Technical Report IRRP-96-1
February 1996

US Army Corps
of Engineers
Waterways Experiment
Station

Installation Restoration Research Program

Recent Developments in Formulating Model Descriptors for Subsurface Transformation and Sorption of TNT, RDX, and HMX

by Dan M. Townsend, North Carolina State University
Tommy E. Myers, WES

Approved For Public Release; Distribution Is Unlimited

Prepared for Headquarters, U.S. Army Corps of Engineers

Installation Restoration
Research Program

Technical Report IRRP-96-1
February 1996

Recent Developments in Formulating Model Descriptors for Subsurface Transformation and Sorption of TNT, RDX, and HMX

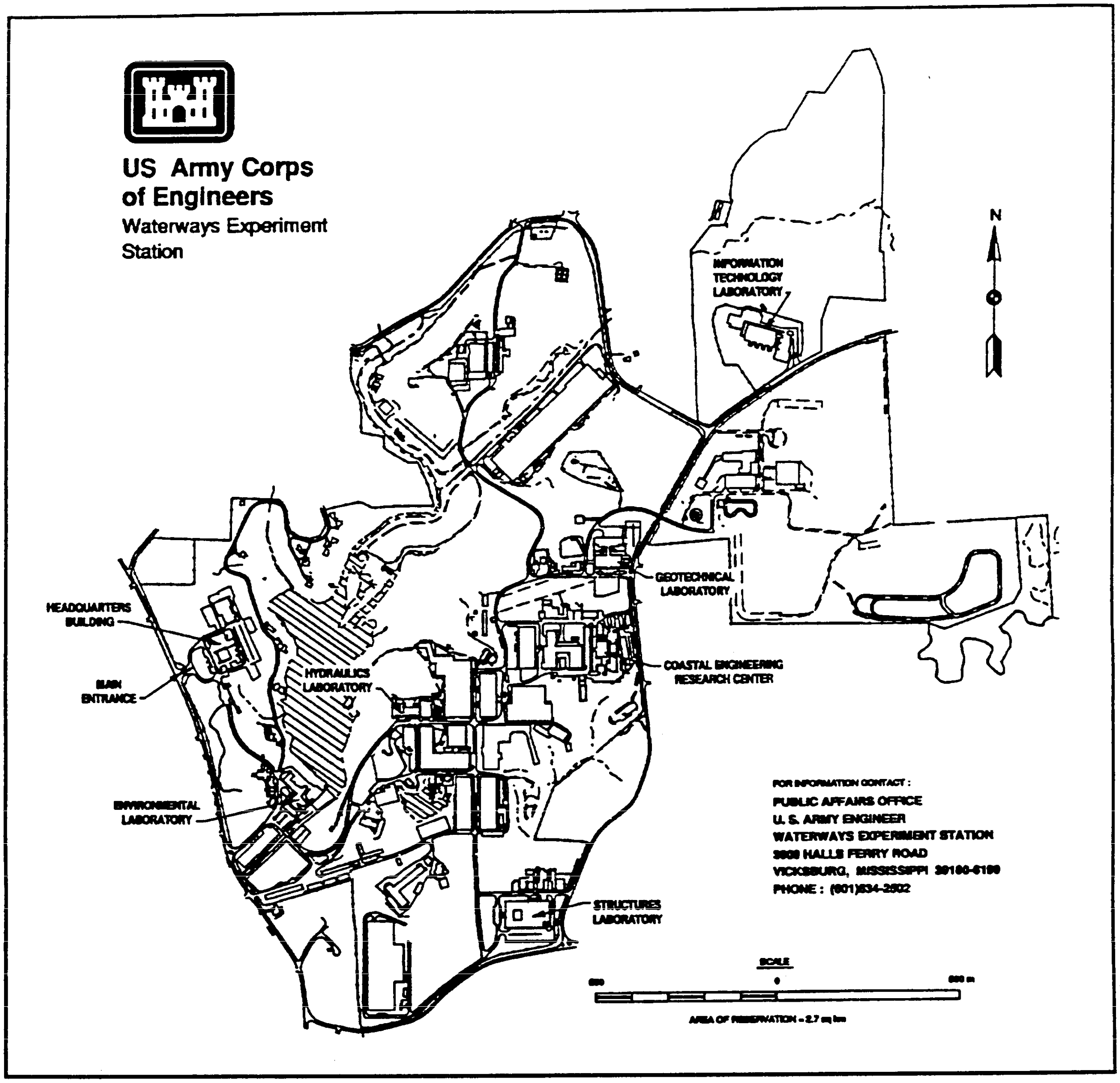
by Dan M. Townsend
North Carolina State University
Raleigh, NC 27650

Tommy E. Myers

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

Final report

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



Waterways Experiment Station Cataloging-in-Publication Data

Townsend, Dan M.
Recent developments in formulating model descriptors for subsurface transformation and sorption of TNT, RDX, and HMX / by Dan M. Townsend, Tommy E. Myers ; prepared for U.S. Army Corps of Engineers.
36 p. : ill. ; 28 cm. — (Technical report ; IRRP-96-1)
Includes bibliographic references.
1. Explosives — Environmental aspects. 2. In situ bioremediation — Research. 3. Groundwater flow — Environmental aspects. 4. Soil absorption and adsorption —Environmental aspects. I. Myers, Tommy E. II. United States. Army. Corps of Engineers. III. U.S. Army Engineer Waterways Experiment Station. IV. Installation Restoration Research Program. V. Title. VI. Series: Technical report (U.S. Army Engineer Waterways Experiment Station) ; IRRP-96-1.
TA7 W34 no.IRRP-96-1

Contents

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, and Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, and Mr. Tommy E. Myers, ERB. 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.

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 Director of WES. Commander was COL Bruce K. Howard, EN.

This report should be cited as follows:

> Townsend, D. M., and Myers, T. E. (1996). "Recent developments in formulating model descriptors for subsurface transformation and sorption of TNT, RDX, and HMX," Technical Report IRRP-96-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

1 Introduction

Background

The Department of Defense is tasked with the cleanup of soils and groundwater at military installations. Subsurface contamination with 2,4,6-trinitrotoluene (TNT), 2,3,5-trinitro-1,3,5-triazine (RDX), and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) has occurred at munitions (manufacturing, loading, packing, and transporting) facilities.

Processes affecting groundwater transport of these explosives include, but are not limited to, convection, hydrodynamic dispersion, biodegradation, abiotic transformations, soil sorption, dissolution, and diffusion (McGrath 1995). Not all processes affect TNT, RDX, and HMX subsurface transport equally, making it important to identify key processes involved and develop accurate descriptors for these processes.

Numerical modeling of contaminant transport, a time- and cost-effective tool for evaluating the effectiveness of remediation alternatives, is based on conceptual models of transport processes. Model formulation for TNT, RDX, and HMX has been hampered by lack of information regarding the key processes involved in subsurface transport of these explosives.

Objectives

The objectives of this report are as follows:

- Present an overview of the processes potentially affecting subsurface transport of TNT, RDX, and HMX.
- Integrate and summarize the laboratory data applicable to modeling subsurface transport of TNT, RDX, and HMX.
- Present values for process descriptors governing subsurface transport of TNT, RDX, and HMX.

- Suggest future research needed to improve the state of knowledge regarding subsurface transport of TNT, RDX, and HMX.

Scope of Report

Laboratory studies have been conducted to improve the state of knowledge regarding subsurface transport of explosives. A review of the early literature was provided by McGrath (1995). Additional studies were conducted during and after preparation of the McGrath (1995) report.

The main focus of this report is transformation and sorption of TNT, RDX, and HMX in the subsurface. A brief overview of other transport processes will also be presented. Table 1 shows the major emphases of the studies reviewed in this report and the type of information provided by each study.

Table 1
Literature Emphasized in This Report

Reference	Batch	Column	TNT	RDX	HMX	Estimated K_d[1]	Estimated μ[2]
McCormick, Feeherry, and Levinson (1976)	✓		✓				
McCormick, Cornell, and Kaplan (1981)	✓			✓			
Leggett (1985)	✓		✓	✓	✓	✓	
Pennington and Patrick (1990)	✓		✓			✓	
Pennington et al. (1992)	✓		✓				
Ainsworth et al. (1993)	✓	✓	✓	✓		✓	✓
Selim and Iskandar (1994)	✓	✓	✓	✓		✓	✓
Pennington et al. (1995b)	✓	✓	✓	✓	✓	✓	✓
Townsend, Myers, and Adrian (1995)		✓	✓			✓	✓
Myers et al. (In Preparation)	✓	✓	✓	✓	✓	✓	✓
Price and Brannon (1995)	✓		✓				

[1] Linear equilibrium distribution coefficient.
[2] Pseudo-first-order transformation rate constant.

