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# Sorption–Desorption and Transport of TNT and RDX in Soils

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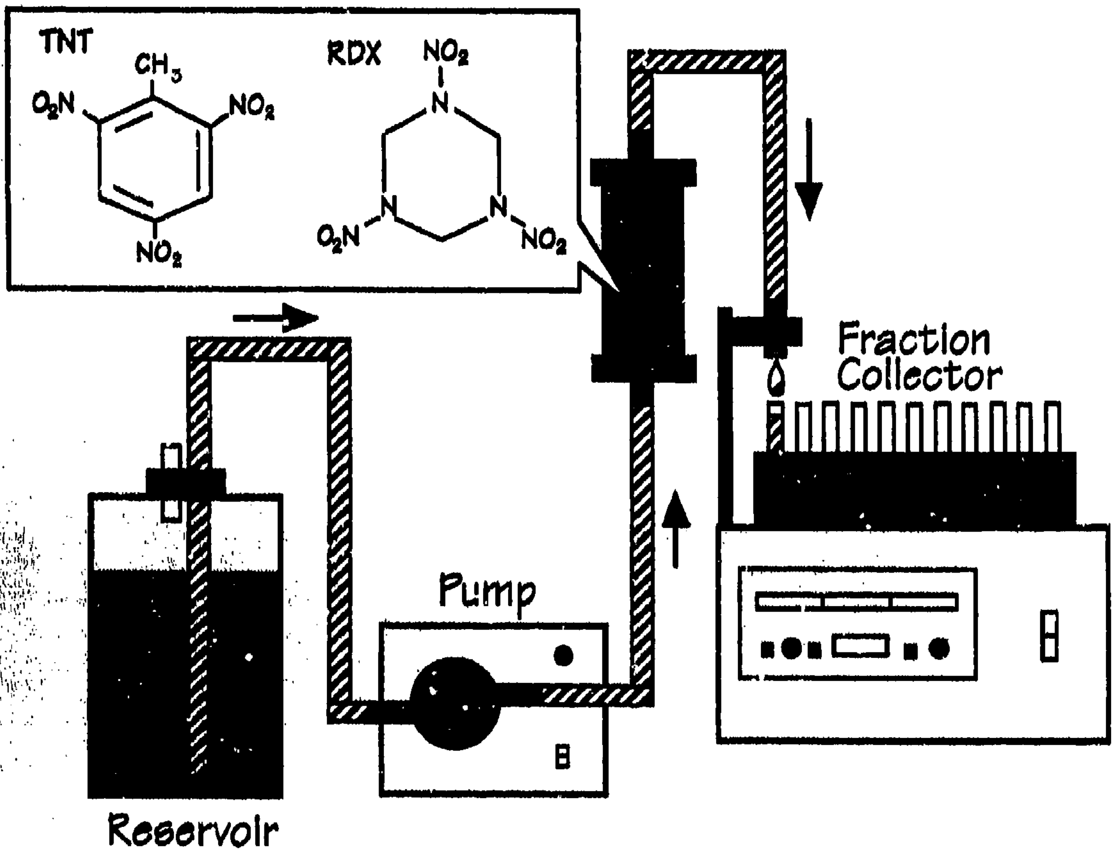
May 1994



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## *Abstract*

Batch and miscible-displacement experiments were conducted to determine the extent of adsorption–desorption and transport of 2,4,6-trinitrotoluene (TNT) and 2,3,5-trinitro-1,3,5-triazine (RDX) in soils. A reference bentonite clay, contaminated (Kolin) soil from the Louisiana Army Ammunition Plant, and two uncontaminated soils were used. The TNT isotherm for bentonite clay was described equally well using linear, Freundlich, Langmuir and modified Langmuir models. TNT adsorption and desorption isotherms showed a lack of hysteric behavior, with TNT retention as a fully reversible mechanism. Transport results from bentonite clay columns indicated that TNT was a highly mobile contaminant and fully conservative in the presence of methanol as the background solution. Mobility of TNT was strongly retarded, with some 50% of the applied TNT retained in the bentonite clay column when 0.005-M $Ca(NO_3)_2$ was the background solution. Transport results in Norwood (fine silty) soil columns revealed that TNT was strongly retained in this low-organic-matter and low-clay-content soil. The use of a transport model with either Freundlich or linear retention and an irreversible mechanism predicted the TNT transport data well. Poor predictions were obtained when model parameters based on batch retention data were used. Reasons for model failure may be attributable to TNT sorption-kinetics and retention because of diffusion into clay lattices. Transport results indicated high mobility of RDX with limited retardation, which is consistent with release and transport data from the contaminated soil.

*Cover: Experimental setup.*

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *Standard Practice for Use of the International System of Units,* published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

## PREFACE

This report was prepared by Dr. H. Magdi Selim, Professor of Soil Physics at Louisiana State University, Baton Rouge, Louisiana, and Dr. Iskandar K. Iskandar, Chief of Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. This work was carried under out the *Strategic Environmental Research Development Program (SERDP), Fate and Transport in Seasonally Frozen Soils and Discontinuous Permafrost,* and the Department of Defense RDT&E Research Program.

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# Sorption–Desorption and Transport of TNT and RDX in Soils

H. MAGDI SELIM AND ISKANDAR K. ISKANDAR

## INTRODUCTION

When the Superfund Program was enacted in 1980, a 1.6-billion-dollar trust fund was authorized for the cleanup of the worst hazardous waste sites. However, in 1986, the Environmental Protection Agency (EPA) estimated the need for five times this amount, and an 8.5-billion-dollar fund was approved. In addition, the Department of Defense (DOD) estimated 24.5-billion dollars for cleanup of DOD sites, while the Department of Energy estimated at least 30-billion dollars for these sites for the next 5 years. EPA (1993) estimated that the entire cost for cleanup will exceed 1-trillion dollars.

One reason for this uncertainty in the cost of cleanup is the lack of knowledge about the environmental fate and toxicity of pollutants such as organics, heavy metals, Army-unique compounds and radioactive nuclides, and their effects on terrestrial and aquatic life forms as well as on humans. While cleanup is required by regulations and statutes, there are no environmental criteria or health advisories available for the military materials of interest. The ability to make economical and timely assessments of the effect of these materials on the environment and subsequent remedial cleanup action is hindered by our inability to predict the forms and amounts of these contaminants in soil, groundwater and plants.

To successfully assess and repair sites contaminated with explosives, we need to quantify the mechanisms governing the retention and transport of these contaminants through the soil to the groundwater. Previous investigations of the fate of explosive contaminants in the soil environment did not emphasize the problem of their potential mobility to the groundwater. The ability to predict such mobility requires knowledge of the retention processes influencing the fate of explosive contaminants during transport in the soil.

Several studies by scientists at CRREL have been devoted to the fate of explosive contaminants in soils. These efforts include the development of analytical methodologies for analyzing explosive contaminants such as TNT as well as DNT, RDX and HMX. Results of this work are available in several publications, including those of Jenkins et al. (1984, 1986, 1988) and Cragin et al. (1985). Extraction techniques for munitions residues in soils have been recently developed by Jenkins and Leggett (1985) and Jenkins and Grant (1987). Palazzo and Leggett (1986) among others showed that TNT and several of its transformation products are toxic to fish and several aquatic fauna.

The retention (adsorption–desorption) characteristics of TNT, DNT, RDX and HMX on pure clay (Wyoming bentonite) were investigated by Leggett (1985). He found that, for all military explosives tested, retention reactions were rapid and fully reversible. He examined the reversibility assumption by desorption of the solute after apparent equilibrium was attained. In addition, sorption isotherms appeared to be linear for RDX and HMX, whereas he observed a moderate nonlinearity for TNT and DNT. Surface sorption was probably the dominant mechanism on the clay studied. Moreover, these contaminants did not degrade in such pure clays, since irreversible behavior was not observed, and thus the total of the sorbed amounts was released. Similarly, Pennington and Patrick (1990) found that TNT was only slightly resistant to desorption. In fact, after three sequential desorptions over 12 hours, some 88 to 93% of adsorbed TNT was released.

The above papers are some of the few that attempted to quantify the retention behavior of TNT and other explosive contaminants in soils and in pure clay. Other researchers have proposed mechanisms governing the fate of TNT and its transformation products. Burlinson (1980) showed that photo-decomposition is the process forming 1,2,5-trinitrobenzene in natural waters. Kaplan and Kaplan (1982) proposed microbial transformation as the dominant mechanism causing the reduction of nitro groups to amino groups.

The primary objective of this investigation is to quantify the potential mobility of TNT (2,4,6-trinitrotoluene) and RDX (2,3,5-trinitro-1,3,5-triazine) in soils. To achieve this, we focused on describing the mobility and retention of TNT and RDX in a pure montmorillonite clay, in two uncontaminated soils, and in contaminated soils from the Louisiana Army Ammunition Plant. Specifically, we attempted to quantify the retention properties of TNT and RDX based on their transport (miscible displacement) behavior in the montmorillonite clay and soils. We also tested the applicability of mechanistic models that incorporate the retention processes with the convection–dispersion transport equation.

## TRANSPORT MODELS

The classical convective–dispersive equation, which is generally accepted for the description of dissolved chemicals in the soil solution (Selim 1992), is

$$\Theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \Theta D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \Sigma_i \Psi_i \quad (1)$$

where

$C$ = solute concentration in solution (µg/mL)
$\Theta$ = soil water content (cm$^3$/cm$^3$)
$t$ = time (hr)
$z$ = depth (cm)
$\rho$ = soil bulk density (g/cm$^3$)
$D$ = hydrodynamic dispersion coefficient (cm$^2$/hr)
$v$ = Darcy's water flux density (cm/hr)
$S$ = solute concentration associated with the solid phase of the soil (µg/g soil)
$\Psi_i$ = rates of solute removal (or supply) from soil solution (µg/cm$^3$ • hr) and not included in $S$.

We consider the ($\partial S/\partial t$) term as a fully reversible process between the solution and the solid phases, while $\Psi_i$ are rates of irreversible reactions, i.e., transformations. Processes governing the interactions of individual solute species need to be identified if prediction of the fate of contaminants in the soil using the convection–dispersion equation (eq 1) is sought. The reversible term ($\partial S/\partial t$) is often used to describe the rate of sorption or exchange reactions with the solid matrix. Sorption or exchange has been described by either instantaneous equilibrium or a kinetic reaction, where concentrations in solution and sorbed phases vary with time; reviews of various forms of equilibrium and kinetic models are given by Murali and Aylmore (1983). Recently, Selim (1992) presented a review of significant features of sorption-exchange reactions of the equilibrium and kinetic type. Linear, Freundlich, and one- and two-site Langmuir equations are most commonly used to describe equilibrium reactions.

The Freundlich equation is perhaps the simplest approach for quantifying the behavior of retention of reactive solute with the soil matrix. It is certainly one of the oldest of the nonlinear sorption equations and has been used widely to describe solute retention by soils (Helfferich 1962, Travis and Etnier 1981, Murali and Aylmore 1983, Sposito 1984). The Freundlich equation is

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

where

$S$ = amount of solute retained by the soil (µg/g)
$C$ = solute concentration in solution (µg/mL)
$K_d$ = distribution coefficient (cm$^3$/g)
$b$ = dimensionless (typically $b < 1$).

The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction. For a $b$ of unity, the Freundlich equation is often referred to as the linear retention equation.

Although the Freundlich equation has been rigorously derived (Sposito 1980), the goodness-of-fit of the Freundlich equation to solute retention data does not provide definitive information about the actual processes involved, since the equation is capable of describing data irrespective of the actual retention mechanism. Often complex retention processes can at least in part be described by relatively simple models such as the Freundlich equation. Therefore, the Freundlich parameters $K_d$ and $b$ are best regarded as descriptive parameters in the absence of independent evidence concerning the actual retention mechanism. Pennington and Patrick (1990) found that best-fit Freundlich $b$ values were consistently greater than 1 for TNT in a wide range of soils. Such a finding indicates a lack of sorption maxima for their range of concentrations.

The Langmuir isotherm is the oldest and most commonly encountered in soils. It was developed to describe the adsorption of gases by solids where a finite number of adsorption sites in the surface is assumed (Langmuir 1918). As a result, a major advantage of the Langmuir equation over linear and Freundlich types is that a maximum sorption capacity is incorporated into the formulation of the model, which may be regarded as a measure of the amount of available retention sites on the solid phase. The standard form of the Langmuir model is

$$\frac{S}{S_{max}} = \frac{\omega C}{1 + \omega C} \tag{3}$$

where $\omega$ and $S_{max}$ are adjustable parameters. Here $\omega$ ($cm^3/\mu g$) is a measure of the bond strength of molecules on the matrix surface and $S_{max}$ ($\mu g/g$ soil) is the maximum sorption capacity or total amount of available sites per unit soil mass. In an attempt to classify the various shapes of sorption isotherms, Sposito (1984) recognized that the Langmuir isotherm, or L-curve isotherm, is the most commonly used. The Langmuir sorption isotherm has been used extensively by scientists for several decades. Travis and Etnier (1981) provided a review of studies where the Langmuir isotherm was used to describe P retention for a wide range of soils. Moreover, Langmuir isotherms were used successfully to describe Cd, Cu, Pb and Zn retention in soils. Leggett (1985) and Pennington and Patrick (1990) successfully used the Langmuir approach to describe batch results of TNT retention on a reference clay and on soils having a wide range of properties.

