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RELATIONSHIP BETWEEN THE LEACHABILITY CHARACTERISTICS OF UNIQUE ENERGETIC COMPOUNDS AND SOIL PROPERTIES

Final Report

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The object of this project was to develop a soil sorption model for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) based on physical-chemical properties of soils in the absence of biotic and abiotic transformation/degradation of the solutes. This was accomplished by conducting a series of batch and column studies with TNT and RDX on a variety of sterilized soils. Abiotic transformation of TNT to several amino compounds, of which 2-amino-4,6-dinitrotoluene was the most common, necessitated direct analysis of the solute in the aqueous phase and extraction/analysis of the sorbed material to be performed on all batch studies to allow for mass balance calculations.

RDX was poorly sorbed to all soils, and steady-state conditions were obtained within 6 h. Linear sorption coefficients (K_d) were generally < 1mL/g. The sorption and desorption limbs of the breakthrough curves were symmetrical and solute breakthrough could be well described by the use of a transport code that accounted for dispersion and fast, reversible sorption described by a linear isotherm.

Munitions, RDX, TNT, Soil Sorption, Soil Transport, and TNT Transformation

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Abstract (continued)
whose values were dependent on a soils CEC, pH, clay content, OC, and DCB extractable Fe. The model developed for RDX estimated the K_d for the soils used in this study to within a factor of 2.25 and most often within a factor of 2 or less.

TNT required more time to reach steady-state conditions in the batch studies, but was more strongly sorbed than RDX. Determination of the solid phase concentration was confounded by the abiotic transformation of TNT to the aminodinitrotoluene isomers and diaminonitrotoluene. Steady-state aqueous phase TNT concentrations were obtained in the soil suspensions in less than 96 h. Sorption data was best fit with the Freundlich model. TNT column experiments exhibited reversible sorption with at least some mass loss occurring in all soils. At the higher pore water velocities, variable degrees of asymmetry between the sorption and desorption limbs of the solute breakthrough curves were observed. At the lower pore water velocities, asymmetry increased and mass loss became evident in all soils and was as much as 19% of the total mass injected. TNT sorption model based on soil properties was best represented as a Fruendlich sorption isotherm with the predicted K_{fp} and $1/n_p$ values being a linear combination of pH and CEC, and OC, respectively. The ability to predict the K_f parameter was reasonable in that all of the measured K_f values were predicted to within a factor of 3.5 and most often better than a factor of 2.

Sorption of both solutes was not solely the result of hydrophobic partitioning to the OC phase of these soils. K_d values calculated via carbon-referenced partitioning were variable and poor predictors of actual sorption in both the batch and column studies. Sorbed RDX and TNT appear to occupy the same set or subset of sorption sites; sorption of either solute is decreased in the presence of the other as a cosolute. Sorption of both compounds appears to be an exothermic process with a substantial isosteric heat of sorption; ΔH_r is about -15 kJ/mol and -25 KJ/mol for RDX and TNT, respectively.

FOREWORD

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EXECUTIVE SUMMARY

The objectives of this research were to: 1) develop a sorption model based on chemical, physical, and mineralogic properties of soil and subsurface materials, 2) validate the effectiveness of the model in static and dynamic systems using a soil material different from those used in model construction, and 3) attempt to determine the basic chemical and geochemical reactions and interactions between TNT and RDX and soil and subsurface materials in the absence of biotic and abiotic degradation/transformation. In order to accomplish these objectives, batch sorption studies were used to provide the necessary data for developing sorption isotherms and sorption relationships based on the physical-chemical properties of soils [extractable Fe, CEC (cation exchange capacity), clay content, pH, OC (organic carbon)]. Regression analysis was used to determine the relationship between the appropriate isotherm parameters and soil properties. In addition, a series of 1-D column experiments were conducted to determine 1) if adsorption parameters determined in the batch studies were effective in describing the sorption process during fluid flow and 2) if simple transport codes accounting for hydrodynamic dispersion and assuming local equilibrium would describe TNT and RDX transport in soils.

RDX sorbed poorly to all soils used in this study. Sorption steady-state conditions in sterilized soils were obtained in about 6 h and remained constant for 24 days. While the sorption of RDX was almost equally well described by the linear and Freundlich isotherm model, the simpler linear model was found to adequately describe RDX sorption to all soils. The K_d values from the linear model were low (typically less than 1); suggesting minimal sorption to soil materials. In addition, sorption was totally reversible with no mass loss noted under the conditions utilized in this study. The sorption coefficient, K_d, was well predicted by a linear combination of three principle components whose values were dependent on a soils CEC, pH, clay content, OC, and DCB extractable Fe:

$$K_d = -0.38 + 0.149(\%OC) + 0.008(\%clay) - 0.0006(DCB\text{-}Fe) + 0.074(pH) + 0.033(CEC).$$

The above model estimated the K_d for the soils used in this study to within a factor of 2.25 and most often within a factor of 2 or less..