2 Theory

General

Processes involved in transformation and sorption of TNT, RDX, and HMX in the subsurface are shown in Figure 1. Processes shown in bold are thought to be major mass transfer mechanisms for these explosives. Transformation products (TPs) of TNT, RDX, and HMX may also be affected by these processes. Not shown in Figure 1 are advection, dispersion, and volatilization. Advection and dispersion typically are important transport processes, but these processes are not the focus of this report. Volatilization has been shown to be relatively unimportant for TNT, RDX, and HMX (Pennington et al. 1992; McGrath 1995).

The general partial differential equation describing one-dimensional solute transport is:

$$\frac{\partial C}{\partial t} = \frac{\partial (VC)}{\partial X} + \frac{\partial\ D(\partial C)}{\partial X^2} + S \tag{1}$$

(Time rate of change = Advection + Dispersion + Sources and sinks)

where

C = solution phase concentration, M/L^3

t = time

V = average pore water velocity, L/t

X = distance, L

D = dispersion coefficient, L^2/t

S = sum of sources and sinks, M/L^3t

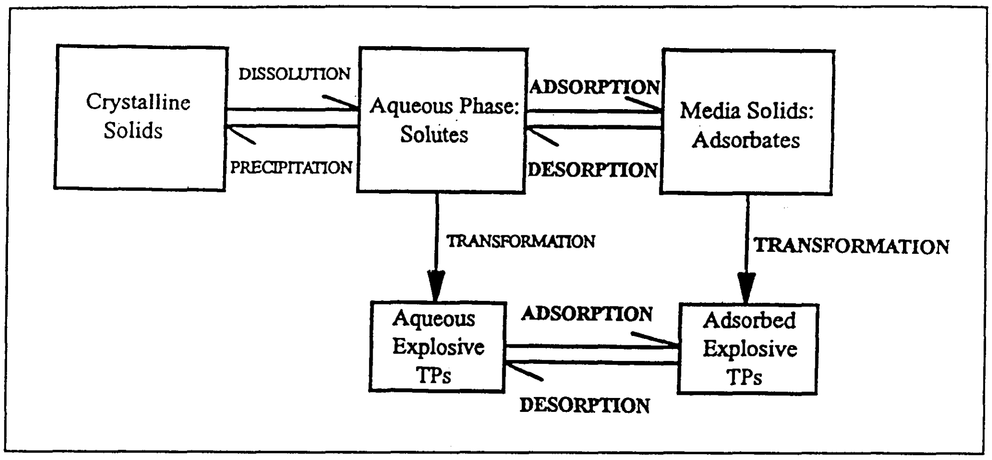


Figure 1. Subsurface phases for TNT, RDX, and HMX

M = mass

L = length

This report focuses on the sources and sinks term in Equation 1. The major source for many contaminated soils is desorption. Dissolution is a major source in highly contaminated soils containing solid explosives. Transformation of parent compounds is the obvious source of TPs. Major sinks include transformation and adsorption. Precipitation can be a sink if dissolved concentrations exceed the solubility limit.

Transformation

Transformation of explosives such as TNT, RDX, and HMX has been observed (McCormick, Feeherry, and Levinson 1976; McCormick, Cornell, and Kaplan 1981; Kaplan and Kaplan 1982; Ainsworth et al. 1993; Pennington et al. 1995b; Townsend, Myers, and Adrian 1995; Myers et al., In Preparation; Price and Brannon, In Preparation). Most of the work on transformation of explosives in soils has focused on TNT transformation. Although there is evidence from mass balance calculations that RDX and HMX also undergo transformation, RDX and HMX transformation products have not been measured due to lack of microanalytical procedures.

TNT

McCormick, Feeherry, and Levinson (1976) found that TNT transforms in both aerobic and anaerobic systems. These transformations, under both aerobic and anaerobic conditions, were found to be reductions of the nitro groups on the TNT molecule. Depending on the reducing potential of the system, one, two, or three of the nitro groups could be reduced to amino groups.

Kaplan and Kaplan (1982) studied the transformation of TNT and suggested the transformation pathways shown in Figure 2. The pathways consist of nitro-to-amino reductions and hydroxylamino intermediates coupling to form azoxy compounds. In their study, the aromatic ring was not cleaved, and nitro-to-amino reduction at the para (4) position was preferred relative to reduction at the ortho (2) positions.

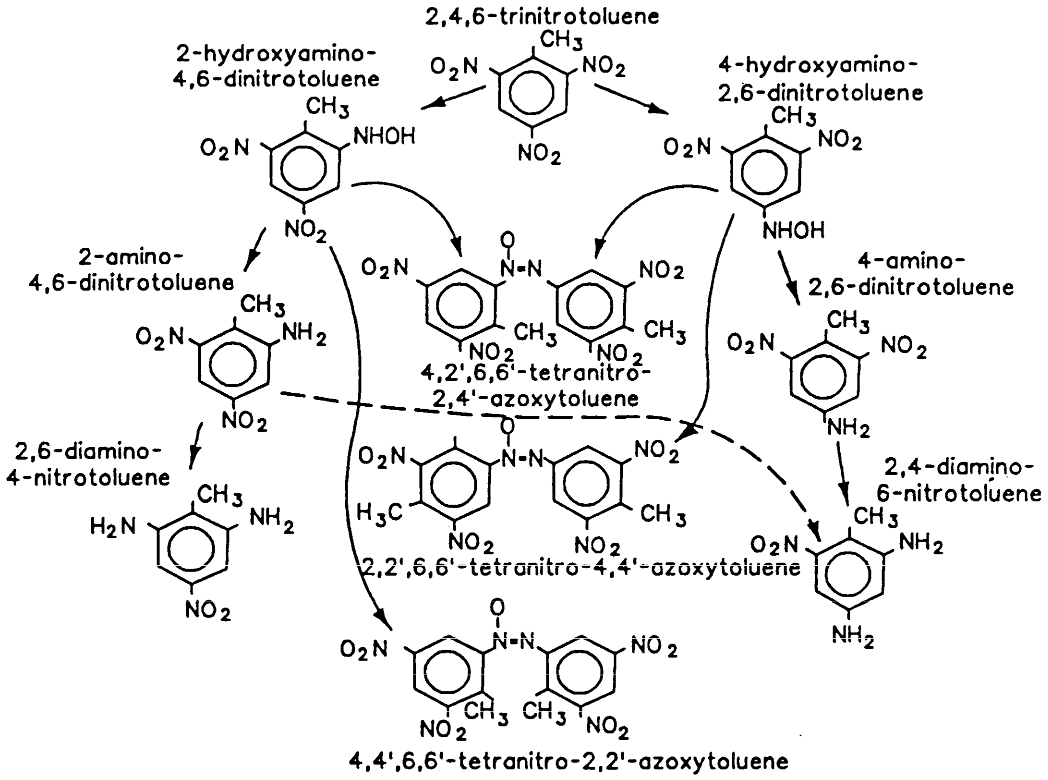


Figure 2. TNT transformation pathway diagram (from McGrath 1995)

Ainsworth et al. (1993) studied five soils, all of which were sterilized, and found that TNT was reduced in all of these. Several amino compounds, 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), and 2,4-diamino-6-nitrotoluene (2,4-DANT) were produced, 2A-DNT being the most common. Estimated TNT pseudo-first-order transformation rate constants (μ) were between 1.7×10^{-3} and 8.7×10^{-3} hr^{-1}. Ainsworth et al. (1993) suggested that the TNT transformation process is diffusional, since TNT transformation was more significant at lower pore water velocities. Their findings indicate that sorption is required before transformation, and that only a portion of TNT sorption sites are involved in TNT transformation. Ainsworth et al. (1993) suggested that iron porphyrins and quinones could be involved in abiotic TNT transformation, and that these compounds could be regenerated under reduced conditions.

In thin-disk experiments (0.32-cm soil length), Townsend, Myers, and Adrian (1995) observed TNT transformation to the products 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-diamino-4-nitrotoluene (2,6-DANT). The product 4A-DNT was the most significant transformation product, as would be expected from Kaplan and Kaplan (1982) work. Transformation to azoxy compounds was insignificant. Of the three soils used (silt loam, clay-rich, and Ottawa sand), the silt showed the most potential for TNT transformation, followed by the clay, and the sand. Measured transformation rate constants ranged from 0.008 to 0.025 hr^{-1}. After pumping over 150 and 200 pore volumes of TNT-contaminated feed solution through the silt and clay soils, respectively, TNT transformations were still occurring, indicating that TNT transformations were biotic, biologically mediated, or if primarily abiotic, that an abiotic soil constituent responsible for TNT transformations was constantly being renewed. Virtually all of the TNT introduced to the columns could be accounted for as TNT and TNT transformation products (100 ± 5 percent).