Multisite or multireaction models deal with the multiple interactions of one species in the soil environment. Such models are empirical and are based on the assumption that a fraction of the total sites is highly kinetic, whereas the remaining sites interact slowly or instantaneously with the chemicals in the soil solution (Selim et al. 1976, Jardine et al. 1985). Nonlinear equilibrium (Freundlich) was assumed to describe retention reactions associated with equilibrium sites, whereas first- or $n^{th}$-order kinetic reactions were the mechanisms associated with the kinetic sites. Such a two-site approach proved successful in describing observed extensive tailing of breakthrough results.

Another two-site approach was proposed by Theis et al. (1988) for Cd mobility and adsorption on geothite. They assumed that the nature of reactions is governed by second-order kinetic reactions. The reactions were assumed to be consecutive where the second reaction was irreversible. Amacher et al. (1988) developed a multireaction model that includes concurrent and concurrent–consecutive processes of the nonlinear kinetic type. The model was capable of describing the retention behavior of Cd and Cr(VI) with time for several soils. In addition, the model predicted that a fraction of these heavy metals was irreversibly retained by the soil. Recently, Amacher et al. (1990) concluded that the multireaction model could also successfully describe adsorption of Hg for several soils.

In the Multi-Reaction and Transport Model (MRTM) of Selim et al. (1990), a solute species was assumed to be present in the soil solution phase ($C$) and in four phases representing solute retained by the soil matrix as $S_e$, $S_1$, $S_2$ and $S_{irr}$. The model further assumed that $S_e$, $S_1$ and $S_2$ were in direct contact with the solution phase and were governed by concurrent type reactions. Here, $S_e$ represents the amount of solute that is sorbed reversibly and is in equilibrium with $C$ at all times. The governing equilibrium retention–release mechanism was that of the nonlinear Freundlich type as discussed previously.

The retention–release reactions associated with $S_1$ and $S_2$ had to be in direct contact with $C$ to be governed by reversible processes of the (nonlinear) kinetic type

$$S_e = K_d C^b \tag{4}$$

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1 \tag{5}$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2 \tag{6}$$

where $k_1$ to $k_4$ are the associated rate coefficients ($hr^{-1}$). These two phases ($S_1$ and $S_2$) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. Moreover, these phases may be characterized by their sorption and release kinetics to the soil solution and thus are susceptible to leaching in the soil. In addition, primary differences between these two phases not only lie in the difference in their kinetic behavior but also in the degree of nonlinearity, as indicated by the parameters $n$ and $m$. The multireaction model also considers irreversible solute removal via a retention sink term $Q$ to account for irreversible reactions such as precipitation–dissolution and mineralization–immobilization, among others. We expressed the sink term as a first-order kinetic process

$$Q = \rho \frac{\partial S_{irr}}{\partial t} = k_s \Theta C \qquad (7)$$

where $k_s$ is the associated rate coefficient ($hr^{-1}$).

We incorporated the above retention mechanisms into the classical convection–dispersion equation (eq 1) to predict solute retention as governed by the multireaction model during transport in soils (Selim et al. 1989). The initial and boundary conditions used were

$$C = 0, \qquad t = 0, \qquad 0 \le z \le L \qquad (8)$$

$$S_e = S_1 = S_2 = 0, \qquad t = 0, \qquad 0 \le z \le L \qquad (9)$$

$$vC_0 = -D \frac{\partial C}{\partial z} + vC, \quad z = 0, \qquad t < T \qquad (10)$$

$$0 = -D \frac{\partial C}{\partial z} + vC, \qquad z = 0, \qquad t \ge T \qquad (11)$$

$$\frac{\partial C}{\partial z} = 0, \qquad z = L, \qquad t \ge 0 \qquad (12)$$

where it is assumed that a solute solution of a concentration ($C_0$) is applied to a soil column having a length $L$ for a given duration $T$ and was thereafter followed by a solute-free solution. The numerical solution for the multireaction and transport model is documented in the program MRTM and is given in Selim et al. (1990).

## EXPERIMENTAL

### Soils and reagents

A contaminated soil was collected from the Louisiana Army Ammunition Plant in north Louisiana. It appeared to be disturbed and mixed; thus, it was not possible to exactly identify soil layers. An uncontaminated (original) soil was also sampled about 300 m from the contaminated site. The surface (0–30 cm) horizon of the uncontaminated (original) soil was sampled to serve as a blank (a check) for soil physical and chemical properties in comparison to the contaminated sample. Two subsamples from the contaminated and uncontaminated soils were forwarded to CRREL for complete analysis of total TNT and RDX contents as well as other explosive contaminants. The contaminant analyses revealed that no TNT, RDX or other contaminants were present in the uncontaminated soil. The soil at the site is Kolin soil (fine-silty, siliceous, Thermic Glossaquic Paleudalfs). Further details may be obtained from the document entitled *Soil Survey of Caddo Parish, Louisiana* (USDA-SCS 1980) and from Amacher et al. (1989).

A reference clay was also used in this study: SWy-1 montmorillonite (Crook County, Wyoming, bentonite) obtained from the Source Clays Repository, University of Missouri. Sposito et al. (1983a,b) and Gaston and Selim (1990) have presented extensive data for ion exchange (of Ca, Mg and Na) on pure montmorillonite fractionated from this material. Most significant is Leggett's (1985) extensive work on the adsorption–desorption of TNT and RDX on pure montmorillonite clay, which indicated fully reversible TNT and RDX retention mechanisms. Based on this knowledge of TNT and RDX in this reference clay, we conducted transport and adsorption–desorption experiments to determine the mobility of these contaminants in soils. Our primary objective was to identify the sorption–release mechanisms of TNT on 2:1 montmorillonitic clays. To predict the potential mobility of TNT and RDX in soils under field conditions, we also evaluated the extent of time-dependent or kinetic behavior of the retention mechanisms. Mineral compositions of the less than 2-µm fractions of the reference clay material were determined from X-ray diffractograms of oriented slide mounts after K-saturation with heat treatments at 300 and 550°C and Mg-saturation with glycolation. X-ray analyses were run from 2–32° 2θ, using Cu-Ka radiation with a vertical goniometer equipped with a 2θ compensator slit and graphite monochronometer. Estimates of composition were based on areas of characteristic diffraction peaks—it was 99% montmorillonite.

A Norwood soil was also chosen for this study for several reasons. This soil is predominant in the Red River valley, which is adjacent to the contaminated site near the Louisiana Army Ammunition Plant. Norwood soil is classified as fine silty, mixed, calcareous, Thermic and Typic Udifluvent with 79% sand, 18% silt and 3% clay. In addition, previous work on this soil indicates that it is of low organic matter content (0.32%), high pH (7.4) and low cation exchange capacity (4.1 $cmol_c/kg$), and it is highly permeable to water infiltration with a low water retention capacity (Amacher et al. 1988, Buchter et al. 1989). The adsorption behaviors of several heavy metals in this soil have been recently documented by Buchter et al. (1989). This soil is a worst case, owing to its high leaching capability and thus the potential for contamination of the groundwater.

Analytical standards for TNT were prepared from a reagent chemical purchased from Eastman Kodak. The RDX used was provided by CRREL scientists. Both RDX and TNT were dried to a constant weight over dry calcium chloride in a desiccator in the dark. Standards were prepared in methanol for TNT and acetonitrile and methanol for RDX. A combined analyte calibration standard was prepared in methanol. Volumetric flasks were stoppered, and the flask closures were wrapped with parafilm to minimize evaporation of solvent. All standards were stored in the dark at 4°C.

All analyses for TNT and RDX in soil water samples were carried out using HPLC methodology as established by CRREL. Briefly, all HPLC analyses were conducted using an IBM LC/9533 Ternary Gradient Liquid Chromograph with an IBM LC/9523 variable-wavelength UV detector set at a wavelength ($\lambda$) of 244 nm. A Rheodyne 7125 injector valve with a 100-$\mu$L sample loop was used and samples were introduced to the column by overfilling the loop. A Supelco 25-cm × 4.6-mm i.d. (5-$\mu$m) reversed-phase column (LC-18) was used with an eluent of methanol and water (50:50) at a flow rate of 1.5 mL/min.

A series of standards was prepared in methanol from the combined analyte calibration standard. The concentrations included 0.5, 1, 2, 5, 10 and 20 mg/L of RDX and TNT. Initial calibration was done by analyzing these concentrations in duplicate and in random order. The calibration curve was determined to be linear, with the slope of the regression line the response factor. Final calibration was done using a single-point working standard, which was analyzed in replicate at the beginning, the middle and the end of analysis daily. The mean peak height was used to calculate the response factor, which was compared to the response factor from the initial calibration.

### Sorption experiments

The retention of applied TNT during sorption was investigated using the batch method as outlined by Amacher et al. (1988). Initial concentrations of TNT in the solution added to the soil were 1.110, 2.275, 5.559, 7.708, 10.22 and 11.31 mg/L. Background solution composition was 0.005-M $Ca(NO_3)_2$. For the SWy-1 montmorillonite, TNT retention was carried out as follows. Triplicate 3.5-g samples, consisting of 0.5-g of SWy-1 montmorillonite and 3 0 g of acid-washed sand, were added to 40-mL polypropylene centrifuge tubes of known weight. The acid-washed sand was assumed to be nonreactive, which was necessary to maintain mixing and distribution of the SWy-1 montmorillonite (see Gaston and Selim 1990). Twenty-five milliliters of TNT solution were added to the triplicate samples, which were vortex mixed. The tubes were placed endwise on a shaker set to shake at 120 oscillations/minute. The samples were shaken for 15 minutes every 2 hours. After 3 days, the samples were centrifuged and the supernatant decanted. Concentrations of TNT in the sample solution were based on the HPLC method described above. Amounts of the TNT sorbed or retained by the SWy-1 montmorillonite samples were calculated from the difference between initial (applied) concentrations of each sample. Correction was also made for the entrained supernatant.

### Desorption experiments

Desorption or release of TNT was carried out following sorption as outlined by Amacher et al. (1988), with successive dilution steps. After the solution was decanted, the first dilution step was carried out by adding 25 mL of $Ca(NO_3)_2$ to each test tube. The tubes were then vortex mixed and placed on the shaker as described in the above section. The samples were shaken for 15 minutes every 2 hours. After a minimum release time of 4 to 6 hours for each step, the samples were centrifuged and the supernatant decanted for TNT analysis. Five dilution steps were carried out using this procedure. In addition to the TNT concentrations after each release or extraction step, the amount of TNT released and that remaining on matrix surfaces were calculated on the basis of solution concentrations and input (initial) amounts added. Release beyond the fifth dilution step was not done because the TNT in the soil solution dropped below detection limits.

For the contaminated soil (samples A and B), the above method was followed except that 3-g soil samples were used. Again, triplicate soil samples were used and the desorption reaction duration was 1 day for each extraction step, after which solutions were analyzed for TNT and RDX. Desorption was carried out for 8 days for eight extractions. Release reaction was terminated after the eighth day, as TNT and RDX levels in the extraction solutions were below the HPLC detection limit.

### Transport experiments

Transport experiments were conducted to describe the potential mobility of TNT and RDX in a standard reference material (pure clay), in contaminated and uncontaminated soils obtained from

**Table 1. Parameters of the various soil columns for the TNT and RDX miscible displacement experiments.**

| *Soil* | *Experiment number* | *Water content* $\Theta$ *($cm^3/cm^3$)* | *Bulk density* $\rho$ *($g/cm^3$)* | *Flux* $v$ *(cm/hr)* |
|---|---|---|---|---|
| Bentonite-sand | 102 | 0.363 | 1.56 | 0.299 |
| Bentonite-sand | 110 | 0.385 | 1.56 | 0.295 |
| Bentonite-sand | 111 | 0.385 | 1.56 | 0.295 |
| Norwood | 103 | 0.403 | 1.46 | 0.906 |
| Norwood | 105 | 0.404 | 1.47 | 0.747 |
| Kolin* | 112 | 0.466 | 1.45 | 0.302 |
| Kolin sample A** | 108 | 0.510 | 1.42 | 0.279 |
| Kolin sample B** | 107 | 0.517 | 1.45 | 0.310 |

* Uncontaminated sample from Louisiana Army ammunition site.