Column experiments with RDX and five soils exhibited rapid breakthrough with sorption and desorption limbs being symmetrical. In general, the sorption/desorption limb determined K_d values were similar and very low; suggesting fast, reversible RDX sorption. The K_d values calculated from the breakthrough curves were at or near our ability to discern differences between the solute and tracer, but were about the same magnitude as those measured in the batch studies. In all cases, solute breakthrough could be accounted for using a transport model incorporating hydrodynamic dispersion and fast, reversible sorption described by a linear isotherm; however, in many cases sorption was so low that solute breakthrough could be described by considering only hydrodynamic dispersion.

There was no way to discern the RDX sorption mechanism or the active site or sites of RDX sorption from these studies. However, it is evident from the results of these investigations that RDX sorption is not solely the result of hydrophobic partitioning to the OC phase of these soils. From temperature studies with three soils, RDX sorption appears to be an exothermic process with a substantial isosteric heat of sorption (ΔH_r is about -10 to -20 kJ/mol) which is similar to that ascribed to hydrogen bonding or van der Walls forces. In addition, K_d values calculated via carbon-referenced partitioning were variable and poor predictors of actual sorption in both the batch and column studies.

TNT sorption to all soils was greater than that observed for RDX. While determination of the solid phase concentration was confounded by the abiotic transformation of TNT to the aminodinitrotoluene isomers (2ADNT, and 4ADNT) and diaminonitrotoluene, steady-state aqueous and solid phase TNT concentrations were obtained in all soils in less than 96 h. TNT sorption was observed to be totally reversible if transformation was taken into account. TNT sorption appears to be an exothermic process with a substantial isosteric heat of sorption (ΔH_r is about -25 kJ/mol) which is similar to that ascribed to hydrogen bonding or van der Walls forces and somewhat higher than RDX. Unlike RDX, TNT sorption data in all soils was curvilinear and was best fit by the Freundlich model ($q = K_f C^{1/n}$). The best predictor of K_f and

1/n were found to be a linear combinations of the soil pH, and CEC, and OC respectively:

$$K_f = -7.69 + 1.6(pH) + 0.35(CEC); \quad 1/n_p = 0.56 + 0.15(OC).$$

The ability to predict the K_f parameter was reasonable in that all of the measured K_f values were predicted to within a factor of 3.5 and most often better than a factor of 2. In addition, predicted values calculated for the soils used in a resent TNT study yielded very reasonable comparisons to the published K_f values (Pennington and Patrick 1990). The 1/n values varied over a greater range than one would hope, but still reasonable considering the calculated value is only dependent on OC.

TNT column experiments on five different soils exhibited reversible sorption with at least some TNT mass loss occurring in all soils. At faster pore water velocities, the majority (95%) of the transport behavior in the soils could be accounted for by using a reversible nonlinear sorption model and knowledge of the hydrodynamic dispersion. Even at the higher pore water velocities, however, variable degrees of asymmetry between the sorption and desorption limbs of the solute breakthrough curves was observed; that is, the K_d values calculated from the sorption limb were invariably larger than those calculated from the desorption limb. The degree of asymmetry appeared to be dependant on the soil being studied, and suggests either irreversible sorption or mass loss. At the lower pore water velocities, asymmetry increased and mass loss became evident in all soils and was as much as 19% of the total mass injected. Sorption coefficients determined from the high pore water velocity experiments were generally in good agreement with those calculated for the batch experiments.

TNT undergoes a reduction of one or more of the NO_2- moieties to NH_2- when in contact with soil. All the soils used in this study exhibited the capability of reducing TNT to 2ADNT, 4ADNT or DANT, although mediation of this reaction appears to be soil dependent. It would appear that the slow step in this process is diffusional in nature since greater TNT mass loss occurred at lower pore water velocities in the column studies. In the batch studies conducted at 25 ^{0}C, steady-state aqueous TNT conditions were reached in 72 to 96 h with TNT mass loss confined to this time frame; at higher temperatures, however, greater mass loss was observed. This suggests that the transformation process is an endothermic process. The findings of the present

present study suggests that sorption is required prior to the transformation of TNT. It is unknown at this time what soil constituent(s) is acting as the electron donor for this reaction; however, it appears that only a subset of the "TNT sorption sites" are active in the transformation of TNT.

