modeling, a time and cost-effective tool for comparing various remediation alternatives, is hampered by lack of information on the significance of TNT transformation and sorption in soils. This study was conducted to estimate TNT transformation and sorption parameters from breakthrough curves (BTCs) for three major soil classes—sand, silt, and clay. An additional objective was to determine if soil transformation of TNT is an exhaustible process. Thin-disk soil columns (0.32-cm soil length) were used to obtain TNT BTCs. Effluent TNT and TNT transformation product concentrations were analyzed as a function of pore volumes eluted. The thin-disk columns produced symmetrical TNT BTCs for each soil. The BTCs were modeled assuming complete-mix, first-order transformation, and linear equilibrium sorption. This model produced excellent curve fits, with only slight discrepancies occurring near the beginning and end of the BTCs. Excellent mole balances were observed for each soil. <div style="text-align: right;">(Continued)</div>			
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Over 99 percent of the input TNT could be accounted for either as TNT in the effluent, transformed TNT in the effluent, or residual TNT remaining in the soil columns at the end of the breakthrough experiments.

First-order transformation rate constants and linear equilibrium distribution coefficients were estimated from fitted BTCs for each soil. TNT transformation rate constants ranged from 0.008 to 0.025 hr⁻¹, and TNT distribution coefficients ranged from 1.5 to 10.0 l / kg. Silt showed the greatest tendency for transformation, and clay showed the greatest tendency for sorption.

TNT transformation products were primarily reduction products resulting from transformation of nitro groups to amino groups. Reduction at the 4-carbon position was favored over reduction at the 2- or 6-carbon position.

None of the TNT BTCs showed evidence of an exhaustible soil constituent responsible for TNT transformation, suggesting that the observed transformations were primarily biotic, or at least biologically mediated.