** Contaminated samples from Louisiana Army ammunition site.

**Table 2. Concentration of TNT and RDX input pulses, background solution and pulse duration for the miscible displacement column experiments.**

| *Soil* | *Experiment number* | *Input pulse* | *Concentration (μg/mL)* | *Background solution* | *Input pulse (pore volumes)* | *Duration (hr)* |
|---|---|---|---|---|---|---|
| Bentonite-sand | 102 | TNT | 100.00 | 50% methanol | 4.33 | 54.6 |
| Bentonite-sand | 110 | TNT | 10.65 | 0.005-M $Ca(NO_3)_2$ | 7.51 | 95.9 |
| Bentonite-sand | 111 | RDX | 10.65 | 0.005-M $Ca(NO_3)_2$ | 4.33 | 90.1 |
| Norwood | 103 | TNT | 100.00 | 0.005-M $Ca(NO_3)_2$ | 7.11 | 30.6 |
| Norwood | 105 | TNT | 10.28 | 0.005-M $Ca(NO_3)_2$ | 5.18 | 28.1 |
| Kolin* | 112 | TNT | 10.35 | 0.005-M $Ca(NO_3)_2$ | 5.00 | 74.5 |
|  |  | RDX | 10.04 | 0.005-M $Ca(NO_3)_2$ | 5.00 | 74.5 |
| Kolin sample A** | 108 | — | — | 0.005-M $Ca(NO_3)_2$ | 37.9 | 693 |
| Kolin sample B** | 107 | — | — | 0.005-M $Ca(NO_3)_2$ | 40.5 | 678 |

* Uncontaminated sample from Louisiana Army Ammunition Plant site. Applied pulse contained both RDX and TNT.

** Contaminated samples from Louisiana Army Ammunition Plant site.

the Louisiana Army Ammunition Plant, and in the highly permeable Norwood soil. For the standard clay, we used a 1:9 bentonite–sand mixture. A mixture with acid-washed sand assured uniformity and allowed water flow through the packed soil columns. Our transport experiments used the miscible displacement approach described by Selim et al. (1989), where leaching through packed soil columns was monitored. Each soil was air-dried and passed through a 2-mm sieve before use. Plexiglas columns (6.4 cm in diameter × 10 cm in length) were uniformly packed with each soil to an appropriate bulk density. Constant flux was maintained with variable-speed piston pumps (fluid metering model RPG6). A fraction collector was used to collect column effluent (ISCO model 68-2180) at different intervals that depended on effluent fluxes.

Initially, soil columns were slowly wet with 0.005-M $Ca(NO_3)_2$ and leached with this solution until negligible Mg, K or Na appeared in the effluent. Analysis of leachate collected in the Ca-saturation step indicated that essentially all initially extractable Mg, K and Na had been removed. Over 20 pore volumes of 0.005-M $Ca(NO_3)_2$ were introduced into each column at a constant flux to equilibrate the soils with the background solution. Comparison of column weights after wetting with Ca solutions to initial air-dry weights indicated that nearly full saturation had been achieved. Experimental parameters of the column leaching studies are given in Tables 1 and 2.

A pulse of TNT having a concentration of either 10 or 100 mg/L in a 0.005-M $Ca(NO_3)_2$ solution was introduced into each column at a constant flux. The applied TNT was followed by several pore volumes of the background solution of 0.005-M $Ca(NO_3)_2$ to elute the columns and obtain a complete TNT breakthrough curve for each soil. The experimental miscible displacement procedure just described was followed for all packed soil columns and the pure clay with only one exception: for soil columns with the contaminated samples A and B, pulse applications of TNT were not made. Instead, we monitored the leaching of TNT and RDX that was already present in the contaminated soils. In addition, the background solution of 0.005-M $Ca(NO_3)_2$ was introduced to the air-dry soil and the extent of leaching or release based on concentrations of TNT and RDX in the effluent solution was monitored.

To determine the hydrodynamic dispersion coefficient ($D$) of eq 1, a pulse of tritium ($^3H_2O$) was applied to the reference clay columns prior to the TNT pulses. The pulse volume was equivalent to one pore volume and the background solution was 0.005-M $Ca(NO_3)_2$, which was maintained at all times. Liquid scintillation spectrometry (Beckman LS7000) was used to count the tritium radio tracers. Best-fit model parameters for $D$ were obtained by use of nonlinear least-squares optimization methods of the tritium results (see van Genuchten 1981). The estimate for $D$ was 0.00134 $m^2\ day^{-1}$, and that for a retardation factor was close to unity.

## RESULTS AND DISCUSSION

### Sorption isotherms

Figure 1 is the sorption isotherm for TNT on the SWy-1 montmorillonite. This figure represents the amount of TNT sorbed vs. that in the soil solution following 1 day of retention reaction. The amount retained by the clay material is expressed in terms of micrograms of TNT retained per gram of SWy-1 montmorillonite (µg/g). The acid-washed sand was considered nonreactive and was thus not included in any of the calculations reported below.

Isotherm results of Figure 1 were described in three different ways. First a linear Freundlich form was used

$$S = K_d C \qquad (13)$$

where

$S$ = amount sorbed (µg/g)
$C$ = solution concentration (µg/mL)
$K_d$ = distribution coefficient ($cm^3/g$).

The linear form is similar to the Freundlich equation (eq 2) with $b = 1$. The $K_d$ parameter describes the partitioning of TNT between the solid and liquid phases over the concentration range and is analogous to the equilibrium constant for a chemical reaction. The best fit $K_d$, which provided the solid line in Figure 1, was $51.722 \pm 2.929\ cm^3/g$.

There is strong deviation from linear behavior, especially for low TNT concentrations (less than 5 µg/mL) as depicted in Figure 1. As a result, the common nonlinear Freundlich form was used (Selim et al. 1990). Nonlinear least-square optimization was carried out to provide estimates for $K_d$ and $b$ based on eq 2. Parameter values that provided the best fit for the isotherm results were $K_d$ of $65.881 \pm 11.046\ cm^3/g$ and $b$ of $0.841 \pm 0.101$.

Isotherm prediction using the nonlinear Freundlich form is shown by the solid curve of

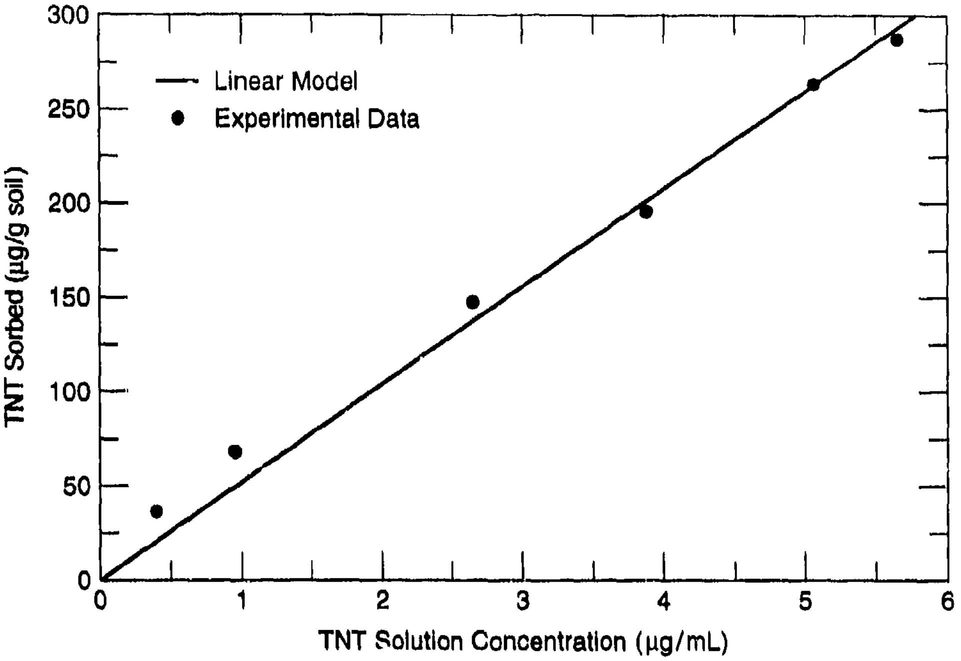


*Figure 1. TNT sorption on bentonite clay (SWy-1 montmorillonite, Crook County, Wyoming). The solid line is a fitted linear model.*

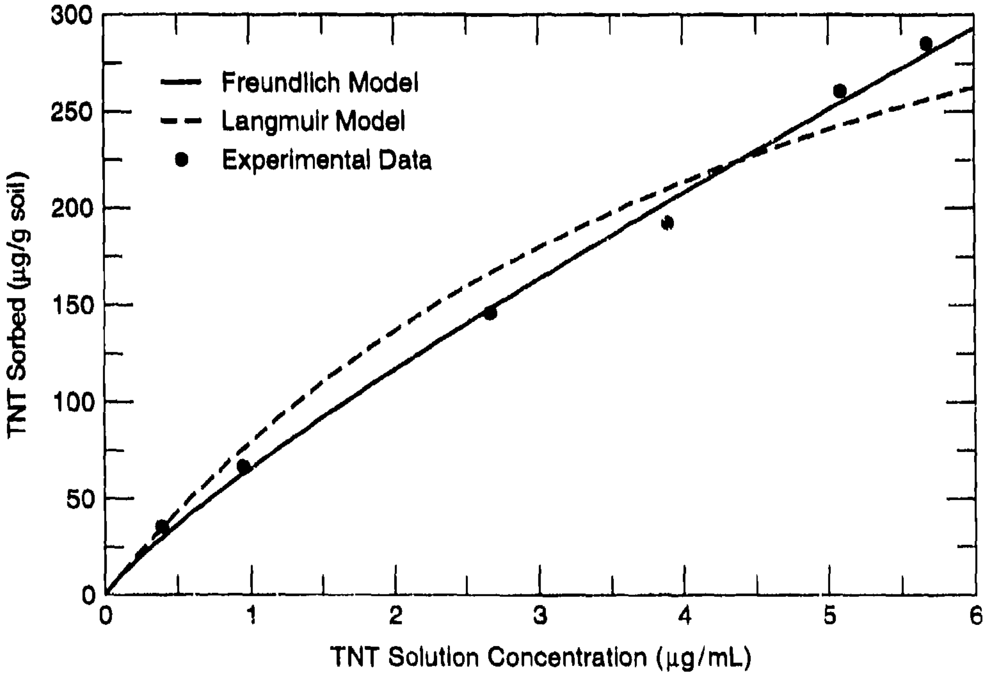


*Figure 2. TNT sorption on bentonite clay (closed circles) and fitted Freundlich and Langmuir models.*

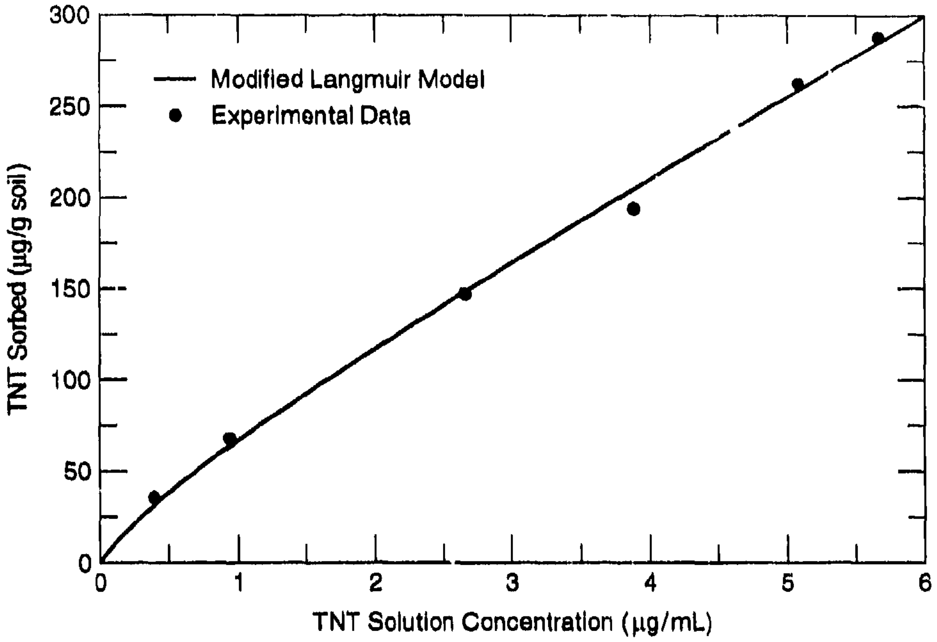


*Figure 3. TNT sorption on bentonite clay (closed circles) and fitted modified Langmuir model.*

Figure 2. Such a nonlinear approach provided good predictions for the low TNT concentration range. Greater discrepancy between predicted and experimental results were obtained as TNT concentrations increased. The *b* value of 0.84 for the nonlinear form is consistent with isotherms for other dissolved chemicals for other soils and pure minerals. In general, the parameter *b* is typically less than unity, as was found in this study (Buchter et al. 1989). In contrast, Pennington and Patrick (1990) found that best-fit Freundlich *b* values for TNT sorption were consistently greater than unity for a wide range of soils.