TABLE OF CONTENTS

REPORT DOCUMENT PAGE iii
FORWARD iv
EXECUTIVE SUMMARY v

1.0 INTRODUCTION 1
    1.1 Status of Knowledge Regarding TNT and RDX Sorption to Soils 1
        1.1.1 RDX sorption in soils 3
        1.1.2 TNT sorption in soils 5
    1.2 Approach 7
2.0 MATERIALS AND METHODS 10
    2.1 Chemicals and Standards 10
        2.1.1 Preparation of aqueous TNT and RDX solutions 11
    2.2 Soil Characterization and Selection 11
    2.3 Soil Studies 13
        2.3.1 Method of sterilization 13
        2.3.2 Sorption time dependence 14
        2.3.3 Soil extraction 15
        2.3.4 Batch sorption studies 15
        2.3.5 Desorption studies 16
        2.3.6 Cosolute Studies 17
        2.3.7 Temperature studies 17
        2.3.8 Column studies 17
    2.4 Chemical/Analytical Procedures 19
3.0 RESULTS OF BATCH SORPTION STUDIES 24
    3.1 Sorption Kinetics, Extraction Methods, and Transformation of TNT and RDX 24
        3.1.1 Sorption kinetics and extraction technique 24
        3.1.2 TNT mass loss 28
    3.2 Batch Soil Sorption Studies 35
        3.2.1 RDX soil sorption/desorption at 23 ^{0}C 36
        3.2.2 TNT soil sorption/desorption at 23 ^{0}C 40
        3.2.3 TNT and RDX cosolute studies 47
        3.2.4 TNT and RDX temperature studies 49
4.0 STATISTICAL ANALYSIS AND MODEL DEVELOPMENT 54
    4.1 Statistical Analysis 54
    4.2 TNT Model Development 58
    4.3 RDX Model Development 64
    4.4 NL-TNT Model Development 67
    4.5 Model Effectiveness 72
5.0 COLUMN STUDIES WITH RDX AND TNT 78
    5.1 RDX Column Studies 81
    5.2 TNT Column Studies 85
    5.3 TNT Pulsed Column Studies at Different Temperatures 94

6.0 SUMMARY AND CONCLUSIONS 99
    6.1 RDX 99
    6.2 TNT 100
    6.3 TNT Transformation 102
    6.4 Research Needs 103
7.0 LITERATURE CITED 105
8.0 APPENDIX A and B........ 113

LIST OF FIGURES

FIGURE PAGE

2-1 Experimental column apparatus.. 22

3-1 Behavior of 3µg/mL RDX in contact with steam sterilized or unsterilized Cloudland Ap soil horizon over a 24 d period; a) aqueous concentration, and b) sorbed concentration.. 25

3-2 Affect of time on TNT aqueous and solid phase concentrations: a) aqueous concentration of TNT in the presence of Norborne C and Cloudland Ap soils at initial concentrations of 10 and 60 µg/mL TNT, and b) the solid phase concentration of TNT at an initial TNT concentration of 10 µg/mL as a function of analysis (HPLC or LSC) and extraction versus aqueous calculation of sorbed concentration on the Norborne C soil horizon 26

3-3 Comparison between the Soxhlet and repetitive MeOH wash soil extractions; 60 µg/mL initial TNT concentration 27

3-4 Mass balance based on HPLC analyses of TNT in the a) Cloudland Ap, and b) Norborne C soil horizons; 60 µg/mL initial TNT concentration.................... 28

3-5 HPLC chromatograms illustrating the concentrated MeOH extractables from three different soils after 24 h of incubation under sterile conditions 30

3-6 GC/MS total ion current chromatogram of a concentrate from the 6-µg/mL aqueous TNT solution used to amend the soils (center), the mass spectrum of TNT (top), and the 197 a.m.u. extracted ion plot............ 31

3-7 Extracted ion plot of a concentrated extract from the Burbank Ap soil (bottom), and the mass spectra of the aminodinitrotoluene isomers (top and center).. 32

3-8 Extracted ion plot of a concentrated extract from the Cloudland Ap soil (bottom), and the mass spectra of the aminodinitrotoluene isomers (top and center).. 33

3-9 RDX sorption isotherms for six selected soils.. 37

3-10 RDX sorption/desorption for the a) Cloudland Ap, and b) Norborne C soils.. 39

3-11 TNT sorption isotherms for six selected soils.. 40

3-12 TNT sorption/desorption isotherms for the a) Cloudland Ap,
and b)Norborne C soil.. 46

3-13 The effect of equal cosolute mass concentrations of TNT and RDX
on the sorption of the TNT or RDX to the a) Cloudland Ap, and b)
Norborne C soils.. 48

3-14 Sorption of TNT to the a) Norborne C and b) Kenoma BC soil horizons
at 10, 23, and 50 ^{0}C.. 50

3-15 Sorption of RDX to a) the Cloundland Ap at 10, 23, and 50 ^{0}C, and b)
the Kenoma BC at 10 and 20 ^{0}C... 50

4-1 Plots of a) TNT sorption isotherm for the Cecil Ap soil showing the
Freundlich isotherm model fit, b) predicted K_{fp} from Eq. 4 versus the
estimated K_f from the Freundlich model.. 60