Myers et al. (In Preparation) reported TNT transformations in both batch and column studies. In batch studies with a clay, TNT transformation to 2A-DNT and 4A-DNT was observed under aerobic-biotic conditions. Accumulation of these products was low and could only account for a small portion of TNT disappearance. Under aerobic-abiotic conditions (irradiated soil), 2A-DNT and 4A-DNT were not found. The appearance of reductive transformation products in the aerobic-biotic test is evidence of microanaerobic regions around soil particles. In the anaerobic-biotic batch test, essentially all TNT disappeared from solution after 24 hr. TNT disappearance was accompanied by the appearance of 2A-DNT, 4A-DNT, and trace amounts of 2,4-DANT and 2,6-DANT. Under anaerobic-abiotic conditions, some TNT disappeared from solution phase, but solution-phase TNT concentrations became steady after 24 hr. The anaerobic-abiotic TNT disappearance was not accompanied by the appearance of transformation products. In both anaerobic tests, TNT in solution declined rapidly, recovered somewhat, and then gradually declined again. In the anaerobic-biotic test, as TNT in solution recovered, 2A-DNT and 4A-DNT increased, suggesting competitive sorption. The disappearance of TNT and the measurement of TNT transformation in batch tests conducted by Myers et al. (In Preparation) has significant implications for the literature on TNT equilibrium sorption coefficients. These implications are discussed in the section on the significance of sorption (p. 17).

Myers et al. (In Preparation) conducted 15-cm length soil column studies with the same soils (silt loam, clay-rich, and Ottawa sand) used by Townsend, Myers, and Adrian (1995) in thin-disk studies. The results showed that TNT disappearance was greatest in the silt, followed by the clay and the sand, which is in agreement with the results of the thin-disk studies by Townsend, Myers, and Adrian (1995). Myers et al. (In Preparation) measured TNT reductive transformation products in each of the column effluents. The product 2,4-DANT was the most significant, indicating that TNT reduction preferentially follows TNT --> 4A-DNT --> 2,4-DANT pathway. This preference has been shown by others (Kaplan and Kaplan 1982; Townsend, Myers, and Adrian 1995). Analyses of the sectioned soil columns after completion of the experiments revealed low concentrations of TNT, 2A-DNT, 4A-DNT, 2,4-DANT, 2,6-DANT in the soil phase. Residual concentrations were highest in the silt, and no residuals were measured in the sand. The silt TNT, 2A-DNT, and 4A-DNT residuals were skewed toward the column inlet, while the silt 2,4-DANT and 2,6-DANT residuals were skewed toward the outlet. The clay residuals showed no skewness.

Myers et al. (In Preparation) calculated TNT mass balances (in molar equivalents) for each column. About 84 percent of the TNT introduced to the silt could be accounted for as the sum of TNT eluted, TNT transformation products eluted, residual TNT, and residual TNT transformation products. Most of this mass was in the form of 2,4-DANT (59.4 percent) and 2,6-DANT (17.3 percent). Only 0.4 percent of the TNT introduced to the silt remained in the form of TNT. In the clay, only 16 percent of the TNT introduced could be accounted for, and most of this was in the form of transformation products, primarily 2,4-DANT and 2,6-DANT. Approximately 3.3 percent of the TNT introduced to the clay remained in the form of TNT. The poor mass balance for the clay was largely due to experimental problems associated with clay swelling during testing. It is also possible that unmeasured transformation products were produced or that disappearance processes other than reductive transformation were operative in the clay soil. In contrast to the silt and clay soils, about 98 percent of the TNT introduced to the sand was accounted for, and virtually all of this was in the form of TNT eluted (97.5 percent). The majority of the remaining mass accounted for was in the form of 2A-DNT (0.4 percent).

Estimated TNT pseudo-first-order transformation rate constants (μ) in the 15-cm soil columns used by Myers et al. (In Preparation) were 14×10^{-2}, 8.3×10^{-2}, and 0.32×10^{-2} hr^{-1} for silt, clay, and sand, respectively. These rate constants are higher than the ones reported by Townsend, Myers, and Adrian (1995) for the same soils and may reflect differences in oxidation-reduction potentials (Eh) related to differences in column lengths. The columns used by Myers et al. (In Preparation) were much longer (15 cm versus 0.32 cm) than the ones used by Townsend, Myers, and Adrian (1995). Although Eh was not measured in either experiment, the longer columns were probably operating at lower Eh.

Price and Brannon (1995) performed batch experiments to determine the effects of Eh and pH on the extent of TNT transformation in soil (clay). The influence of selected soil constituents (Fe^{2+}, kaolinite, and montmorillonite) on TNT transformation was also studied. Four Eh levels (+500, +250, 0, and -150 mV) and four pH levels (5.0, 6.0, 7.0, and 8.0) were studied. This study showed that reducing conditions promote TNT transformation and disappearance of TNT transformation products.

Results indicated that TNT was not stable at any Eh/pH combination. TNT was most stable at Eh = 0 mV and pH 5.0, and was most susceptible to transformation (total disappearance in 1 day) under highly reduced conditions (Eh = -150 mV), regardless of pH. After 1 day, the transformation products 2A-DNT and 4A-DNT were present in solution at all Eh/pH combinations, and the products 2,4-DANT and 2,6-DANT were present in the solution phase of the Eh = 0 and Eh = -150 mV tests. Concentrations of 2,4-DANT and 2,6-DANT increased in the Eh = -150 mV treatment compared with the Eh = 0 mV treatment with a corresponding decrease in 2A-DNT and 4A-DNT. After 14 days, TNT was not present in any of the soils at all Eh/pH combinations.

In addition to the studies with soil, Price and Brannon (1995) performed experiments designed to test the abilities of specific soil components to mediate TNT transformation. The soil components tested included Fe^{2+}, kaolinite, and montmorillonite. No significant disappearance of TNT was observed from treatments with any of the soil components alone. Rapid disappearance of TNT from solution was observed in treatments with montmorillonite + Fe^{2+} and in treatments with kaolinite + Fe^{2+}. In these treatments, 90 percent of added TNT disappeared within 24 hr. These results support the idea that Fe^{2+} is a key component in TNT transformation. Under reduced conditions, Fe^{2+} provides the electrons needed to reduce nitro groups to amines. The Fe^{3+} that results may be used as an electron acceptor by microbes. Microbial reduction of Fe^{3+} yields Fe^{2+}, and the cycle is complete. The disappearance of TNT in the batch studies of Price and Brannon (1995) has significant implications for TNT sorption and transformation modeling as will be discussed in the section on the significance of sorption (p. 17).

RDX and HMX

A scheme for the biodegradation of RDX (Figure 3) has been proposed (McCormick, Cornell, and Kaplan 1981). In this scheme, RDX degrades through a series of nitro group reductions to a point where ring fragmentation occurs. RDX degradation was found to occur only under anaerobic conditions.

Myers et al. (In Preparation) conducted aerobic RDX batch experiments with clay under both biotic and abiotic conditions. Differences in RDX recoveries between the biotic (63 percent) and abiotic (91 percent) tests suggest significant amounts of RDX biodegradation. If aerobic RDX biodegradation does not occur (McCormick, Cornell, and Kaplan 1981), it may be that observations by Myers et al. (In Preparation) are due to microanaerobic regions around soil particles within a macroaerobic environment.

Myers et al. (In Preparation) performed column studies with RDX and HMX. Mass balance analysis indicated that disappearance of both RDX and HMX occurred in the silt and clay. About 67, 62, and 108 percent of the RDX introduced to the silt, clay, and sand, respectively, could be accounted

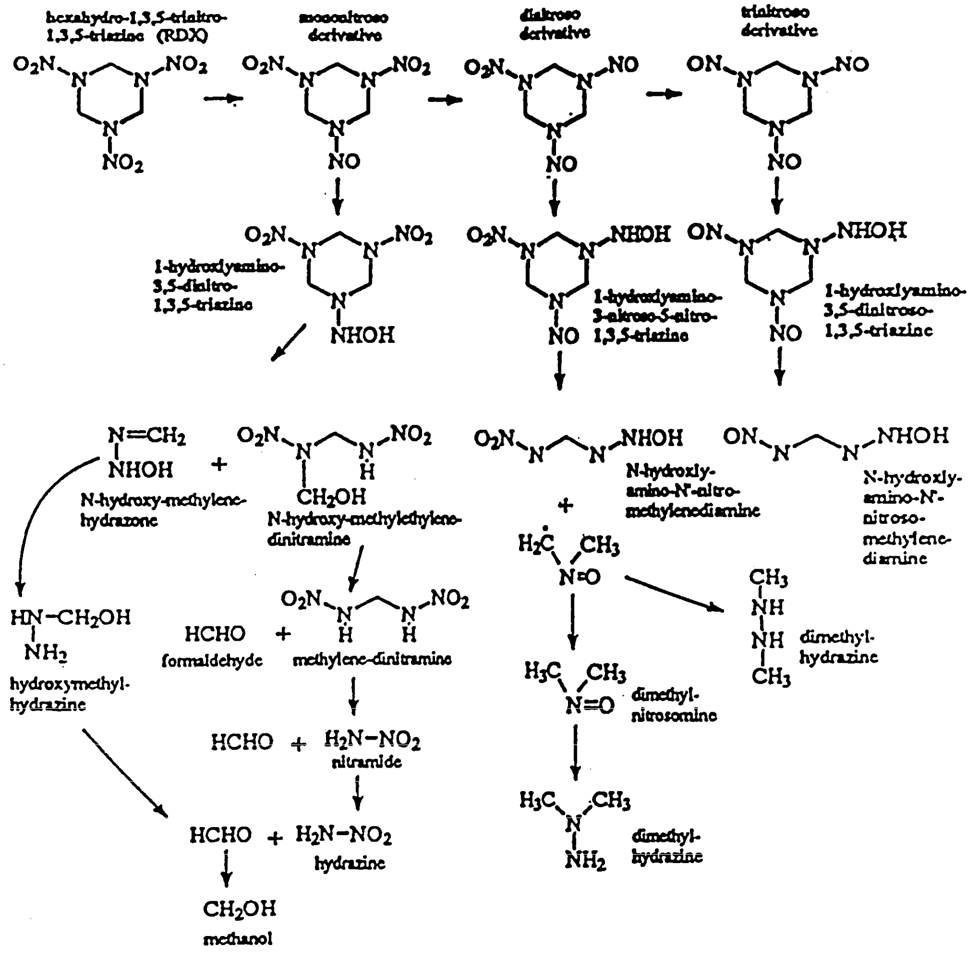


Figure 3. RDX biodegradation scheme (from McGrath 1995)