Langmuir predictions were also used to describe the isotherm data for TNT sorption on the clay. The best-fit prediction is indicated by the dashed curve in Figure 2. It is obvious that this approach is inappropriate for describing the isotherm results in the concentration range shown. The values for $\omega$ and $S_{max}$, which provided the best fit shown, are 0.196 ± 0.036 (mL/µg) and 493.467 ± 47.905 (µg/g) respectively. Leggett (1985) found that the use of an extended Langmuir form as

$$\frac{S}{S_{max}} = \frac{\omega C}{(1 + \omega C)} + \kappa C \qquad (14)$$

provided the best predictions of TNT, DNT, RDX and HMX isotherms for a similar concentration range ($\kappa$ is an arbitrary parameter). The above formulation may be regarded as a two-site approach, where a combination of linear plus Langmuir processes describes the retention mechanisms. For our TNT sorption isotherm, the use of the combined approach improved the prediction capability of the experimental data, as shown in Figure 3. Parameter estimates that provided best-fit predictions of Figure 3 were 37.258 ± 22.698, 1.502 ± 1.189 and 44.477 ± 4.681 for $S_{max}$, $\omega$ and $\kappa$ respectively. In fact, the predicted curve was closely similar to that for the Freundlich approach. However, the large values for the parameter standard errors given in Table 3 are indications that the modified Langmuir approach provides inadequate representation of the TNT retention mechanisms on the reference clay.

**Desorption and hysteresis**

Following the sorption step, TNT was desorbed using the successive dilution method as outlined by Amacher et al. (1988). Desorption isotherms for two initial applied concentrations are shown in Figure 4. Each desorption curve is a

**Table 3. Best-fit model parameters for batch sorption data of TNT on reference clay (SWy-1 montmorillonite).**

| *Model* | *Rate coefficient* | *Parameter estimate* | *Standard error* | $r^2$ |
|---|---|---|---|---|
| Linear | $K_d$ (cm$^3$/g) | 51.722 | 1.197 | 0.995 |
| Freundlich | $K_d$ (cm$^3$/g) | 65.881 | 4.297 | 0.996 |
| | $b$ | 0.841 | 0.039 | |
| Langmuir | $S_{max}$ (μg/g) | 493.46 | 19.579 | 0.976 |
| | $\omega$ (mL/μg) | 0.917 | 0.0146 | |
| Modified Langmuir | $S_{max}$ (μg/g) | 37.258 | 8.8307 | 0.998 |
| | $\omega$ (mL/μg) | 1.502 | 0.4624 | |
| | $\kappa$ (mL/μg) | 44.477 | 1.8209 | |

result of several dilution steps, each followed by equilibration for 4 to 6 hours. Another way of representing the desorption results is in terms of concentration of TNT in the soil solution and in the sorbed phase vs. the number of extractions (i.e., the desorption step). These results are shown in Figures 5 and 6 respectively. As extraction continued, the amount released for the various TNT initial concentrations—i.e., the amount desorbed to the soil solution—continued to decrease. The initial TNT concentrations ranged from 1.11 to 11.31 μg/mL. In the meantime, owing to the successive dilutions, TNT concentrations and the total TNT content retained by the clay continued to decrease.

A mass balance was attempted for each batch experiment and for all TNT initial concentrations using the total amount released vs. that applied. These mass-balance calculations indicated that TNT retention is fully reversible. Thus, for the

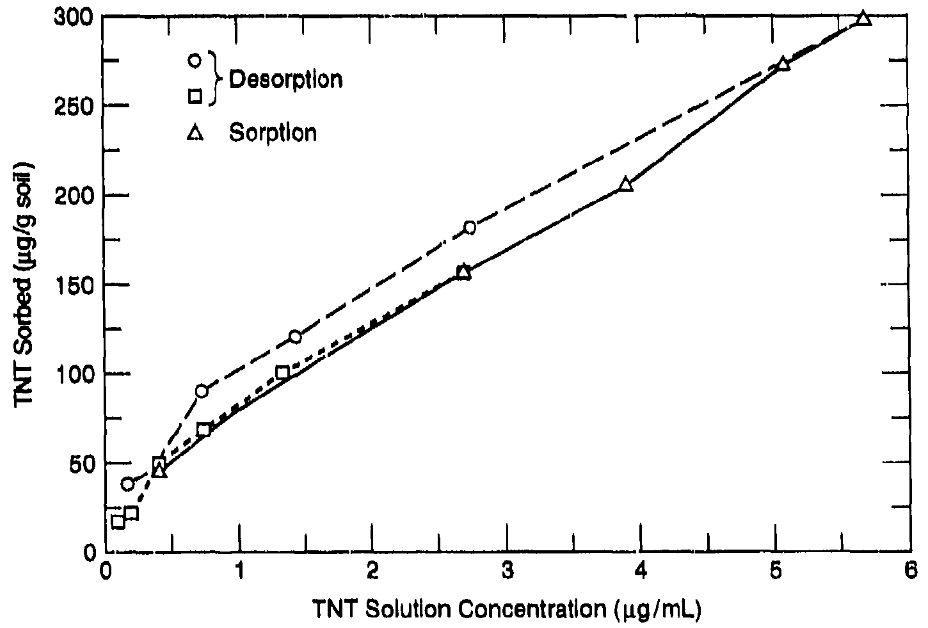


*Figure 4. TNT sorption–desorption isotherms for bentonite clay.*

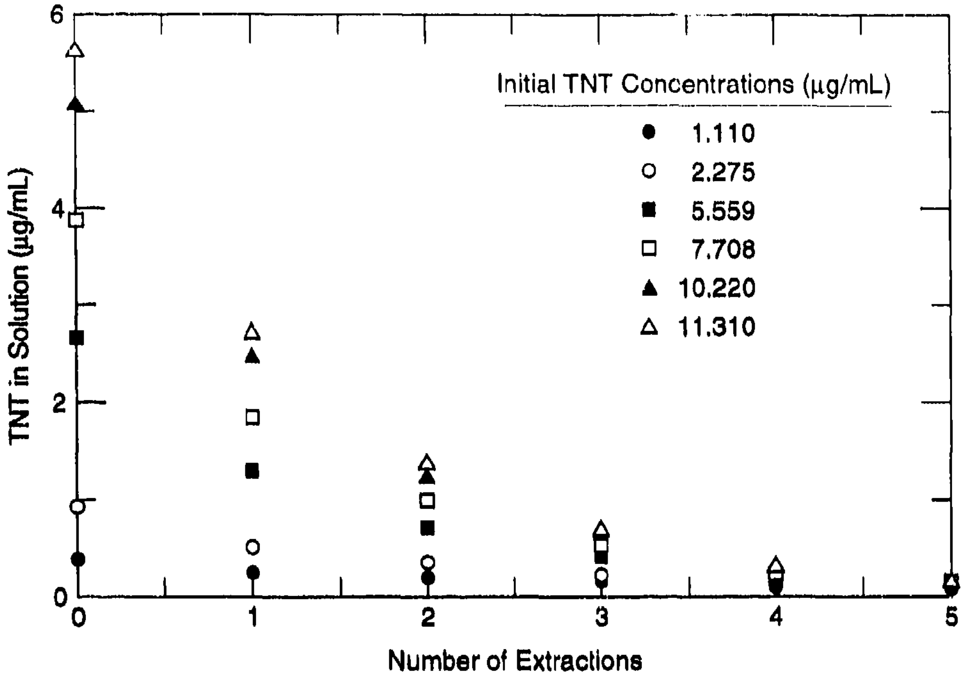


*Figure 5. TNT concentration in solution in the bentonite clay vs. number of dilutions–extractions during desorption.*

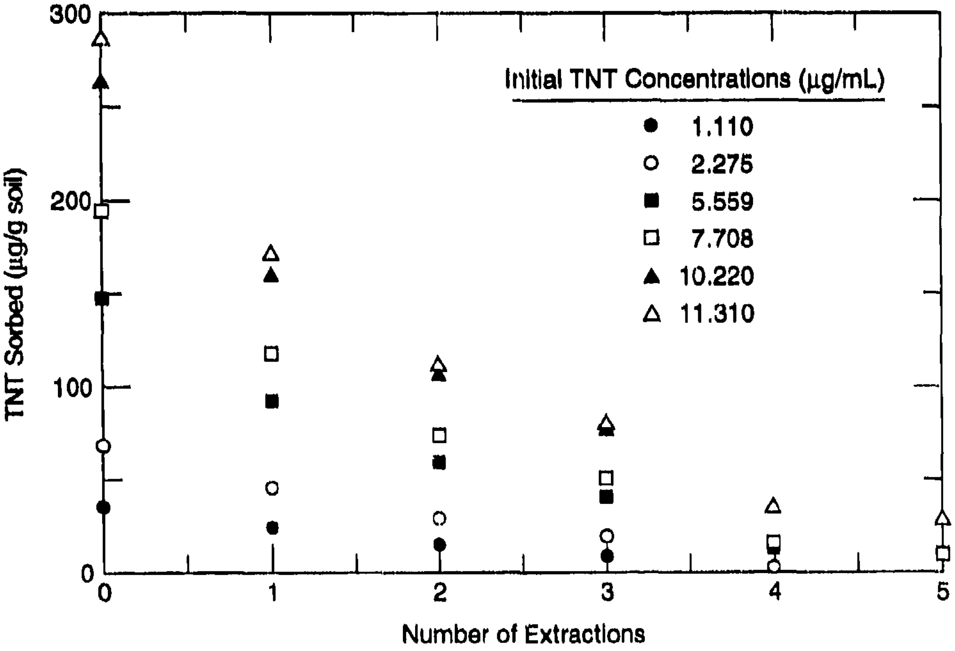


*Figure 6. Amount of TNT sorbed on bentonite clay vs. number of dilutions–extractions during desorption.*

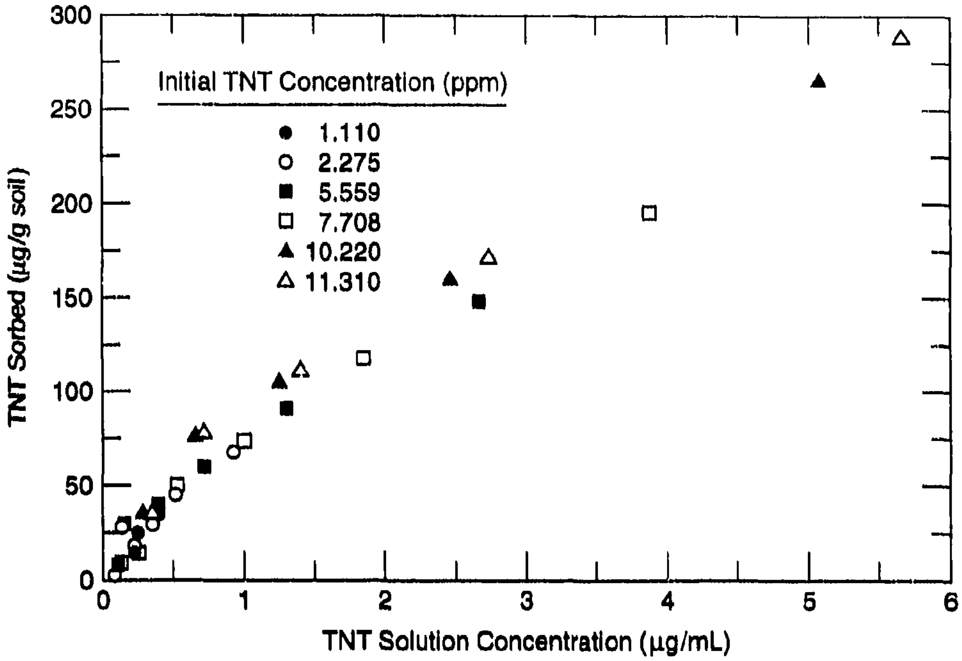


*Figure 7. TNT sorption–desorption isotherms for bentonite clay for all initial TNT concentrations used.*

bentonite clay used here, there were no apparent irreversible interactions of TNT such as degradations. However, this is not the case for inhomogeneous soils, where organic matter at various levels of decomposition and various clay minerals and oxides play significant roles in the chemical, physical and biological interactions within the soil environment. The level of biological activities in nonhomogeneous soils is demonstrated by the extent of degradation potential of military explosives (for a review see final report by Weston 1988).