4-2 Plots of a) predicted K_{fp} from Eq. 5 versus estimated K_f from the
Fruendlich model, and b) predicted 1/n values from Eq. 6 versus
estimated 1/n values from the Freundlich model... 62

4-3 Plots of a) RDX sorption isotherm for the Cecil Ap soil showing the
linear model fit, and b) the predicted Kd from Eq. 7 versus the estimated
Kd from the linear isotherm model (Eq. 1).. 64

4-4 Plots of a) TNT sorption on the Cecil Ap soil using the NL-TNT solid phase
concentration data, and b) predicted Langmuir Q parameter from
the Langmuir model.. 69

4-5 Predicted b parameter from Eq. 9 for NL-TNT versus the estimated
parameter from the Langmuir isotherm.. 72

5-1 Comparison of the sorption and desorption limbs of RDX breakthrough
curves on four different soils at the same velocity (0.012 cm/sec) and
aqueous RDX concentration (4.18 µg/mL).. 82

5-2 Comparison of the sorption and desorption limbs of TNT breakthrough
curves for four different soils at the same velocity (v = 0.012 cm/sec)
and TNT aqueous concentration (4.35 µg/mL)... 85

5-3 TNT breakthrough curve for the Norborne C soil horizon..................................... 86

5-4 TNT breakthrough curves in the Ocala C4/alumina mixture at
two different velocities and model fits to the data.. 89

5-5 TNT breakthrough curves for the Burbank Ap soil horizon 91

5-6 TNT pulsed column experiments with the Norborne C soil at 4 temperatures 97

5-7 TNT pulsed column experiments with the Cloudland C soil at 4 temperatures 98

LIST OF TABLES

Table		Page
1-1	Selected chemical and physical properties of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	9
2 - 1	Selected physical-chemical properties of soils selected for study	23
3 - 1 .	The resulting mean squared error from fitting each model to the independent variable of the concentration of RDX (µg/mL solution) and the dependent variable of the concentration of RDX (µg/g soil)	37
3-2	Parameter estimates (K_f and 1/n) and approximate 95% confidence limits (CL) for soils best fit by the Freundlich isotherm Modelfor RDX phase concentration data	38
3-3	Parameter (K_d) estimate and approximate 95% confidence limits (CL) for RDX sorption to those soil horizons best described by the Linear Model parameter and those soils whose Freundlich 1/n values where statistically no different from 1	38
3-4	The resulting mean squared error from fitting each model to the independent variable of the concentration of TNT (µg/mL solution) and the dependent variable of the concentration of TNT (µg/g soil)	41
3 - 5	Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Freundlich Isotherm Model for TNT phase concentration data	41
3 - 6	The resulting mean squared error (MSE) from fitting each model to the NL-TNT independent variable of the concentration of TNT (µg/mL solution) and the dependent variable of the concentration of NL-TNT (µg/g soil)	42
3 - 7	Parameter estimates and approximate 95% confidence limits (CL) for each soil that was best fit by the Freundlich Isotherm Model using NL-TNT phase concentration data	43
3 - 8	Parameter estimates and approximate 95% confidence limits (CL) for each soil that was best fit by the Langmuir Isotherm Model using NL-TNT phase concentration data	43

3 - 9 Percent recovery of TNT added to the Norborne C and Cloudland Ap soil horizons after a 4 day sorption period as a function of initial TNT concentration 45

3 - 10 Parameter estimates and approximate 95% confidence limits (CL) for each isotherm and soil using the Freundlich Isotherm Model and the cosolute (CoS) or single solute (S) phase concentration data 48

3 - 11 The percentage of TNT recovery from the Kenoma BC, Cloudland Ap, and Norborne C soils as a function of initial concentration and temperature 53

4 - 1 Correlation matrix of the average soil properties........ 57

4 - 2 First three principal components (P_1 - P_3) for the average soil properties. The principal components are linear combinations of the standardized soil properties [i.e., $(X_i - X_{ave})/S_x$; where X_{ave} is the mean X, S_x=standard deviation of X and X_i the individual values of X]........ 57

4 - 3 Analysis of variance of the regression of the estimated K_f for TNT against the first two principal components........ 60

4 - 4 Parameter estimates for the predictive model for K_f for TNT (eq. 4)........ 60

4 - 5 Estimated (O) and Predicted (P) K_f values for TNT using Eq.4 and a measure of their deviation........ 61

4 - 6 Analysis of variance of the regression of the estimated K_f for TNT against pH (X_4) and CEC (X_5) (Eq. 5)........ 61

4 - 7 Parameter estimates for the TNT K_f predictive model (Eq. 5); X_4 is pH, X_5 is CEC for K_f 61