for in the effluent. About 97, 55, and 109 percent of the HMX introduced to the silt, clay, and sand, respectively, could be accounted for in the effluent. Although RDX and HMX transformation product analysis was not conducted, biodegradation was suspected in the disappearance of these compounds. Analysis of the sectioned soil columns after the end of the experiments revealed no RDX or HMX remaining in the soil phase. Estimated first-order RDX transformation rate constants were 0.65 × 10^{-2}, 1.4 × 10^{-2}, and 0.0 hr^{-1} for silt, clay, and sand, respectively. Estimated first-order HMX transformation rate constants were 0.36×10^{-2}, 3.2×10^{-2}, and $0.0\ hr^{-1}$ for silt, clay, and sand, respectively.

Soil Sorption

Soil sorption is an important process that retards the movement of contaminant plumes in the subsurface. Factors affecting sorption include the chemical characteristics of the inorganic and organic fractions of the medium, chemical characteristics of the solute, temperature, and pH (Tchobanoglous and Schroeder 1985).

Many mathematical formulations for sorption are available (McGrath 1995). Sorption models are broadly classified as equilibrium or nonequilibrium. Equilibrium sorption implies that the rates of adsorption and desorption are equal. In order for equilibrium to be attained, groundwater flow must be slow relative to the reactions taking place (Valocchi 1985). The equilibrium assumption greatly simplifies the mathematics of contaminant transport, making it very attractive. However, for some combinations of pore water velocity and sorption kinetics, the equilibrium assumption may not be valid. In these cases, nonequilibrium models may better describe sorption.

Research on soil sorption of TNT, RDX, and HMX has addressed the following questions:

- Can TNT, RDX, and HMX sorption be modeled with equilibrium-type equations; and if so, what type of isotherm should be used?
- What soil parameters/environmental controls are important in determining the extent of TNT, RDX, and HMX sorption?
- How is the sorption of TNT, RDX, and HMX influenced by the presence of cosolutes?

Sorption of explosives such as TNT, RDX, and HMX has been investigated in several studies (Leggett 1985; Pennington and Patrick 1990; Ainsworth et al. 1993; Selim and Iskandar 1994; Pennington et al. 1995b; Townsend, Myers, and Adrian 1995; Myers et al., In Preparation). Results from these studies have varied. Reported linear equilibrium distribution coefficients (K_d) are tabulated in Appendix A.

TNT

Leggett (1985) studied the sorption of TNT on bentonite drilling muds in batch tests. Leggett (1985) suggested a dual component sorption model for TNT, fitting a Langmuir isotherm to low concentration data and a linear isotherm to high concentration data. This type of formulation suggests that

TNT sorption is a simultaneous combination of two separate sorption mechanisms. TNT sorption on bentonite was similar to TNT sorption on sediments, suggesting that the clay content of natural sediments is important in the sorption of these compounds.

Cosolute effects on TNT sorption were also studied (Leggett 1985). Results showed that the sorption of TNT was lower when dinitrotoluene (DNT) was present as a cosolute, suggesting that TNT and DNT compete for the same sorption sites and that TNT sorption may also be affected by the presence of other contaminants in groundwater.

Pennington and Patrick (1990) performed TNT batch tests on 16 soils and found that the Langmuir isotherm gave the best fit to their data. In their study, TNT sorption correlated well with extractable iron, cation exchange capacity (CEC), and percent clay. TNT sorption correlated poorly with fraction of organic carbon (f_{oc}), extractable calcium, aluminum, and manganese, pH, and electrical conductivity.

Ainsworth et al. (1993) performed TNT batch experiments and found that the Freundlich model best fit the data. In their study, TNT sorption correlated well with pH, CEC, and f_{oc}.

Ainsworth et al. (1993) also performed continuous flow (column) tests with TNT. They found that at fast pore water velocities (0.012 cm/s), TNT sorption could be described with a reversible, nonlinear (Freundlich) model. At lower pore water velocities (0.0056 cm/s), breakthrough curve (BTC) asymmetry was observed. The BTC tailing (asymmetry) is evidence of some type of nonequilibrium process.

Cosolute effects on the sorption of TNT and RDX were studied by Ainsworth et al. (1993). Their data suggest that both solutes utilize at least a fraction of the same sorption sites. Competition by these solutes for sorption sites reduced the sorption of individual solutes compared with their single solute sorption values.

Selim and Iskandar (1994) performed batch and column tests with TNT. They found that a TNT sorption isotherm for pure bentonite clay could be described equally well using linear, Freundlich, Langmuir, and extended Langmuir (Leggett 1985) models. Desorption studies indicated that TNT sorption was reversible. In column studies with a Norwood soil and average pore water velocities of 2.1×10^{-4} and 2.5×10^{-4} cm/s, Selim and Iskandar (1994) found that use of a transport model with either Freundlich or linear retention and an irreversible mechanism predicted TNT elution reasonably well.

Townsend, Myers, and Adrian (1995) performed TNT column studies using three major soil classes: silt, clay, and sand. They found that TNT retention was higher in the clay than in the silt, and higher in the silt than in the sand. The data indicated that a linear equilibrium sorption model could be used to capture the essence of the BTCs at the velocities used (4.96×10^{-5} to 9.44×10^{-5} cm/s).

Myers et al. (In Preparation) conducted batch experiments under both biotic and abiotic conditions, and under both aerobic and anaerobic conditions. Batch data indicated rapid sorption of TNT, followed by disappearance from the soil phase. The biotic data indicated correlation of TNT sorption to clay content and f_{oc}. The abiotic data were too inconsistent for comparisons between the biotic and abiotic experiments to be drawn. Myers et al. (In Preparation) were not able to obtain steady TNT concentrations in either the sorbed or dissolved phases.

In aerobic tests, TNT sorption was rapid under both biotic and abiotic conditions. In anaerobic tests, larger differences in biotic and abiotic solution-phase TNT concentrations were observed, suggesting anaerobic biodegradation of TNT. In all batch tests, TNT transformation products were formed that competed with TNT for sorption sites.

Column tests were also performed by Myers et al. (In Preparation) using the same soils (silt, clay, sand) as Townsend, Myers, and Adrian (1995). Linear equilibrium sorption provided good fits to the data for the pore water velocities used (1.2×10^{-4} to 1.6×10^{-4} cm/s).

RDX and HMX

Leggett (1985) studied the sorption of RDX and HMX on bentonite drilling muds in batch and found that the sorption of these explosives was linear. RDX sorption on bentonite was similar to RDX sorption on sediments, suggesting that the clay content of natural sediments is important in the sorption of RDX. Leggett (1985) found that the sorption of RDX and HMX was unaffected by the presence of each other in solution, probably because of their low sorption potential compared with the sorption capacity of the soil.

Ainsworth et al. (1993) performed batch and column tests with RDX. In both the batch and column tests, RDX sorption fit a linear model. RDX sorption was found to be reversible.

Selim and Iskandar (1994) studied the sorption of RDX and found RDX to be extremely mobile.

Myers et al. (In Preparation) performed batch tests with RDX and column tests with RDX and HMX. Batch experiments were performed under both biotic and abiotic conditions. Sorption of RDX under biotic conditions was rapid, occurring on the order of minutes. Differences in the recoveries of RDX between the biotic and abiotic tests suggested RDX biodegrades.

In column tests (Myers et al., In Preparation), sorption of RDX and HMX was low. RDX sorption could be modeled using linear equilibrium sorption.

Some breakthrough curve tailing was observed for HMX, suggesting that HMX sorption may be nonlinear or nonequilibrium controlled.

Dissolution

Explosives may be present in some soils as crystalline solids. Mobility of explosives from soils containing crystalline solids is controlled primarily by the aqueous solubility of the explosives. The aqueous solubility of a given explosive represents the maximum concentration of explosive that could be in solution. Once dissolved, explosives can be moved from the crystal surface into the bulk solution by diffusive transport. The aqueous solubilities and molecular diffusion coefficients of TNT, RDX, and HMX are generally low (Tables A1, A2, A3).