Since retained TNT was completely desorbed during a reaction time of only 2 days, one may regard the retention process as fast or instantaneous, where local equilibrium is reached in a relatively short reaction time (Rubin 1983). To further test the hypothesis that the Local Equilibrium Assumption (LEA) is valid for TNT retention with the bentonite clay, one may examine the sorption and desorption isotherms shown in Figure 4. The fact that the desorption isotherms do not deviate appreciably from the sorption isotherm is a definite indication of reversibility as well as of local equilibrium conditions as the dominant retention mechanism. The nonsingularity or hysteretic behavior of the TNT isotherms may be a result of kinetic behavior of reversible reaction mechanisms, irreversible mechanisms such as degradation, or artifacts from the technique used for the desorption–release process. Selim et al. (1976) have shown the effect of kinetic behavior on the observed nonsingularity of sorption–desorption isotherms. The TNT results for all desorption isotherms are given in Figure 7 and indicate limited deviations between the sorption and desorption curves for all initial TNT concentrations investigated.

## Transport

The transport of TNT in miscible displacement columns packed with a bentonite–sand mixture is illustrated by the results shown in Figure 8. In this case, we introduced into the bentonite–sand column a pulse of TNT having a concentration ($C_0$) of 100 mg/L in a background solution of 50% methanol in distilled water. The volume of the pulse input and other characteristics of the miscible displacement column are given in Table 2. In Figure 8, the results are presented in terms of the relative TNT concentration ($C/C_0$) versus number of pore volumes ($V/V_0$), where $V_0$ is the volume of pore space in the column.

The results indicate the early arrival of TNT in

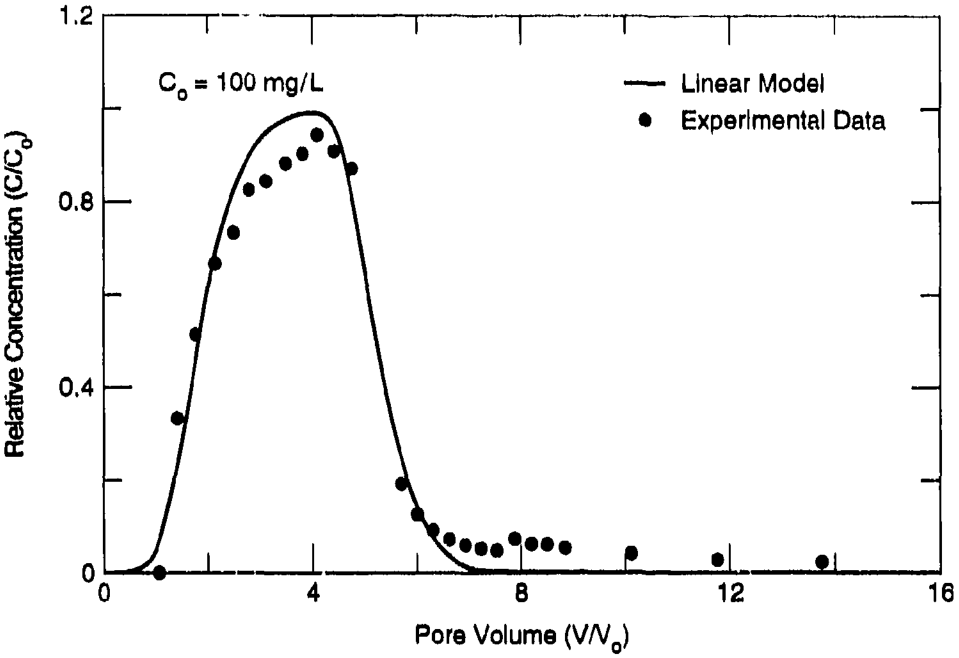
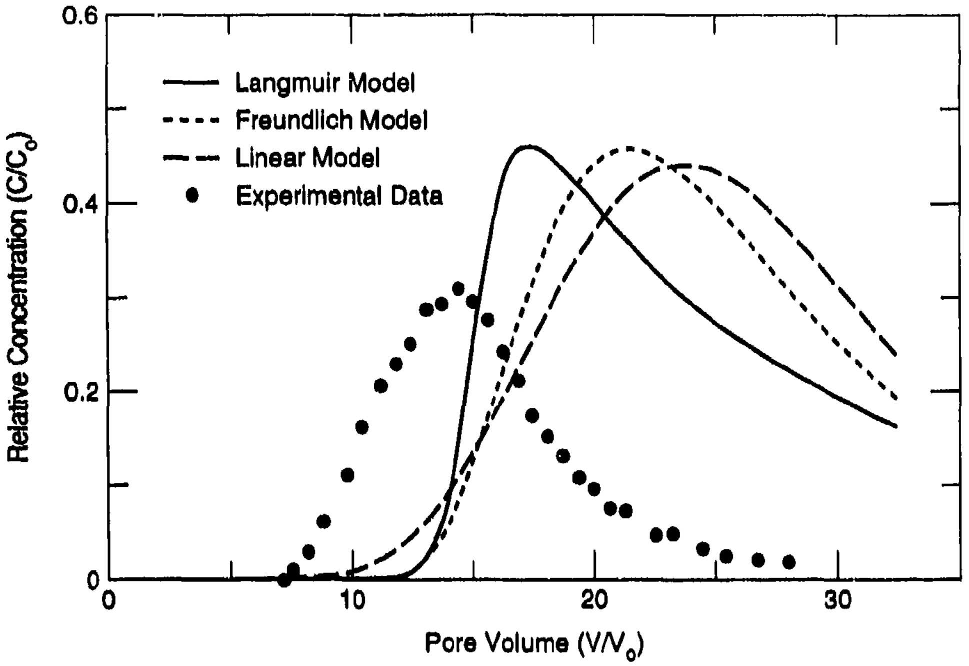


*Figure 8. TNT breakthrough results (closed circles) for a bentonite–sand column with input TNT concentration ($C_0$) of 100 μg/mL in a 50% methanol background solution. The solid curve is a model prediction using the transport equation with a linear retention model.*

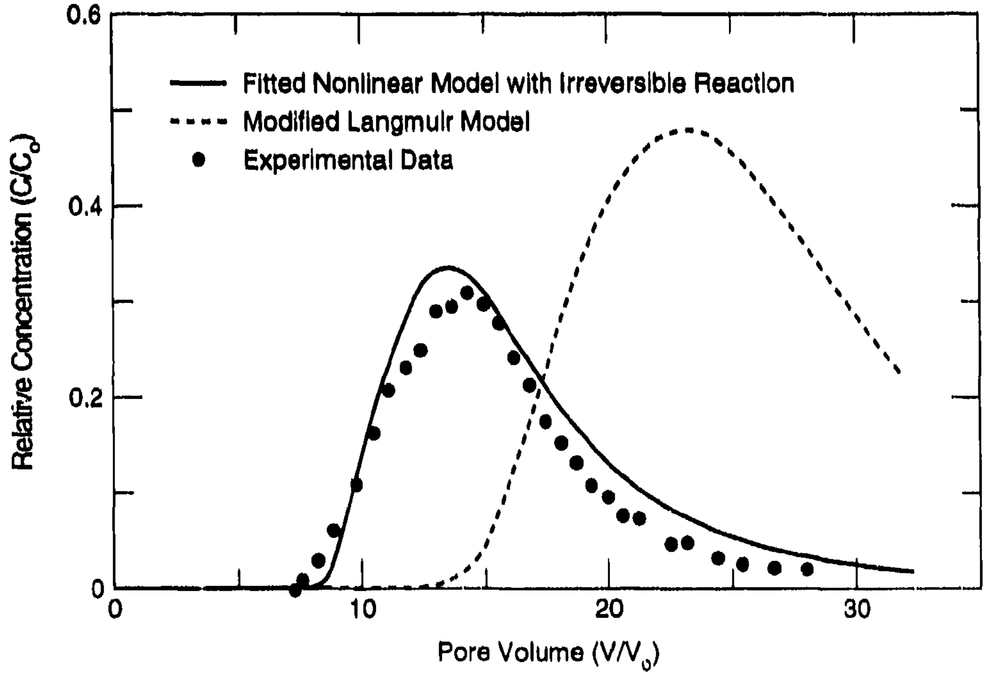
the effluent solution. Moreover, the peak concentration exceeded 95% of the input concentration ($C_0$). The TNT mobility for this case resembles that of a nonreactive solute, where the recovery of applied TNT in the effluent solution exceeded 95%. The amount of TNT recovery was estimated based on the area under the breakthrough results. Very little retardation of the TNT pulse was observed here. This is confirmed by the relative TNT concentration in the effluent ($C/C_0$) reaching 0.50 after only 1.7 pore volumes ($V/V_0$). For a nonreactive solute, such relative concentration is achieved at approximately $V/V_0$ of unity. Such results directly indicate the effect of methanol as a solvent on the extent of reaction of TNT in the bentonite–sand column.

Attempting to describe the transport behavior of TNT in the bentonite–sand column when methanol was present (Fig. 8), we found that a simple linear retention model provided a good description of the breakthrough results. The $K_d$ value that gave the best fit to the data was 0.2036 ± 0.0193 $cm^3/g$, which indicates a low parameter standard of error for the estimated $K_d$. The goodness of fit of the linear model to the experimental data was based on $r^2$ values as calculated using the principle of extra sum of squares (Amacher et al. 1988). The $r^2$ value for the results of Figure 8 was 0.987. We should point out that the linear model could not describe the slow release of TNT, as indicated by the tailing of the breakthrough results. It is conceivable that a small proportion of the desorbed TNT was strongly sorbed by the clay matrix surfaces. Such strongly held TNT forms may account for the slow release during leaching in the bentonite–sand column.

The TNT breakthrough results shown in Figure 9a reflect the mobility of TNT where the applied pulse concentration ($C_0$) was 10.65 mg/L and the background solution was 0.005-M $Ca(NO_3)_2$. Figure 9a shows that the TNT movement was retarded: arrival in the exit solution was not detected until after seven pore volumes, and peak concentration did not reach $C/C_0$ of 0.35. Slow release of TNT was also shown by the tailing of the desorption (right) side of the breakthrough results. Total recovery of applied TNT was not obtained. In fact, on the basis of the area under the curve, we estimated that only some 40% of the applied TNT pulse was recovered in the effluent solution. Figure 9a illustrates that, in the presence of 0.005-M $Ca(NO_3)_2$ as the background solution, the mobil-



*a. Solid and dashed curves are predictions using the transport equation with linear, Freundlich and Langmuir retention models.*



*b. Dashed and solid curves are predictions using the transport equation with a modified Langmuir model and a multireaction model (nonlinear model with irreversible reaction).*

*Figure 9. TNT breakthrough results (closed circles) for a bentonite–sand column with an input TNT concentration ($C_0$) of 10.65 μg/mL in a 0.005-M $Ca(NO_3)_2$ background solution.*

ity of TNT in the bentonite–sand column was much more retarded than when methanol was present (Fig. 8).

We found that the use of linear, Freundlich or Langmuir retention with the convective–dispersion equation poorly described the transport data of Figure 9. For all three predictions, the extent of retardation or the arrival time of TNT in the effluent solution was overpredicted. In addition to delayed arrival of TNT, the maximum predicted concentration was higher than that experimentally measured. The retention parameters associated with the equilibrium models were based on batch results on the bentonite clay (see Table 3 and Fig. 1–3). It should be emphasized that the three models considered here are equilibrium-type models and do not account for irreversible or slowly reversible retention reactions. As a result, the failure of these fully reversible equilibrium models to describe this data set was not surprising. In addition, the modified Langmuir model eq 14 failed to describe the data (Fig. 9b).

Model predictions shown in Figure 9 illustrate the inadequacy of the equilibrium models in describing the TNT results in a clay–sand column in the presence of 0.005-M $Ca(NO_3)_2$ as the background solution. Despite equilibrium models of the Freundlich and Langmuir type providing good predictions of the batch data, one should not automatically assume the validity of such models to transport experiments. We suggest that the batch data of TNT on bentonite clay did not account for possible retention mechanisms of the slow adsorption–desorption or transformation during the 2-day reaction time of batch equilibration.