4 - 8 Estimated (O) and Predicted (P) K_f values for TNT using Eq.5 and a measure of their deviation 62

4 - 9 Analysis of variance of the regression of the estimated 1/n for TNT against organic carbon (X_1) (Eq.6)........ 63

4 - 10 Parameter estimates for the predictive model for 1/n for TNT (Eq. 6)........ 63

4 - 11 Estimated (O) and Predicted (P) 1/n values for TNT using Eq. 6 and a measure of their deviation 63

4 - 12 Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Linear Model (Eq. 1) for RDX phase concentration data 65

4-13 Analysis of variance of the regression of the estimated K_d for RDX against the first three principal components 66

4-14 Parameter estimates for the predictive model for K_d for RDX (Eq. 7) 66

4-15 Estimated (O) and Predicted (P) K_d values for RDX using Eq. 7 and a measure of their deviation 67

4-16 Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Langmuir Isotherm Model and NL-TNT phase concentration data 69

4-17 Analysis of variance of the regression of the estimated Q for NL-TNT against the iron content of the soil (X_3) (Eq. 8) 70

4-18 Parameter estimates for the predictive model for Q for NL-TNT (Eq. 8); X_3 is DCB iron content 70

4-19 Estimated (O) and Predicted (P) Q values for NL-TNT using Eq. 8 and a measure of their deviation 70

4-20 Analysis of variance of the regression of the estimated b for NL-TNT against the soil CEC (X_5) (Eq. 9) 71

4-21 Parameter estimates for the predictive model for b for NL-TNT (Eq. 9); where X_5 is CEC 71

4-22 Estimated (O) and Predicted (P) b values for NL-TNT using Eq. 9 and a measure of their deviation 71

4-23 Comparison between the predicted Langmuir parameters (Q_p and b_p;Eq. 8 and 9) and Q and b values determined by Pennington and Patrick (1990) 75

4-24 Comparison between the predicted Fruendlich parameters (K_{fp} and $1/n_p$) using Eq. 5 and 6 and the parameters (K_f and $1/n$) determined by Pennington and Patrick (1990) 76

5-1 Chemical and physical properties of those soils used in the column studies 82

5-2 Comparison of the column study determined K_d values from the sorption limb and K_d values calculated from the batch sorption isotherms 92

5-3 Comparison of serial pulsed injection data for the Norborne C and Cloudland C soil horizons at 4 temperatures; contact time and injection mass are 10.5 min and 8.2 µg, respectively 96

1.0 INTRODUCTION

Munitions material currently used as propellants or explosive charges include 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). These two compounds are present in soils, the vadose zone, and groundwaters at a number of active, inactive, and abandoned munitions sites as a result of manufacturing, packing, and loading processes that generate large volumes of munitions contaminated wastewater (Palazzo and Leggett 1986; Layton et al. 1987). The United States Army is currently involved in the remediation of these sites. While only limited field studies have been conducted, the available information suggests a gradual movement through soils and vadose zone materials to groundwater of RDX, and of TNT and its photolysis and biodegradation products (see Layton et al. 1987). These compounds could pose a hazard to public health due to their toxic and carcinogenic nature (Layton et al. 1987). Sorption to surface soil, vadose zone, and groundwater solid materials influences solute mobility, aqueous concentrations, and may adversely effect the time and cost of subsurface remediation of contaminated sites.

1.1 STATUS OF KNOWLEDGE REGARDING TNT AND RDX SORPTION TO SOILS

Reference to RDX and TNT sorption via carbon-referenced hydrophobic partitioning (sorption) has been made throughout the literature (Pennington and Patrick 1990; Tucker et al. 1985; Sikka et al. 1980; Spanggord et al. 1980). Sorption of nonionic organic compounds (NOC) with fairly low aqueous solubilities ($< 10^{-3}$ M) (e.g., pesticides, polyaromatic hydrocarbons, heterocyclic compounds, and unique energetic compounds such as TNT, and RDX), by soils and sediments should result from their partitioning from the aqueous phase into the solid-phase organic carbon fraction (f_{OC}) (Karickoff 1984; Chiou et al. 1983, 1989). Additionally, the intensity of sorption should be correlated to a compound's water solubility (WS) (Chiou et al. 1979; Karickoff 1981; Hassett et al. 1980) and its octanol/water partition coefficient (Kow)(Brown and Flagg 1981; Hassett et al. 1980; Schwarzenbach and Westall 1981). It has been shown from the above correlations that predictive relationships based on a sorbents f_{OC} provides a reasonable estimate (within a factor of 2) of NOC sorption over a range of soils and sediments (Karickoff 1981; Chiou et al., 1983). The major characteristics of carbon-reference partitioning reactions are: 1) linear sorption isotherms ($K_P = S_e/C_{e;}$ where K_P is the sorption distribution coefficient, and S_e and C_e are the solid and aqueous solute concentration), 2) the organic carbon normalized K_P [$K_{OC} = K_P/(f_{OC})$; where K_P is the linear partition constant or K_d] is approximately the same across a diverse range of soils and sediments, 3) the K_{OC} exhibits an inverse linear relationship to a solutes water solubility and a direct relationship to its octanol/water partition coefficient, and 4) little or no interaction between cosorbates (Chiou et al. 1983; Choiu 1989; Karickoff 1984, 1981; Karickoff et al. 1979; Dzombak and Luthy 1984). The major driving forces in the sorption of NOC by the f_{OC} are attractive solvation forces that are entropic in nature (Vansant and Uytterhoeven 1972; Chiou et al. 1983), and therefore, does not exhibit a significant sorbate density variation due to changes in temperature or the presence of cosolute as a result of solute competition (Chiou et al. 1989).