Pennington et al. (1995b) conducted batch desorption kinetics studies with four field-contaminated soils. Each of the soils contained TNT, and two of the soils contained RDX and HMX. Solution phase concentrations were measured periodically as soils were equilibrated with distilled deionized water. In three of these soils, TNT solution-phase concentrations reached the aqueous solubility of TNT and remained steady, indicating solubilization of crystalline TNT from the soil. RDX and HMX solution-phase concentrations showed the same type of behavior in one of the soils.

Sequential batch tests were also conducted (Pennington et al. 1995b) with these four soils. Sequential desorption isotherms were vertical for each soil, indicating that the solution phase was saturated with each successive dilution by solubilization of crystalline TNT. The isotherm for one soil suggested that the soil was becoming exhausted of TNT and that the solution concentrations were becoming governed by desorption from the soil solids. Pennington et al. (1995b) suggested that dissolved TNT concentrations are solubility limited when soil TNT concentrations exceed 1,500 mg/kg.

Pennington et al. (1995b) conducted column desorption experiments with a field-contaminated soil containing TNT, RDX, and HMX. The TNT elution curve rapidly declined and then held steady at about 1/3 of the initial effluent concentration. Chemical analysis of the sectioned column after elution revealed a high TNT concentration in a section near the column outlet. In spite of thorough mixing, the soil column was not homogeneous, and the shape of the TNT elution curve and the dissolved TNT concentrations in the effluent were affected by dissolution of crystalline TNT.

Volatilization

Volatilization is usually viewed as an insignificant environmental pathway for TNT, RDX, and HMX due to their low vapor pressures and Henry's Constants (Tables A1, A2, A3) (McGrath 1995). Pennington et al. (1992)

found that volatile losses of TNT and TNT transformation products in a series of wetting and drying experiments were limited (approximately 1 percent or less). Volatilization may be important for some explosive reaction products with lower molecular weights than TNT, RDX, and HMX.

3 Discussion

Significance of Transformation

TNT

Reductive transformation has been established as a key mechanism in TNT subsurface transport. Measured transformation products (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982; Ainsworth et al. 1993; Townsend, Myers, and Adrian 1995; Myers et al., In Preparation; Price and Brannon 1995) provide unequivocal evidence of reductive transformation of TNT in soils. Pseudo-first-order TNT transformation rate constants (μ) have been measured from 0.17×10^{-2} to 14.0×10^{-2} hr^{-1} (Table A1).

TNT transformation involves sequential nitro group to amino group reductions. Generally, observed transformation products include 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT. Transformation to azoxytoluene compounds are insignificant compared with nitro group to amino group reductions (Townsend, Myers, and Adrian 1995; Myers et al., In Preparation), but these transformations have been identified (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982). Azoxy compound formation may be intermediate to further polymerization, making detection of azoxy compounds less likely if polymerization is a fast reaction. In the majority of studies where transformation products were measured, either 4A-DNT or 2,4-DANT was the most significant product formed, indicating that the TNT --> 4A-DNT --> 2,4-DANT pathway is the preferred reduction route.

The body of evidence suggests that TNT transformations are biologically mediated. Townsend, Myers, and Adrian (1995) pumped over 150 and 200 pore volumes of TNT-contaminated feed solution into silt and clay, respectively, and found that TNT transformations were still occurring at the end of the loading step. These data suggest a nonexhaustible transformation process, which is consistent with biological transformation. Furthermore, Price and Brannon (1995) tested several specific soil components for their abilities to transform TNT. When montmorillonite, kaolinite, or Fe^{2+} alone were tested, no transformations were observed. However, when montmorillonite or kaolinite was combined with Fe^{2+}, significant amounts of transformation were observed, suggesting that Fe^{2+} plays an important role in TNT reductions. The fact that Fe^{2+} alone could not transform TNT suggests that microorganisms and/or surfaces are also needed. Price and Brannon (1995) suggested that under anaerobic conditions, Fe^{3+} is biologically reduced to Fe^{2+}, which in turn reduces nitro groups to amino groups and Fe^{3+}, thus forming a cycle. This idea has also been postulated by Ainsworth et al. (1993). In experiments where both sterilized and unsterilized soils were used (Pennington and Patrick 1990; Myers et al., In Preparation), transformations were observed under both conditions, indicating the presence of a purely abiotic transformation component. Since transformations are far more extensive in unsterilized soils than in sterilized soils, the abiotic transformation component is small compared with the biotic transformation component.

TNT transformations are significantly enhanced under anaerobic conditions, as would be expected since the predominant transformations in soils are reduction reactions. Data from Price and Brannon (1995) indicated that TNT was not stable at any Eh tested (+500, +250, 0, -150 mV), and that TNT was the most unstable at Eh = -150 mV and pH 8.0.

Generally, mass balances indicate that TNT disappearance cannot be fully accounted for as measured reductive transformation products (2A-DNT, 4A-DNT, 2,4-DANT, 2,6-DANT, and azoxytoluenes), which suggests other transformation products (triaminotoluenes, etc.) are being produced and/or some of the TNT is being bound to the soil in unmeasured and, perhaps, unextractable forms (i.e., chemisorption). Evidence for binding loss is shown in the radioisotope work of Price and Brannon (1995) and the composting studies by Pennington et al. (1995a). There is also the possibility of azoxy compound polymerization. TNT mineralization to CO_2 and H_2O has not been significant in laboratory studies. The radiolabeled work of Price and Brannon (1995) showed that a small amount of TNT was mineralized as CO_2 (0.09 to 2.7 percent). Pennington et al. (1992) found that less than 1 percent of the TNT introduced to their system was mineralized as CO_2.

RDX and HMX

Research has indicated that RDX is also affected by transformation (McCormick, Cornell, and Kaplan 1981; Myers et al., In Preparation). McCormick, Cornell, and Kaplan (1981) proposed a pathway scheme for the biodegradation of RDX (Figure 3) and suggested that RDX degradation occurs only under anaerobic conditions. This scheme involves reduction of nitro groups until destabilization and breakage of the ring occurs. Mass balances for column experiments (Myers et al., In Preparation) indicated that RDX disappearance occurred. Although column eluates were not analyzed for RDX transformation products, soil analysis for RDX showed that RDX was not retained in the columns. HMX disappearance was also observed by Myers et al. (In Preparation), suggesting that HMX biodegradation may also have occurred. First-order RDX transformation rate constants (μ) have been reported from 0 to 1.0×10^{-1} hr^{-1} (Table A2). First-order HMX transformation rate constants (μ) have been reported from 0 to 9.0×10^{-2} hr^{-1} (Table A3).

Significance of Sorption

TNT

Several investigators (Leggett 1985; Pennington and Patrick 1990; Ainsworth et al. 1993; Selim and Iskandar 1994) have reported batch-determined equilibrium sorption coefficients. The isotherm plots in all these studies are well behaved and in all respects appear to be reliable data. The batch experiments of Myers et al. (In Preparation) and Price and Brannon (1995), however, show that TNT in batch tests does not reach nonzero steady concentrations in either soil or dissolved phases due to transformation reactions. Thus, a portion of the literature on TNT sorption highlights measurement of constants for equilibrium partitioning of TNT between soil and water phases, and another portion of the literature emphasizes TNT transformation and the absence of equilibrium concentrations in soil and water phases. Causes for these radically different perspectives include confusion over sorbed TNT concentrations, ill-defined redox conditions during batch testing, and variable exposure time of the soil to water.

Ainsworth et al. (1993), Myers et al. (In Preparation), and Price and Brannon (1995) measured both dissolved and soil phase TNT concentrations. In the batch studies of Leggett (1985), Pennington and Patrick (1990), and Selim and Iskandar (1994), only TNT dissolved-phase concentrations were measured. In the absence of measured soil-phase TNT concentrations, sorbed concentrations are calculated by difference, that is, the TNT that disappears from the water phase is assumed to have been sorbed by the soil phase. Thus, calculated sorbed concentrations reflect both TNT disappearance from solution by sorption and transformation (unmeasured). Ainsworth et al. (1993) suggested that soil-phase concentrations be measured directly. TNT transformations were occurring, but that modeling results appeared to be independent of TNT mass transformed. The direct measurements of soil-phase TNT concentrations by Myers et al. (In Preparation) and Price and Brannon (1995) showed that equilibrium in the sorbed phase is not reached because TNT continues to transform, especially under anaerobic conditions.

Redox conditions have not been measured during batch testing with the exception of the Price and Brannon (1995) study, which showed that redox is a major environmental factor affecting TNT transformation. Redox conditions in an uncontrolled batch test are highly variable and depend on the head space gas, initial concentration of oxygen in the water and soil organic matter, iron, manganese, sulfur, and numerous other substances. TNT transformation is more rapid when nitrogen is the head space gas and deaired water is used than when air is the head space gas and air-equilibrated water is used (Myers et al., In Preparation). Since TNT is not stable under any redox conditions (Price and Brannon 1995), TNT transformation probably occurred in the studies of Leggett (1985), Pennington and Patrick (1990), Ainsworth et al. (1993), and Selim and Iskandar (1994), but the significance of transformation on the sorption data is not known.