We attempted further prediction of the TNT data set of Figure 9b using the Multi-Reaction and Transport Model (MRTM) described earlier, where two mechanisms were assumed to govern the retention reactions of TNT. The first mechanism was a fast reaction of the nonlinear (Freundlich) equilibrium type (see eq 2) and the second an irreversible mechanism of the first-order type (see eq 7). Because of lack of complete TNT recovery in the effluent solution from the bentonite–sand miscible displacement column, incorporation of an irreversible reaction was necessary to account for TNT phases that were not in soil solution. Incomplete TNT recovery is ascribable to possible transformation reactions as well as slow release of sorbed TNT phases on the clay surfaces. Other mechanisms include inter-particulate diffusion in clay lattices or other inaccessible sites. A diffusion mechanism involving clays has been postulated for other ions by Sparks and co-workers (see Sparks 1989).

Model parameters that provided best-fit predictions of the TNT results of Figure 9b are given in Table 4. The MRTM model was capable of predicting the peak concentration and the extent of TNT retardation in the soil column. The goodness of fit of the MRTM model as given by the value of $r^2$ was 0.836. In addition, the standard errors of model parameters were small, which adds credence to the applicability of the mechanisms considered in describing the Breakthrough Curves (BTCs). Based on model calculations, the amount of TNT recovery was 41.9% following 35 pore volumes, which compares well with experimental data. Estimates for $K_d$ and $b$ were much smaller than those based on batch results, however.

Results for RDX concentration in the effluent, as shown by the breakthrough results in Figure 10, reveal that there is a limited retention of RDX by the bentonite–sand column. This is attributable to the retardation of the BCT, with the arrival of RDX in the effluent after two pore volumes and a relative concentration ($C/C_o$) of 0.5 corresponding to approximately three pore volumes. In addition, RDX in the effluent indicates that there is a sharp rise of the sorption front and on the desorption side, which is commonly known as self-sharpening. This is a strong indication that, for RDX, the local equilibrium is the dominant cause of retention of RDX in the bentonite–clay column.

The use of an equilibrium Freundlich retention with a fully reversible reaction in the MRTM to describe RDX results is indicated by the solid and dashed curves shown in Figure 10. Although the predictions did not fully describe the shape of the curve for RDX in the effluent, they predicted the arrival time of the RDX in the effluent. For the solid curve, RDX predictions were obtained using nonlinear least-square optimization of MRTM, where $k_s$ was set to zero. This is because it appeared that a total recovery of the applied RDX pulse input was obtained in the effluent solution. Estimates for the Freundlich parameters $K_d$ and $b$ that provided the best-fit of RDX results were 0.8203 $cm^3/g$ and 0.8048 respectively. The errors of estimation for both parameters were relatively small (see Table 4). It is possible that the deviation from the sharp rise of the BTC may be caused by the effect of a large dispersion coefficient or nonlinearity of the Freundlich retention mechanisms. It is known that a large $D$ value (or small Peclet number) or a small $b$ value, or both, results in a sharpening of the BTC

**Table 4. Best-fit model parameters for the TNT and RDX miscible displacement experiments.**

| *Soil* | *Experiment number* | *Model* | $K_d$ *(cm³/g)* | *SE*† | b | *SE* | $k_s$ *(hr⁻¹)* | *SE* | $r^2$ |
|---|---|---|---|---|---|---|---|---|---|
| ***TNT pulse*** | | | | | | | | | |
| Bentonite–sand | 102 | LIN* | 0.204 | 0.009 | — | — | — | — | 0.987 |
| Bentonite–sand | 110 | MRTM* | 4.374 | 0.073 | 0.745 | 0.008 | 0.072 | 0.003 | 0.836 |
| Norwood | 103 | MRTM* | 0.357 | 0.019 | — | — | 0.095 | 0.007 | 0.978 |
| Norwood | 105 | MRTM* | 0.400 | 0.010 | — | — | 0.158 | 0.003 | 0.970 |
| ***RDX pulse*** | | | | | | | | | |
| Bentonite–sand | 112 | FRN* | 0.802 | 0.036 | 0.805 | 0.029 | — | — | 0.919 |
| Kolin | 112 | MRTM* | 0.725 | 0.024 | 0.821 | 0.014 | 0.002 | 0.002 | 0.971 |

† SE = Standard error.

* LIN = linear model, MRTM = multireaction and transport model, FRN = Freundlich model.

(Selim et al. 1990). We did not attempt to adjust *b* or *D* values in this study, however. In fact, the use of a smaller *b* value to produce a sharper front requires further adjustments to the $K_d$ value. Since the *D* value used is based on that determined using tritium breakthrough results, we made no attempts to adjust the *D* value used in the predictions.

To study the extent of irreversible retention of RDX, we examined a range of values of the irreversible rate coefficient ($k_s$) for transport predictions based on eq 1. Selected predictions are shown by the dashed curves of Figure 10 for $k_s$ values of 0.01 and 0.02 hr$^{-1}$, which resulted in 10.5 and 21% irreversible retentions of RDX. More significantly, it is apparent that the use of $k_s$ of 0 produced the best predictions. This is also supported by a visual estimation of the area under the curve. Therefore, we conclude that RDX was highly mobile with little retardation and that kinetic or slow retention processes were absent. Moreover, we did not de-

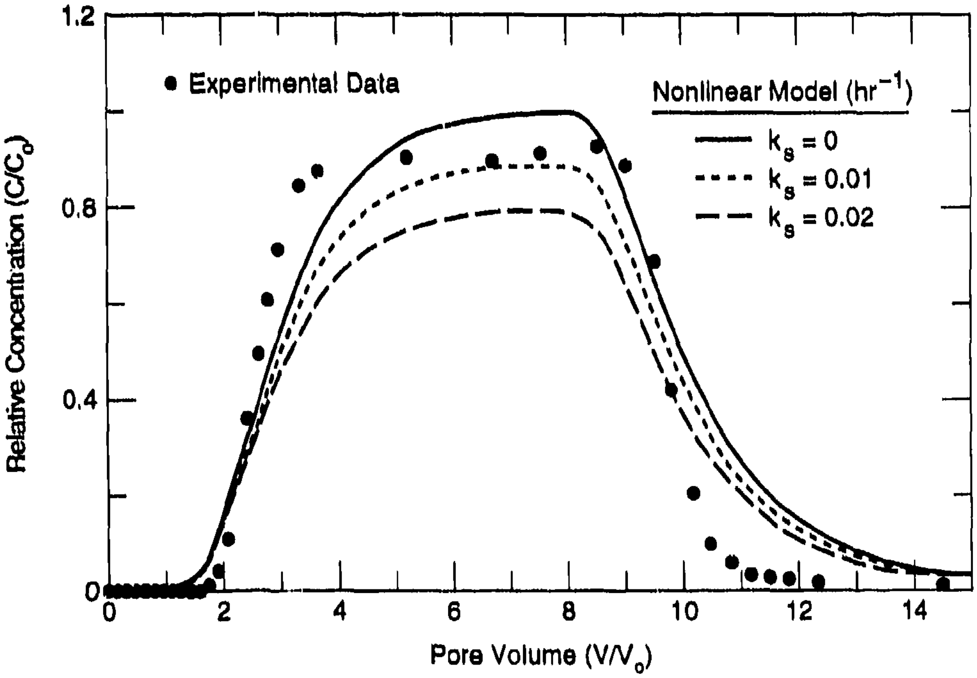


*Figure 10. RDX breakthrough results (closed circles) for a bentonite–sand column with input RDX concentration ($C_0$) of 10.65 µg/mL in a 0.005-M $Ca(NO_3)_2$ background solution. The curves are calculations using the transport equation with nonlinear equilibrium retention and an irreversible reaction for $k_s$ of 0, 0.01 and 0.02 hr$^{-1}$.*

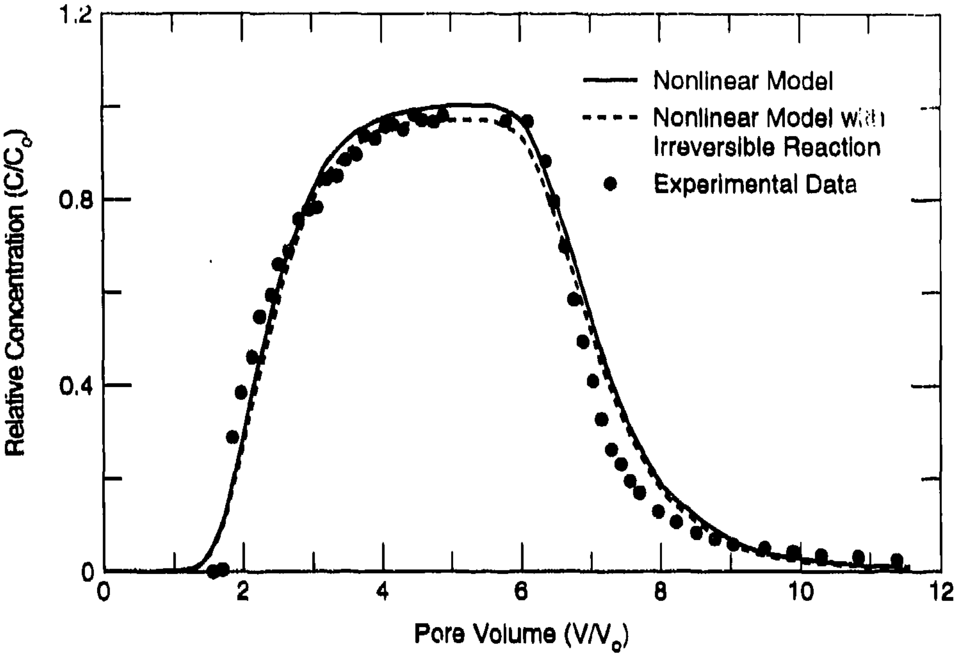


*Figure 11. RDX breakthrough results (closed circles) for Kolin uncontaminated soil column with input RDX concentration ($C_0$) of 10.04 μg/mL in 0.005-M $Ca(NO_3)_2$. The solid curve is calculated using the transport equation with nonlinear retention whereas the dashed curve includes irreversible reaction.*

tect irreversible retention of RDX on bentonite clay surfaces or transformation reactions. Other investigators (Leggett 1985, Pennington and Patrick 1990) have obtained low retention of RDX by clays and several soils during adsorption–desorption.

We investigated the mobility of RDX and TNT in uncontaminated soil samples obtained from near the contaminated site at the Louisiana Army Ammunition Plant. Here, we introduced a pulse of a mixture of TNT and RDX, having concentrations of 10.65 and 10.04 mg/L in 0.005-M $Ca(NO_3)_2$ as the background solution, to a packed column of the uncontaminated soil after a steady water flux condition was achieved. We introduced approximately five pore volumes of the TNT and RDX mixture to the packed column. Breakthrough results for RDX concentration in the effluent are shown in Figure 11 and indicate the arrival of RDX in the effluent after about two pore volumes, where peak (maximum) RDX concentration in the effluent reached that of the input pulse concentration ($C/C_0 = 1$). This was followed by a gradual RDX concentration decrease and is indicated in the figure by the tailing of the desorption side of the breakthrough results. Comparison of data for the uncontaminated soil and those for the bentonite–sand column (Fig. 10) illustrates the similarity of RDX mobility in the two systems. Major differences were found in the overall shape of the breakthrough results rather than in the arrival time of the RDX fronts. Specifically, the RDX effluent and desorption sides for the uncontaminated soil did not exhibit the sharp rise (self-sharpening) seen in the bentonite–sand column. This may be ascribable to a larger dispersion coefficient ($D$) for the uncontaminated soil or the presence of nonlinear or kinetic-type retention reactions. The extent of RDX retention was similar for both systems, however.

The use of a nonlinear retention of the Freundlich type with no irreversible retention in the transport model produced good prediction of RDX movement in the uncontaminated soil, as indicated by the solid curve of Figure 11. Parameter estimates for $K_d$ and $b$ that provided the best-fit of RDX results were 0.7249 cm$^3$/g and 0.8209 respectively. The corresponding estimation errors for $K_d$ and $b$ were small. When the model was extended to include irreversible retention, the estimated $k_s$ value was 0.00212 ± 0.00214 hr$^{-1}$, which is a poor estimate. Moreover, the area under the curve indicated a 3% irreversible retention only. Therefore, the RDX transport data shown for the uncontaminated soil are consistent with those for the bentonite–sand column, indicating extremely high potential mobility of RDX in soils with little or limited retardation.

Analysis for TNT, using our HPLC procedure, did not detect TNT in the effluent solution until some six pore volumes eluted through the uncontaminated soil column (data not shown). The TNT concentration did not exceed 0.05 mg/L (or $C/C_0$ = 0.005). After 12 pore volumes, the TNT decreased and was no longer detectable by HPLC. To investigate the extent of retention of TNT in this soil, we continued application of the background solution (0.005-M $Ca(NO_3)_2$) for 24 pore volumes. Since no appreciable amounts of TNT were recovered, we applied a pulse containing 50% methanol in the 0.005-M $Ca(NO_3)_2$ background solution at a constant flux, finding that TNT concentrations reached a maximum of 0.34 mg/L at $V/V_0$ of 2. We observed no higher TNT concentrations in the effluent solution after 10 pore volumes of 50% methanol were applied; however, HPLC analyses indicated the presence of other possible degradation products of TNT. Specifically, a definable peak on the chromatographic chart was consistently observed following the TNT peak. It is possible that TNT degradation along with strong retention reactions are responsible for the lack of TNT mobility in the original, uncontaminated soil.