Aside from the above characteristics of OC referenced sorption, there are several simplifying assumptions inherent in its use in representing RDX and TNT sorption to soils. The principal assumptions are 1) equilibrium is obtained, 2) linearity of sorption isotherms, 3) sorption is reversible, 4) sorption is limited to the organic fraction of the soil, and 5) soil OC sorption capacity is invariant with soil (Green and Karickoff 1990). Clearly, none of these assumptions are valid in the strictest sense. Further, Mingelgrin and Gerstl (1983) challenged the concept that NOCs are partitioned between water and soil OC in a fashion analogous to partitioning between two immiscible solvents (i.e., n-octanol and water). They contended that other solute-solid interactions (such as solute-clay interactions) may play an important or dominant role in the sorption of NOC. This hypothesis may be extended beyond just NOCs to neutral organic compounds with polar functional groups by examining the "threshold ratio" where below a particular value of clay fraction/OC fraction (f_{CM}/f_{OC}) the mineral contribution to solute sorption becomes important. For NOCs, f_{CM}/f_{OC} was shown to be about 25, however, this increased to as much as 60 for neutral organic compounds with polar functional groups (Koskinen and Harper 1990). This variation in f_{CM}/f_{OC} would suggest uncertainty in the dominant soil component(s) associated with sorption to soils, particularly when the solute exhibits a significant dipole moment or polar moieties.

MacCarty et al. (1981) and Karickoff (1984) proposed a two-phase model for sorption of

NOC to mineral surfaces and OC; significant sorption contributions of one or both sorbents (mineral surfaces and OC) are dependent on the sorbates K_{OW}, the sorbents f_{OC}, surface area, and type of mineral solids. Curtis et al. (1986) found that nonpolar halogenated organic solutes, at low f_{OC} (0.0002), were sorbed in excess of that predicted by K_{OW}. Similarly, Schwartzenbach and Westall (1981) also reported that sorption of nonpolar halogenated and aromatic solutes to silica, alumina, non-expanding clays, and low f_{OC} aquifer material was greater than predicted from the compounds K_{OW}. In contrast to the above studies, however, the sorption of carbazole, dibenzothiophene, and anthracene to soils, subsoils, and deep subsurface sediments was always highly correlated to f_{OC} ($r^2 \geq 0.92$) even at f_{OC} levels below 0.0002, but observed that K_{OC} values varied by as much as an order of magnitude less than the K_{OC} values predicted from K_{OW} (Ainsworth et al., unpublished data). The latter observations were probably due to differences in OC aromaticity and polarity, and structure of the OC associated with the soil mineral phase.

1.1.1 RDX sorption in soils

RDX is a small neutral nonpolar molecule with a low K_{OW}, and a concomitantly low K_{OC} (Table 1-1). RDX under goes photolytic transformations (Spanggord et al. 1980), and is microbially degraded under anaerobic conditions but aerobic biotransformation is not observed (McCormick et al. 1981). However, Spanggord et al. (1980) found that aqueous solutions of RDX could be aerobically degraded in the presence of a Holston river sediment, but only after a lag time of 20 days.

As a first approximation, sorption of RDX to soils and subsurface materials would be expected to be controlled by organic carbon-referenced partitioning, and hence, sorption intensity would be low and directly related to the f_{OC} of the sorbent. However, sorption mechanisms of related compounds such as the triazine herbicides have been suggested to include hydrophobic interactions, cation exchange, van der Waals forces, cation bridging, and charge transfer; and both organic carbon and clay minerals have been viewed as sorption sites (Hayes 1970; Koskinen and Harper 1990). Sorption to soils by the triazine herbicides have been shown to be dependent on their side chain functionality, and hence their dipole moment (Talbert and Fletchall 1965; Weber 1970). However, conclusions drawn from the soil adsorption studies of these herbicides may not be directly applicable to RDX due to the difference in the nature of the ring substitutions; RDX is nonpolar, and nonionizable, but due to the three $-NO_2$ moieties, is typically more hydrophilic than most of the triazine herbicides. In addition, the $-NO_2$ moieties may behave as weak proton acceptors, and hence participate in hydrogen bonding (Vinogradov and Linnell 1971).