The validity of batch equilibrium sorption coefficients for TNT is even more questionable when it is realized that their determination involved the assumption that equilibrium has been reached. Merely separating dissolved and particulate phases does not answer the question of whether or not equilibrium is achieved within the time in which the two phases are in contact.

However, some type of sorption formulation, in addition to a transformation component, is needed to obtain good fits for TNT soil column breakthrough curves (Ainsworth et al. 1993; Selim and Iskandar 1994; Townsend, Myers, and Adrian 1995; Myers et al., In Preparation). In soil column studies, linear equilibrium-controlled sorption has been the preferred model formulation for sorption. TNT sorption in soil columns has been studied under a variety of flow conditions. Good fits were obtained using linear equilibrium-controlled sorption for average pore water velocities ranging from 10^{-5} to 10^{-2} cm/s (Ainsworth et al. 1993; Selim and Iskandar 1994; Townsend, Myers, and Adrian 1995; Myers et al., In Preparation).

The apparent disparity between the soil column data (TNT sorption is equilibrium controlled) and the batch data of Myers et al. (In Preparation) and Price and Brannon (1995) (equilibrium between soil and water phases is not possible for TNT) can be explained as rapid TNT sorption relative to soil column pore water velocities and transformation rates. Equilibrium-controlled sorption in a soil column model implies instantaneous adsorption-desorption. TNT transformation after sorption is not contradictory to model structure (governing partial differential equation). The good fits imply that the model structure is properly formulated. It is also possible that equilibrium sorption coefficients obtained from soil column studies are calibration or curve-fitting parameters and are of questionable value for field transport models.

RDX and HMX

Studies have indicated that RDX sorption can be described well using linear equilibrium sorption (Leggett 1985; Ainsworth et al. 1993; Selim and Iskandar 1994; Myers et al., In Preparation). Much less data are available on the sorption of HMX; but in column studies (Myers et al., In Preparation), HMX sorption was approximately described using a linear equilibrium approach, although some evidence of nonequilibrium or nonlinearity was observed. Measured RDX K_ds have been reported from 0 to 6.75 ℓ/kg (Table A2). Measured HMX K_ds have been reported from 0 to 13.25 ℓ/kg (Table A3). Both RDX and HMX have been observed to be affected by transformations. These transformations have been shown to be much less significant than TNT transformation.

4 Summary

Transformation and sorption are key processes involved in the subsurface transport of TNT, RDX, and HMX. Research has focused on model structure identification and obtaining estimates of process parameters. The important information gathered from previous works is as follows:

- Comparison of observed and fitted soil column breakthrough curves shows that models formulated to describe sorption as linear equilibrium-controlled and transformation as first-order adequately describe TNT and RDX transport in porous media. Soil column breakthrough curves for HMX are only approximately described by linear controlled sorption and first-order decay models.

- TNT and RDX disappearance in soils is a two-step process, rapid adsorption followed by transformation.

- Reductive transformation is a major process affecting TNT transport in the subsurface. TNT transformation is redox and pH sensitive with the highest transformation rates occurring under anaerobic conditions. RDX and HMX subsurface transport are also affected by transformation, but much less so than TNT. The order of transformation significance is TNT > > RDX ≈ HMX.

- Reductive TNT transformation is biologically mediated and probably involves ferrous-ferric iron cycling either in aqueous solution or in organometallic compounds.

- The primary TNT transformation products include 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT. The TNT --> 4A-DNT --> 2,4-DANT is the preferred pathway. Azoxytoluenes have also been reported. Triaminotoluene is potentially an important TNT transformation product, but this product has not been measured due to inadequate chemical analytical capability.

5 Suggestions for Future Research

Research has answered some questions about TNT, RDX, and HMX subsurface transport. Additional questions remain to be answered. An improved understanding in the following areas is needed in order to accurately model TNT, RDX, and HMX subsurface transport:

- Experiments should include analysis of explosive transformation products. It should not be assumed that transformations are inoperative. This is especially important for TNT, where transformation can be extensive. Without measured transformation products, valid mass balances cannot be calculated, and misinterpretation of data is possible.

- Chemical analytical capability for measuring triaminotoluene should be developed to support mass balance calculations for TNT. Development of analytical procedures for RDX and HMX transformation products is also needed.

- Additional work on oxidation-reduction potential (Eh) as a critical parameter in controlling the extent of TNT, RDX, and HMX transformation is needed.

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

References

Ainsworth, C. C., Harvey, S. D., Szecsody, J. E., Simmons, M. A., Cullinan, V. I., Resch, C. T., and Mong, G. H. (1993). "Relationship between the leachability characteristics of unique energetic compounds and soil properties," Final Report, Project Order No. 91PP1800, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD.

Kaplan, D. L., and Kaplan, A. M. (1982). "Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions," *Applied and Environmental Microbiology* 44(3), 757-760.

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

McCormick, N. G., Cornell, J. H., and Kaplan, A. M. (1981). "Biodegradation of hexahydro-1,3,5-trinitro-1,3,5-triazine," *Applied and Environmental Microbiology* 42(5), 817-823.

McCormick, N. G., Feeherry, F. E., and Levinson, H. S. (1976). "Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds," *Applied and Environmental Microbiology* 31(6), 949-958.

McGrath, C. J. (1995). "Review of formulations for processes affecting the subsurface transport of explosives," Technical Report IRRP-95-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Myers, T. E., Brannon, J. M., Pennington, J. C., Townsend, D. M., Davis, W. M., Ochman, M. K., Hayes, C. A., and Myers, K. F. "Laboratory studies of soil sorption/transformation kinetics for explosives," Technical Report in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Pennington, J. C., Hayes, C. A., Myers, K. F., Ochman, M., Gunnison, D., Felt, D. R., and McCormick, E. F. (1995a). "Fate of 2,4,6-trinitrotoluene in a simulated compost system," *Chemosphere* 30, 429-438.

Pennington, J. C., Hayes, C. A., Price, C. B., and McCormick, E. (1992). "Effects of wet and dry cycles on TNT losses from soils," Technical Report EL-92-37, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Pennington, J. C., Myers, T. E., Davis, W. M., Olin, T. J., McDonald, T. A., Hayes, C. A., and Townsend, D. M. (1995b). "Impacts of sorption on in situ bioremediation of explosives-contaminated soils," Technical Report IRRP-95-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

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

Price, C. B., and Brannon, J. M. (1995). "Transformation of 2,4,6-trinitrotoluene under controlled Eh/pH conditions," Technical Report IRRP-95-5, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Selim, H. M., and Iskandar, I. K. (1994). "Sorption-desorption and transport of TNT and RDX in soils," CRREL Report 94-7, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Tchobanoglous, G., and Schroeder, E. D. (1985). *Water quality*. Addison-Wesley Publishing Company, Reading, MA.

Townsend, D. M., Myers, T. E., and Adrian, D. D. (1995). "2,4,6-trinitrololuene (TNT) transformation/sorption in thin-disk soil columns," Technical Report IRRP-95-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Valocchi, A. J. (1985). "Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils," *Water Resources Research* 21(6), 808-820.

Appendix A
Physical, Chemical, and Environmental Data for TNT, RDX, and HMX (adapted from McGrath 1995)[1]

Physical, chemical, and environmental data for TNT, RDX, and HMX are presented in a series of tables as follows:

Table A1: 2,4,6-TNT
Table A2: RDX
Table A3: HMX

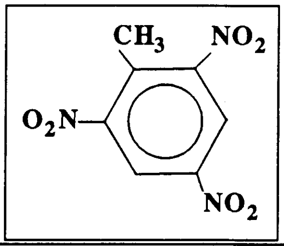
These tables were developed from files provided by C. McGrath (McGrath 1995).

---

[1] References cited in this appendix are located at the end of the main text.