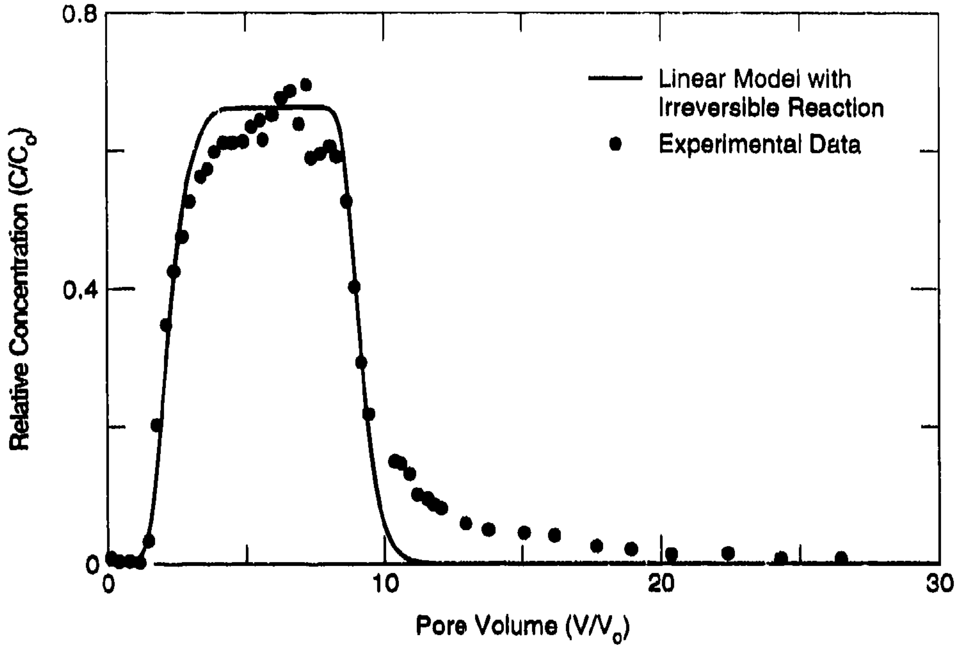
To further examine the leaching potential of TNT in other soils, we selected the Ap horizon from the Red River valley, which is adjacent to Louisiana Army Ammunition Plant. The soil chosen was a Norwood soil (fine silty, mixed, calcareous, Thermic Typic Udifluvent), with 79% sand, 18% silt and 3% clay. Breakthrough results for TNT (in 0.005-M $Ca(NO_3)_2$ background solution) in two different columns of Norwood soil are shown in Figure 12. The fluxes of applied TNT pulses along with soil moisture contents and bulk densities in the soil columns were somewhat similar for both breakthrough results (see Table 1). The primary difference between the data sets shown in the figure is the concentration of TNT in the input solution ($C_0$). The shapes of the BTCs were generally similar. Specifically, the arrivals of TNT in the column effluent solutions were similar regardless of $C_0$. In addition, the shapes of the desorption (right) sides were also similar, with a gradual decrease in concentration. The two data sets also indicate that TNT retention behavior is likely to be nonlinear or kinetic, or both, because peak concentrations, as well as the extent of TNT recovery in the effluent, depended on $C_0$.

The areas under the BTCs show that less than half of the TNT applied into the Norwood soil column was recovered when $C_0$ was 10.64 mg/L in comparison with over 60% recovery for $C_0$ of 100 mg/L (see Fig. 12). Irreversible retention, transformation reactions or slow release of TNT, or all three, are possible mechanisms that may explain the amounts of TNT not recovered in the effluent. Therefore, we applied the MRTM to describe the BTC data for TNT in the presence of an irreversible reaction or a sink term, along with a fast (i.e., equilibrium) type reaction.

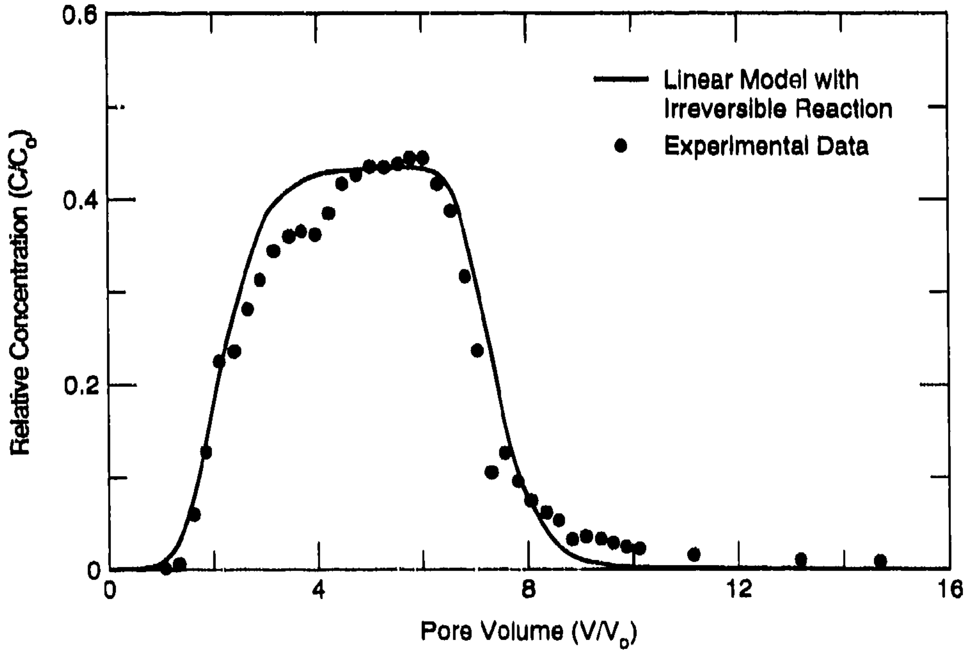
Model predictions are indicated by the solid curves in Figure 12. For both cases, we found that a linear approach (eq 15), along with a first-order irreversible reaction, adequately described the BTCs. Attempts to describe the BTCs using nonlinear (Freundlich) retention resulted in $b$ values close to unity with relatively small standard errors. As a result, we used the nonlinear least-squares optimization technique to fit the BTCs, where $K_d$ and $k_s$ were the only two parameters to be estimated. The estimated $K_d$ parameter was somewhat similar for both columns regardless of $C_0$. In contrast, a higher $k_s$ value was estimated for the case with the low TNT input concentration ($C_0$ = 10.28 mg/L).

The dependency of the irreversible rate coefficient on $C_0$ has been observed for other solute species by other investigators (Amacher et al. 1988). Moreover, for all parameters, the standard errors of estimates were small. Based on model calculations, the amounts of TNT in the slowly reversible or irreversible phase were estimated as 56.5 and 33.8% of that applied for $C_0$ of 10.28 and 100 mg/L respectively.

The model results in Figure 12 indicate that it was incapable of describing the slow release of TNT during leaching, regardless of the TNT concentration in the pulse input $C_0$. Kinetic behavior of a chemical, biological or physical nature may be responsible for the slow release of TNT in the effluent. Moreover, the reason for such high retention capacity of TNT in Norwood soil is not completely understood. Norwood soil has a high pH with low cation exchange capacity, a low clay content and an extremely low organic matter content. We thought that TNT would behave as a nonreactive solute, with little if any TNT retained irreversibly within the soil column. Therefore, additional investigations are needed to determine the behavior of TNT in soils such as the Norwood soil under flow conditions.



*a. Input concentration (C$_0$) of 100 μg/mL in 0.005-M Ca(NO$_3$)$_2$.*



*b. Input concentration (C$_0$) of 10.28 μg/mL in 0.005-M Ca(NO$_3$)$_2$.*

*Figure 12. TNT breakthrough results for a Norwood soil column. The solid curve is the prediction using the transport equation with a linear retention and irreversible reaction.*

**Table 5. Concentrations (μg/g) of explosive residues released from contaminated (Kolin) soil samples from the Louisiana Army Ammunition Plant.**

| | *HMX* | *RDX* | *TNB* | *TNT* | *AmDNT sample* |
|---|---|---|---|---|---|
| Sample A | 39.8 | 175 | 18.4 | 164 | 30.6 |
| Sample B | 36.3 | 127 | 32.4 | 76.1 | 35.2 |

### Contaminated soil

We studied the release of TNT and RDX from the contaminated (Kolin) soil samples (A and B) obtained from the Louisiana Army Ammunition Plant. The uncontaminated (original) samples, along with duplicate uncontaminated samples, were analyzed by CRREL scientists for the total contaminants.

The results for HMX, RDX, TNB, TNT and AmDNT are shown in Table 5. Contaminated soil A contained considerably higher amounts of RDX and TNT than sample B. The reasons for such differences are not known and may be a reflection of the spatial heterogeneity of contaminant concentration in the site. Uncontaminated samples did not show detectable amounts of TNT or RDX.

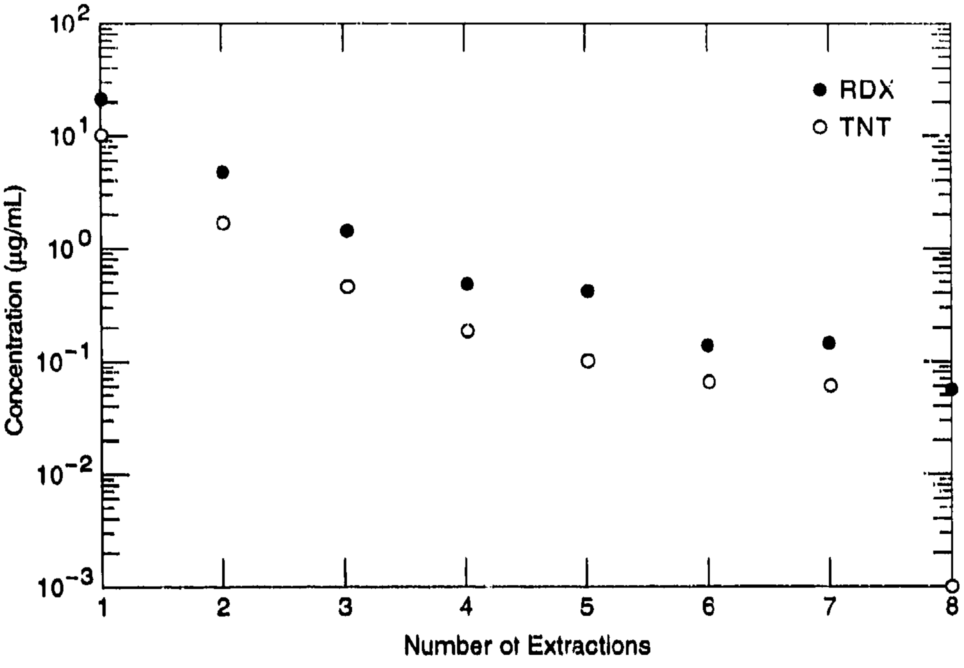
Results of the release study from the contaminated samples are shown in Figure 13. The RDX and TNT release data represent averages of three replications. For each extraction step, i.e., following decanting and additions of $Ca(NO_3)_2$ solution, the time of release reaction was 1 day. For sample A, the release of RDX and TNT continued for 8 days until concentrations below the detection limits of HPLC measurements were reached. Integration of the total amount released indicated that more than 90% of the TNT and RDX release took place within the first 3 days of reaction. This observation was consistent for both samples A and B. Differences in the rates of release are perhaps caused by the total initial TNT and RDX being considerably higher in sample A. The concentration levels were lowered by two orders of magnitudes after 4 to 5 days of continued release–extraction.

An important aspect of release studies is that one can estimate a mass balance of the contamination at different release times. Based on our release results, the total TNT amounts released were 103 and 42 μg/g soil for samples A and B respectively (on the basis of an average of the three replications of concentration at each release step). These amounts represent 60% of the total initial amounts present in the contaminated samples. On the other hand, for RDX, the amounts released were 215 and 155 μg/g soil for samples A and B respectively—amounts that were somewhat higher than the initial values.