The few investigations to date of RDX transport and sorption in soils (Layton et al. 1987; Tucker et al. 1985; Spaggord et al. 1980; Sikka et al. 1980) suggests that RDX does not strongly interact with soil constituents. However, the results of these studies would also suggest that RDX is not sorbed via a single mechanism; that is , carbon-referenced hydrophobic partitioning (as discussed above) does not appear to be the sole RDX sorption process. RDX sorption to soil material is not always characterized by linear sorption isotherms (Tucker et al. 1985), and experimentally determined K_{OC} values have been reported to ranged from 7.7 to 420 (Spanggord et al. 1980; Sikka et al. 1980; Tucker et al. 1985). The K_{OC} calculated from solubility and melting point data is 61. The use of K_{OC} as a normalized sorption coefficient (K_p/f_{OC}) *suggests that 1) linear sorption* isotherms were observed, 2) values for K_{OC} do not vary greatly over a range of soils and 3) partitioning of RDX from the aqueous phase to the soil OC was the dominant mechanism of sorption. In the case of RDX, however, these three empirical assumptions do not appear to be applicable at all times for RDX.

Tucker et al. (1985) observed that the K_d values for the sorption of RDX in various soils were poorly correlated with f_{OC} ($r^2 = 0.293$). However, RDX sorption could be described by a multiple regression analysis equation with soil f_{OC}, cation-exchange-capacity (CEC), pH and silt content as independent variables. Interestingly, Tucker et al. (1985) also concluded that a critical soil f_{OC} ($f_{OC} > 0.0025$) is necessary in order for carbon-referenced sorption to act as a critical process affecting the mobility of RDX. The latter conclusion by Tucker et al. (1985) seems to suggest that sorption is dominated by a carbon-referenced partitioning reaction; however this conclusion is not consistent with the regression analysis or recent observations of NOC sorption at low f_{OC}.

The above discussion suggests that sorption intensity of RDX in soils is low, but is dependent on the soil f_{OC}, and possibly the clay content; however, the dependence on both of these soil properties is poorly documented. In addition, no temperature or cosolute sorption studies of RDX have been performed. Consequently, sorption reactions are poorly understood, and the data currently available is not adequate to identify the soil constituents active in RDX sorption, nor to construct a model descriptive of RDX sorption that is valid across a diverse set of soil materials.

1.1.2 TNT sorption in soils

Similar to RDX, TNT is a small neutral organic compound (Table 1-1), and undergoes photolytic transformations (Layton et al. 1987). Unlike RDX, it is a polar compound with a small dipole moment (1.37 debye), and is known to be degraded by indigenous microflora under aerobic and anaerobic conditions (Layton et al. 1987). Recent investigations using soils sterilized by gamma-radiation suggested that abiotic transformation/degradation of TNT occurs (Cataldo et al. 1990), but the rate of transformation is apparently soil type dependent; however, the primary focus of the Cataldo et al. (1990) studies was not soil sorption, and hence, limited quantitative information directly impacting this hypothesis is available. Data for TNT sorption to autoclave-sterilized sediments exhibited a decrease in recoverable TNT after 240 hr (Spanggard et al. 1980); the sediments were analyzed for possible nonsterile conditions after the 240 hr period and the sediments were considered to be sterile. Major transformation products identified from the sterilized systems were the 2- and 4-aminodinitrotoluene (Cataldo et al. 1990). These results, if typical of TNT sorption in all soil materials, intimate an abiotic degradation pathway.

Similar to the K_{OC} determinations for RDX, the experimentally determined TNT K_{OC} values were variable. Spanggard et al. (1980) calculated K_{OC} values to range from 910 to 2500 for 6 determinations on the same sediment. However, different experimental conditions were employed in the collection of data used to calculate the reported K_{OC} values (i.e., sterile, and unsterile conditions; with and without $HgCl_2$; different times of equilibration). Also similar to RDX, Tucker et al. (1985) found that OC and CEC accounted for 64% and 78% of the variance in

TNT K_d values, respectively. Pennington and Patrick (1990) observed that TNT K_d values (as measured by ^{14}C liquid scintillation counting) correlated with extractable Fe (R = 0.892), CEC (R = 0.866), % clay (R = 0.701), and OC (R = 0.402). Interestingly, Pennington and Patrick (1990) performed the correlation analysis to determine the relationship between the sorption coefficient and soil properties utilizing the linear sorption coefficient (K_d) even though the Langmuir model fit the sorption data better.