Table A1
2,4,6-Trinitrotoluene (TNT) Physical, Chemical, and Environmental Properties

CAS Reg. No.: 118-96-7
Other names: α-trinitrotoluene, *sym*-trinitrotoluene,
1-methyl-2,4,6-trinitrobenzene
Formula (semistructural, empirical): $C_6H_2CH_3(NO_2)_3$ or $C_7H_5N_3O_6$
Molecular Mass: 227.13 g·mol^{-1}



Parameter	Value / Comment	Reference
Density	1.654 g·cm^{-3} 1.654 - 1.663 g·cm^{-3}	Dean (1985) Urbanski (1964)
Melting Point	80.1 °C 80.65 °C	Dean (1985) Urbanski (1964)
Crystallography	Monoclinic rhombohedra from ethanol: colorless Commercial form: yellow needles or columns	Verschueren (1983) Merck (1983)
Dipole Moment	1.37 D	Merck (1983)
Vapor Properties (TNT)		
Henry's Law Constant, K_H	0.18 torr L mol^{-1} < 0.02 torr L mol^{-1} 1.1 E-08 atm·m^3·mol^{-1} [25 °C]	Spanggord et al. (1980a) Haynes and Smith (1981) Rosenblatt et al. (1989)
Vapor Pressure (solid)	20.0 °C 1.28 E-06 torr 25 °C 5.51 E-06 torr (est.)	Leggett, Jenkins, and Murrmann (1977) Rosenblatt et al. (1989)
Aqueous Solubility (TNT)		
0 °C	100 mg·L^{-1}	Urbanski (1964)
10 °C	110 mg·L^{-1}	Urbanski (1964)
15 °C	200 mg·L^{-1} 120 mg·L^{-1}	Verschueren (1983) Urbanski (1964)
20 °C	130 mg·L^{-1}	Urbanski (1964)
25 °C	~100 mg·L^{-1} (~0.01%) 150 mg·L^{-1}	Merck (1983) Urbanski (1964)
Hygroscopy	Non-hygroscopic; 0.05% water	Urbanski (1964)
EPA Drinking Water Std. (DWEL)	0.020 mg·L^{-1}	(in Rosenblatt et al. 1989)
RMCL (Recc. Max. Contam. Lev.)	44 μg·L^{-1}	DOA (1980; Spalding and Fulton 1988)

TNT Solubility in Organics Solvents [g L^{-1}]

	10 °C	15 °C	20 °C	25 °C	
Acetone	780	920	1090	1320	Urbanski (1964)
Benzene	360	500	670	880	"
Toluene	380	450	550	670	"
Ethanol (95%)	8.5	10.7	12.3	14.8	"

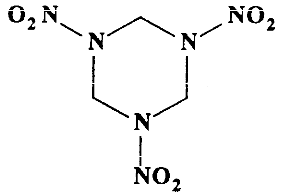
(Continued)

Table A1 (Concluded)

Parameter	Value / Comment	Reference
Environmental Processes (TNT)		
Linear Partitioning Coefficients	log K_{ow} = 2.06; 1.86	Rosenblatt et al. (1989), Jenkins (1989)
	log K_{oc} = 2.72	Rosenblatt (1986)
	K_d = 53 ± 20 $mL{\cdot}g^{-1}$ 2 - 56 $mL{\cdot}g^{-1}$	Spanggord et al. (1980a)
	4.0 (average of 16 soils)	Pennington and Patrick (1990)
	1.6 - 16.6 (batch) 0.5 - 5.5 (column)	Ainsworth et al. (1993)
	52 (batch) 0.0204 - 0.400 (column)	Selim and Iskandar (1994)
	6.16 (batch)	Pennington et al. (1995)
	1.5 - 10.0 (column)	Townsend et al. (1995)
	0.0 - 1.8 (column)	Myers et al. (In Preparation)
Diffusion	Water: 6.71 E-06 $cm^2{\cdot}s^{-1}$ (25 °C; est.) Air: 0.064 $cm^2{\cdot}s^{-1}$ (25 °C; est.)	Rosenblatt et al. (1989)
Biotransformation	Major process in surface and groundwaters. Successive reduction of nitro ($R\text{-}N[+V]O_2$) to amine ($R\text{-}N[-I]H_2$) groups is most common.	Rosenblatt et al. (1989)
	A few reports of microbial growth on and mineralization of TNT *via* elimination reactions; these microorganisms use TNT as the sole nitrogen, and carbon source.	Boopathy and Kulpa (1992), Duque et al. (1993), Unkefer et al. (1990)
	Half-life in groundwater (est.): 8640 hr (12 mo.) to 672 hr (4 weeks).	Howard et al. (1991)
	Aerobic: Major transformation process in surface water; significant in soils as well; slow rates Products: hydroxamino and azoxytoluene compounds	Kaplan and Kaplan (1982) Spanggord et al. (1980a)
	Anaerobic: Primarily nitro-to-amino reduction; moderate rates	
Pseudo-First Order Transformation Rate Constants in Groundwater	1.7 E-03 - 8.7 E-03 hr^{-1}	Ainsworth et al. (1993)
	8.0 E-03 - 2.5 E-02 hr^{-1}	Townsend et al. (1995)
	3.2 E-03 - 1.4 E-01 hr^{-1}	Myers et al. (In Preparation)
Toxicity	EPA possible human carcinogen; May absorb through skin; can cause headache, weakness, anemia, liver injury; Vapors are toxic.	(in Rosenblatt et al. 1989); Merck (1983)
Photosensitivity	Significant. To: 2,4,6-trinitrobenzaldehyde, 1,3,5-trinitrobenzene, 3,5-dinitroaniline, 2-amino-4,6-dinitrobenzoic acid, azoxydicarboxylic acid	Kaye (1980), Burlinson (1980)
Hydrolysis	Alkaline sensitive	
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	Forms complexes with surfactants.	Kaplan and Kaplan (1982)
Abiotic Reduction	Apparent major reaction pathway; anaerobic or aerobic conditions.	—
Polymerization	No reports. Reduction products may form azo or azoxy compounds *via* amino intermediates.	—
Binding to Soil Solids	No reports. Reduction products appear to bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).	Weber et al. 1992; Wolfe and Macalady 1992; Bollag et al. 1983; Parris 1980; Hsu and Bartha 1974.

Table A2
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) Physical, Chemical, and Environmental Properties

CAS No.: 121-82-4
Other names: hexogen; cyclotrimethylenetrinitramine; cyclonite; RDX ≡ Royal Demolition eXplosives (or Research & Development eXplosives)
Formula (semistructural and empirical): $(NO_2)_3N_3C_3H_6$ or $C_3H_6N_6O_6$
Molecular Mass: 222.26 g·mol^{-1}



Parameter	Value / Comments	Reference
Density	1.82 g·cm^{-3}	Kaye (1980)
Melting Point	204-206 °C	Meyer (1977); Banerjee, Yalkowsky, and Valvani (1980); Merck (1983)
Crystallography	Orthorhombic crystals (from acetone); colorless	Verschueren (1983), Meyer (1977)
Dipole Moment	Low (≈ 0); molecule is nearly symmetrical (out of plane configurations have non-zero dipole moment)	
	Vapor Properties (RDX)	
Henry's Law Constant, K_H	1.96 E-11 atm·m^3·mol^{-1} (25 °C; est.) 2 E-05 torr·L·mol^{-1} (°C; est.)	Rosenblatt et al. (1989) Spanggord et al. (1980a,b)
Vapor Pressure	4.03 E-09 torr (25 °C; est.)	Rosenblatt et al. (1989)
	Aqueous Solubility (RDX)	
10 °C	28.9 ± 1.0 mg·L^{-1}	Sikka et al. (1980)
20 °C	42.3 ± 0.6 mg·L^{-1}	Sikka et al. (1980)
25 °C (?)	45 mg·L^{-1}	Spalding and Fulton (1988)
25 ± 0.2 °C	59.9 ± 1.2 mg·L^{-1}; 269 μM	Banerjee, Yalkowsky, and Valvani (1980)
26.5 °C	59.9 ± 1.4 mg·L^{-1}	Sikka et al. (1980)
30 °C	75.7 ± 1.1 mg·L^{-1}	Sikka et al. (1980)
EPA Drinking Water Std. (DWEL)	0.10 mg·L^{-1}	(from Rosenblatt et al. 1989)
RMCL Recc.Max.Contam.Lev.	35 μg·L^{-1}	DOA (1980; from Spalding and Fulton 1988)
	Solubility in Organic Solvents (RDX)	
Acetone	1 g / 25 mL (40 000 mg·L^{-1}) 4.18 g / 100 g @ 0 °C 8.38 g / 100 g @ 30 °C	Merck (1983) Urbanski et al. (1983)
Benzene	0.055 g / 100 g @ 25 °C 0.085 g / 100 g @ 30 °C	Urbanski et al. (1983)
Toluene	0.016 g / 100 g @ 0 ° 0.025 g / 100 g @ 25 °C 0.050 g / 100 g @ 30 °C	Urbanski et al. (1983)

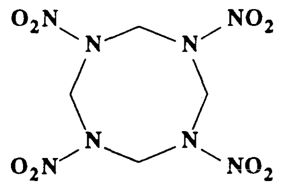
(Continued)

Table A2 (Concluded)