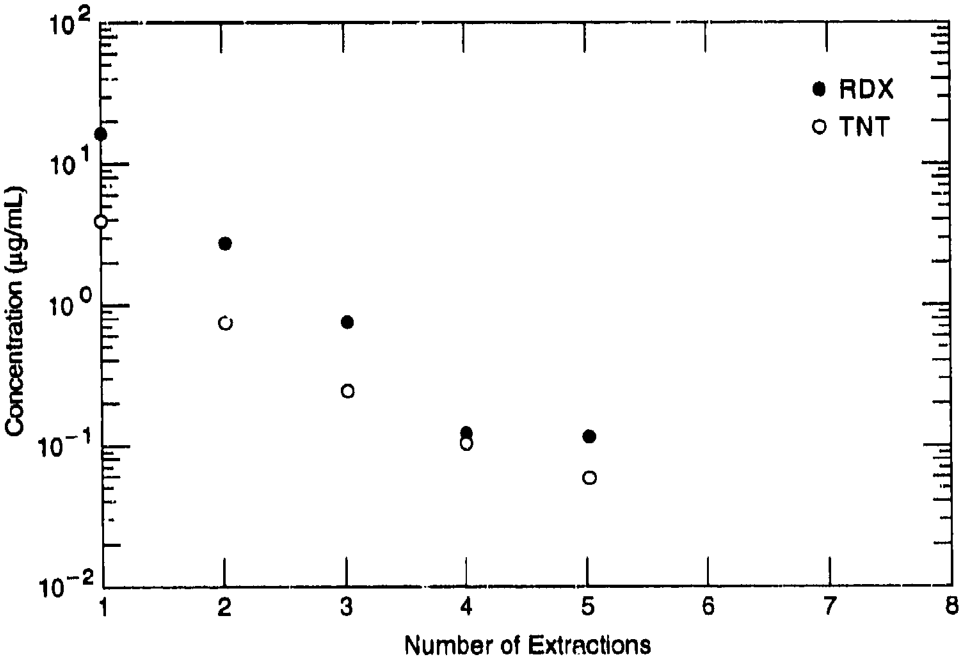
Transport of TNT and RDX in contaminated soil samples A and B is shown in Figure 14. To closely represent the ionic strength of the soil solution in the top soil layers, the background solution applied was 0.005-M $Ca(NO_3)_2$. The results clearly show an initial rise in concentrations of both TNT and RDX in the effluent solution because the contaminated soils were initially air-dried. As the background solution was introduced to the dry soil and water movement in the unsaturated state commenced, the solutes present (TNT and RDX) dissolved in the soil solution as the wetting front advanced in the soil column. This process continued until the wetting front reached the end of the column and effluent was collected.

The results of Figure 14 show higher concentrations of TNT and to a lesser extent RDX from contaminated soil sample A than from sample B. These results are consistent with the release data from the batch studies and reflect total higher initial amounts of TNT in contaminated soil A. From the area under each BTC, we also found that 100% of the RDX initially present in each soil sample was released. In fact, only 10 pore volumes of applied background solution were required for approximately 90% of the RDX contamination to leach out from the contaminated soil column. These results are also consistent with earlier findings for the bentonite–sand and Norwood soil columns, indicating that RDX is not strongly retained. As a result, we conclude that RDX is strongly susceptible to leaching losses to lower soil depths.

Release and movement of TNT in the contaminated soil columns indicate a slow release process and a gradual decrease in effluent concentration (Fig. 13). Such a slow release behavior is often associated with kinetic retention of the linear and nonlinear mechanisms. In contrast to RDX, the

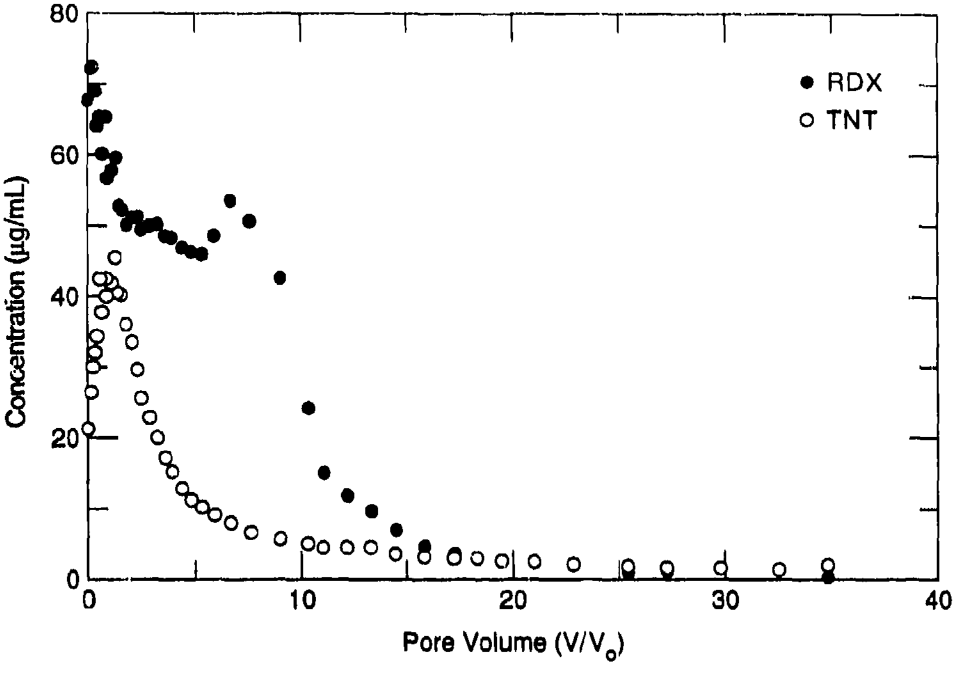


*a. Sample A.*

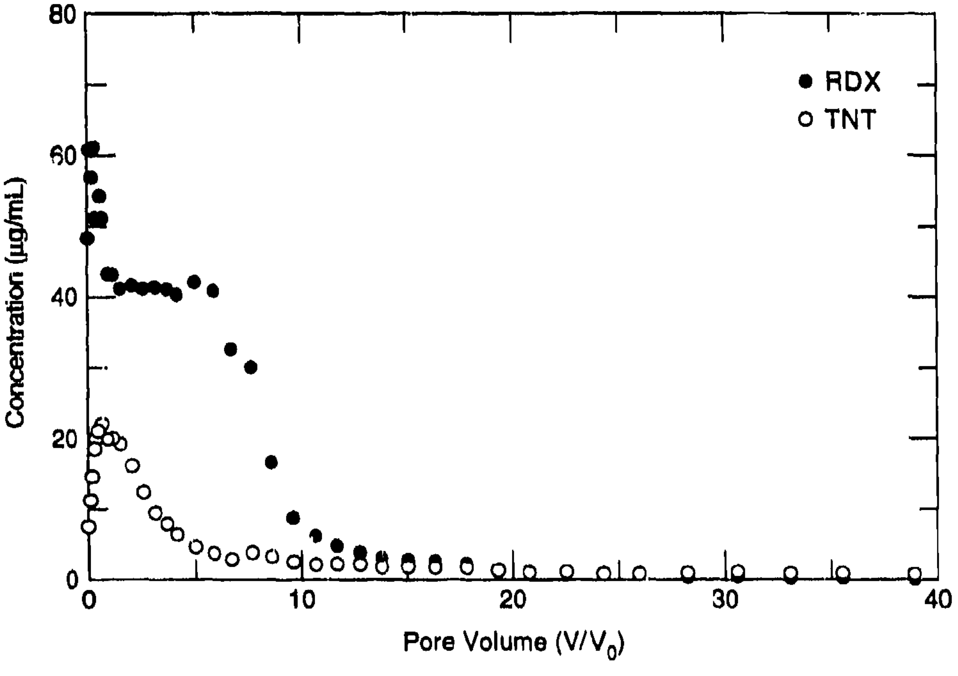


*b. Sample B.*

*Figure 13. Desorption or release of RDX and TNT from the contaminated soil samples obtained from the Louisiana Army Ammunition Plant. Each extraction step represents 1 day of desorption–release time.*



*a. Sample A.*



*b. Sample B.*

*Figure 14. TNT and RDX breakthrough results (pore volume, V/V$_o$, vs. relative concentration, C/C$_0$) for the contaminated soil samples obtained from the Louisiana Army Ammunition Plant. The input solution was 0.005-M Ca(NO$_3$)$_2$.*

extent of TNT recovery was considerably less than 100%. In fact, after some 40 pore volumes, only 50% of TNT in contaminated soil A and 65% of that in soil B were leached out.

## SUMMARY AND CONCLUSIONS

The objective of this investigation was to determine the potential mobility of explosive contaminants in the soil to the groundwater. To achieve this, TNT and RDX sorption–desorption and transport experiments were conducted on a reference clay, contaminated soil from the Louisiana Army Ammunition Plant and two uncontaminated soils. Standard batch experiments were used to determine the extent of adsorption and release of TNT for a wide range of concentrations. In addition, miscible-displacement techniques were used to study the transport of TNT and RDX in soil columns under steady water flow. We found that TNT isotherms for bentonite clay after 1 day of sorption can be described equally well with linear, Freundlich, Langmuir and modified Langmuir models. Results of several desorption steps from successive dilutions indicated that both adsorption and desorption isotherms coincided closely. This indicated a lack of hysteretic behavior of TNT in bentonite clay. Mass balance calculations indicated that TNT retention is also fully reversible. As a result, for the bentonite clay used in this study, there were no irreversible interactions of TNT, such as degradations, within the time of the batch experiments.

Transport results from bentonite–sand miscible-displacement columns indicated that TNT was a highly mobile contaminant and was considered fully conservative in the presence of methanol as the background solution. In fact, TNT transport closely resembled that of a nonreactive species in porous systems. In contrast, TNT was strongly retained (more than 50% of the amount applied) within the bentonite–sand column for a prolonged period when the applied TNT pulse was in 0.005-M $Ca(NO_3)_2$ as the background solution. The use of a convection–dispersion equation with Freundlich (equilibrium) retention and a first-order irreversible reaction adequately predicted the TNT transport results. Poor model predictions were obtained when best-fit parameter values, based on batch retention results, were used to describe the behavior of TNT during transport in the bentonite–sand column. Reasons for this failure were not completely understood and may be attributable to kinetic or time-dependent TNT reactions as well as physical retention by diffusion into clay lattices.

Transport results from Norwood (fine silty) soil columns revealed that TNT was strongly retained in this low-organic-matter (0.32%) and low-clay-content (3%) soil in a manner similar to that in the bentonite–sand columns. We found that the use of a linear reversible retention along with a first-order irreversible (sink) provided a good description of breakthrough results regardless of TNT input pulse concentrations ($C_0$'s). However, the observed slow release of TNT from the miscible displacement columns was not well predicted by the model, nor was it observed for the bentonite–sand column. Slow release is indicative perhaps of kinetic retention of TNT in this soil.

RDX and TNT were released from the contaminated Kolin soil for 8 days before reaching concentrations below the detection limits of experimental (HPLC) measurements. In excess of 90% of the TNT and RDX from the contaminated soil was released within the first 3 days of reaction. Based on our results from two subsamples and three replications, the amount of TNT released from the contaminated soil represented 60% of the amount originally present. In contrast, RDX was completely released. This finding supports transport data from the miscible–displacement experiments, which indicated that 100% of RDX in the contaminated sample was released when a solution of 0.005-M $Ca(NO_3)_2$ was continuously applied for 20 pore volumes. The extent of TNT recovery was considerably less than that for RDX. In fact, after some 40 pore volumes of continuous leaching, about 50% of TNT remained in the contaminated soil samples.

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Batch and miscible-displacement experiments were conducted to determine the extent of adsorption–desorption and transport of 2,4,6-trinitrotoluene (TNT) and 2,3,5-trinitro-1,3,5-triazine (RDX) in soils. A reference bentonite clay, contaminated (Kolin) soil from the Louisiana Army Ammunition Plant, and two uncontaminated soils were used. The TNT isotherm for bentonite clay was described equally well using linear, Freundlich, Langmuir and modified Langmuir models. TNT adsorption and desorption isotherms showed a lack of hysteric behavior, with TNT retention as a fully reversible mechanism. Transport results from bentonite clay columns indicated that TNT was a highly mobile contaminant and fully conservative in the presence of methanol as the background solution. Mobility of TNT was strongly retarded, with some 50% of the applied TNT retained in the bentonite clay column when 0.005-M $Ca(NO_3)_2$ was the background solution. Transport results in Norwood (fine silty) soil columns revealed that TNT was strongly retained in this low-organic-matter and low-clay-content soil. The use of a transport model with either Freundlich or linear retention and an irreversible mechanism predicted the TNT transport data well. Poor predictions were obtained when model parameters based on batch retention data were used. Reasons for model failure may be attributable to TNT sorption-kinetics and retention because of diffusion into clay lattices. Transport results indicated high mobility of RDX with limited retardation, which is consistent with release and transport data from the contaminated soil.

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