Parameter	Value / Comments	Reference
Solubility in Organic Solvents (RDX) (Continued)		
Methanol	0.140 g / 100 g @ 0 °C 0.325 g / 100 g @ 30 °C	Urbanski et al. (1983)
Ethanol	0.040 g / 100 g @ 0 °C 0.155 g / 100 g @ 30 °C	Urbanski et al. (1983)
Acetic Acid (glacial)	slight	Merck (1983)
Environmental Fate and Transport (RDX)		
Linear Partitioning Coefficients	log K_{ow}: 0.87 ± 0.028	Banerjee et al. (1985)
	0.81	Major (1984)
	0.86	Jenkins (1989)
	log K_{oc}: 2.00	Rosenblatt (1986; CAAP)
	2.13	Tucker et al. (1985)
	0.89, 1.87, and 2.43	Sikka et al. (1980)
	1.62 and 2.10	Spanggord et al. (1980b)
	K_d: 0.2, 1.8, 6.4, and 7.8 0.8, 3.06, and 4.15 1.4 and 4.2 1.6 (nondimensional; kg-water / kg-soil); CAAP aquifer material with very low f_{oc}	Hale, Stanford, and Taft (1979) Sikka et al. (1980) Spanggord et al. (1980b) Tsai et al. (1985)
	4.92 - 6.75	Leggett (1985)
	< 1	Ainsworth et al. (1993)
	0.0 - 0.8	Myers et al. (In Preparation)
Diffusion	Water: 7.15 E-06 $cm^2 \cdot s^{-1}$ Air: 0.074 $cm^2 \cdot s^{-1}$	Rosenblatt et al. (1989)
Biodegradability	Aerobic: negligible	McCormick et al. (1981)
	Anaerobic: significant cometabolism Transformation products: methanol, hydrazine, formaldehyde, dimethylhydrazine (1,1-, 1,2-) which are mutagens	McCormick et al. (1981)
First Order Transformation Rate Constants in Groundwater	0 - 6.5 E-03 hr^{-1} 1.0 E-01 hr^{-1}	Myers et al. (In Preparation) Pennington et al. (1995)
Toxicity	Possible carcinogen (USEPA); not mutagen; transformation products may be toxic	McCormick et al. (1981)
Photosensitivity	Rapid; not enhanced by humics substrate (sensitizer) Transformation products: nitrite, nitrate, formaldehyde, N_2, triazine (?)	Sikka et al. (1980) McCormick et al. (1981)
Hydrolysis	Insignificant	Rosenblatt et al. (1989)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	No reports; probable, but weak.	—
Abiotic Reduction	No reports; perhaps under anaerobic systems; probably not under aerobic conditions.	—
Polymerization	No reports; perhaps in reduced (amino compounds) transformation products.	—
Binding to Soil Solids	No reports; perhaps amino compounds.	—

Table A3
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) Physical, Chemical, and Environmental Properties

CAS No.: 2691-41-0
Other names: Octagon; cyclo.tetramethylene.tetranitramine
Formula (semistructural and empirical): $C_4H_8N_4(NO_2)_4$ or $C_4H_8N_8O_8$
Molecular Mass: 296.2 g mol^{-1}



Parameter	Value / Comment	Reference
Density	1.90 g cm^{-3} (β form)	Rosenblatt et al. (1989)
Melting Point	286 °C	Rosenblatt et al. (1989)
Crystallography	Colorless crystals	Meyer (1977)
Dipole Moment	Low ($\approx$ 0); molecule is nearly symmetrical; non-zero DM may arise from out of plane configurations	—
Vapor Properties (HMX)		
Henry's Law Constant, K_H	2.60 E-15 atm m^{-3} mol^{-1} (25 °C; est.)	Rosenblatt et al. (1989)
Vapor Pressure	25 °C 3.33 E-14 torr 100 °C 3 E-09 torr	Rosenblatt et al. (1989) Tucker et al. (1985)
Aqueous Solubility (HMX) Leggett et al. (1977)		
10 °C	1.21 ± 0.04 mg·L^{-1}, 4.09 μM	Spanggord et al. (1982b)
20 °C	2.6 ± 0.01 mg·L^{-1}, 8.78 μM	Spanggord et al. (1982b)
22-25 °C	5 mg·L^{-1}, 16.8 μM	Glover and Hoffsommer (1973)
30 °C	5.7 ± 0.1 mg·L^{-1}, 19.2 μM	Spanggord et al. (1982b)
Solubility in Organic Solvents (HMX)		
Acetone	n.d.	—
Benzene	n.d.	—
Ethanol	n.d.	—
Acetic Acid (glacial)	n.d.	—
Environmental Fate and Transport (HMX)		
Linear Partition Coefficients	log K_{ow}: 0.26 0.06	Major (1989) Jenkins (1989)
	log K_{oc}: 0.54 (est.) log K_{oc}: 2.83; for Holston River sediment (f_{oc}=0.013) based on measured k_p = 8.7	Rosenblatt et al. (1989); Spanggord et al. (1982b)
	K_d: 8.87 - 13.25 0.0 - 1.2	Leggett (1985) Myers et al. (In Preparation)
	K_B: 63 (measured biosorption partitioning)	Spanggord et al. (1982b)

(Continued)

Table A3 (Concluded)

Parameter	Value / Comment	Reference
Environmental Fate and Transport (HMX) — Continued		
Volatilization	Minor; k_v = 2.4 E-04 to 7.2 E-04 day^{-1} (1st-order rate constant); $t_{1/2}$ = 3,000 to 1,000 days (est. from experiments)	Spanggord et al. (1982b)
Diffusion	Water: 6.02 E-06 $cm^2 \cdot s^{-1}$ (est.) Air: 0.063 $cm^2 \cdot s^{-1}$ (est.)	Rosenblatt et al. (1989)
Biodegradation	Aerobic: negligible	Spanggord et al. (1982b)
	Anaerobic: slow; accelerated, 1° kinetics in the presence of primary substrate (cometabolism)	Spanggord et al. (1982b)
First Order Transformation Rate Constants in Groundwater	0 - 3.6 E-03 hr^{-1} 9.0 E-02 hr^{-1}	Myers et al. (In Preparation) Pennington et al. (1995)
Toxicity	Not carcinogenic	(in Rosenblatt et al. 1989)
Photolysis	Significant; 1^{st}-order k = 0.15 d^{-1} ($t_{1/2}$= 5 d); for Hoston River water	Spanggord et al. (1982b)
Hydrolysis	Not significant	Spanggord et al. (1982b)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	No reports; probable, but weak.	—
Abiotic Reduction	Not under aerobic conditions; perhaps in anaerobic systems.	Spanggord et al. (1982b)
Polymerization	No reports; perhaps in reduced transformation products (amino compounds).	—
Binding to Soil Solids	No reports; perhaps in amino reduced compounds.	—

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY ***(Leave blank)***

2. REPORT DATE
February 1996

3. REPORT TYPE AND DATES COVERED
Final report

4. TITLE AND SUBTITLE
Recent Development in Formulating Model Descriptors for Subsurface Transformation and Sorption of TNT, RDX, and HMX

5. FUNDING NUMBERS

6. AUTHOR(S)
Dan M. Townsend, Tommy E. Myers

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
North Carolina State University, Raleigh, NC 27650

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

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report IRRP-96-1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

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

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

Subsurface contamination with 2,4,6-trinitrotoluene (TNT), 2,3,5-trinitro-1,3,5-triazine (RDX), and oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is a problem at military installations where these explosives were manufactured or used in loading munitions. Recent laboratory batch and column studies conducted to identify processes affecting subsurface transport of TNT, RDX, and HMX provide new information on the relative significance of transformation and sorption for these explosives and yield estimates of key process descriptors. This report assesses the current state of knowledge regarding subsurface transformation and sorption of TNT, RDX, and HMX, provides estimates for subsurface transport descriptors, and recommends further research.

Transformation and sorption are important processes in the subsurface transport of TNT, RDX, and HMX. Measurement of transformation products has provided unequivocal evidence of TNT transformation. Research has also indicated that RDX and HMX are affected by subsurface transformations, but RDX and HMX transformation products have not been measured due to lack of chemical analytical capability. The order to magnitude of transformation is TNT >> RDX ≈ HMX, and the order of magnitude of sorption in TNT > HMX > RDX.

(Continued)

14. SUBJECT TERMS

Breakthrough curves	RDX
Explosives	Sorption
Groundwater	TNT
HMX	Transformation

15. NUMBER OF PAGES
36

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

13. (Concluded).

Sorption of TNT by soils has been described with equilibrium-type approaches, although there is substantial evidence that TNT transforms to the extent that equilibrium, at least in batch, is not attainable under reducing conditions. Equilibrium sorption parameters for TNT may be no more than fitting parameters that compensate for inadequately formulated transformation/sorption kinetics. Therefore, caution is advised when extrapolating laboratory-based equilibrium sorption parameters for TNT to field situations. The available data indicate that TNT transformation is a first-order process and is highly dependent on redox conditions.

RDX sorption is equilibrium controlled and can be modeled using a linear isotherm. RDX transformation appears to be first order and slow relative to TNT. Limited information on HMX suggests that HMX sorption may be nonlinear (if equilibrium controlled) or may not be equilibrium controlled. HMX transformation appears to be first order and slow, like RDX.

Finally, of the three explosives (TNT, RDX, HMX), formulation of field models for RDX subsurface transport is anticipated to be the least complicated, since RDX sorption is a linear equilibrium process and RDX transformation is slow and probably first order. HMX transport modeling may be more complicated due to nonlinear or nonequilibrium sorption. TNT-transport modeling is complicated by potentially rapid transformation, depending on redox conditions, and competition with transformation products for sorption sites.