TNT sorption to soil materials has been studied somewhat more extensively than RDX, both through the use of static batch (Pennington and Patrick 1990), soil column (Kaplan and Kaplan 1982), and soil lysimeter techniques (Hale et al. 1979). The column and lysimeter studies were conducted using nonsterile soils resulting in the biotic transformation/degradation of the TNT; both 2- and 4-aminodinitrotoluene were identified (Kaplan and Kaplan 1982; Hale et al. 1979). The presence of these ionizable amino compounds could affect TNT sorption due to co-contaminant enhanced sorption (Traina and Onken 1991; Ainsworth et al. 1989). Both clay content and OC levels appear to impact retardation of TNT breakthrough in column and lysimeter studies (Kaplan and Kaplan 1982; Hale et al. 1979).

Pennington and Patrick (1990) performed static batch equilibration studies with TNT and 14 surface soils collected from Army ammunition plants. While these researchers determined that near-equilibrium conditions were obtained in less than 2 h, continued disappearance of TNT from solution was observed and was attributed to gradual formation and adsorption of transformation products. Importantly, they showed that the sorption reaction was reversible and that the desorption process was almost as rapid as the adsorption process. Adsorption data was fit to a linear and two non-linear models that relate the solutes solid and aqueous phase concentrations; the models where 1) the linear (K_d) model, 2) the Freundlich model, and 3) the Langmuir model. Regression analysis for the model fit showed that the Langmuir model best described the adsorption data; the authors suggested that this indicated that TNT sorption reached a maximum as soil sorption sites where filled (Pennington and Patrick 1990). However, they did not suggest what these "sites" might be, but the use of a "single-site" Langmuir model would intimate a single suite of sites.

That the Langmuir model fits the TNT adsorption data best(Pennington and Patrick 1990) suggests that the major sorption mechanism is not carbon-referenced partitioning as detailed by Chiou et al. (1979), Karickoff (1981) and Hassett et al. (1980). Further, the correlation analyses of Pennington and Patrick (1990) and Tucker et al. (1985) would suggest that clay mineralogy and iron oxide content would be of considerable importance in the sorption of TNT to soils in the absence of abiotic transformations. The TNT sorption dependence on clay, OC, and extractable Fe may be the result of its slight polarity, and the presence of the -NO_2 moieties and the unpaired electrons associated with its oxygen. These factors could have a profound effect on TNT sorption by soils.

From the above review of the pertinent literature, it is evident that sorption has the capacity to affect TNT and RDX transport in soils and subsurface systems. Past research, however, has not developed a clear scientific understanding of how to describe and predict the intensity of these compounds' sorptive behavior on unconsolidated geologic media. Consequently, the purpose of this research is: 1) develop a sorption model based on chemical, physical, and mineralogic properties of soil and subsurface materials, 2) validate the effectiveness of the model in static and dynamic systems using a soil material different from those used in model construction, and 3) attempt to determine the basic chemical and geochemical reactions and interactions between TNT and RDX and soil and subsurface materials in the absence of biotic and abiotic degradation/transformation.

1.2 APPROACH

In order to address the primary objective of this project, batch sorption studies are used to provide the necessary data for developing sorption isotherms and sorption relationships based on the properties of the soils (extractable Fe, CEC, Clay content, pH, OC). Regression analysis is used to determine the relationship between the appropriate isotherm parameters and soil properties. The present study also addresses several aspects of soil selection, isotherm model use, and batch sorption studies protocol, including the following:

- To develop the most stable and accurate regression model possible the present study used correlation analysis to aid in choosing the set of soils for which the key characteristics such as iron, organic carbon and clay contents are least correlated; and hence would produce the most stable regression model.

- Three isotherm models, one linear and two nonlinear (The Freundlich, and Langmuir), commonly used to relate solid and aqueous phase contaminant concentrations are evaluated to determine which model best describes the sorption data.

- Determine the most efficient sterilization technique (steam, gamma-radiation, addition of Hg) to minimize microbial decomposition, evaluate the potential for chemical (abiotic) transformation, and the effect of time on solute sorption/transformation.

- Evaluate the effect of temperature on the magnitude of sorption, and abiotic transformation of TNT.

- Evaluate the effect of cosolute on the sorption of TNT and RDX.

Both direct HPLC analysis and radiolabelled tracers are utilized in the present study to determine recovery of the solute by extraction and desorption; in addition, when transformation products are observed, gas chromatography-mass spectrometry is utilized for identification. Sorption data is collected under the general guidelines of the U.S. EPA isotherm procedure (U.S. EPA 1985).

Table 1-1. Selected chemical and physical properties of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)(a).

Property	Unit	TNT	RDX
Chemical Formula	--	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$
Molecular Weight	g/mol	227.13	222.26
Boiling Point	^0C	240	Decomposes
Melting Point	^0C	80.1	205
Density	g/mL	1.65	1.82
Vapor Pressure	torr	1.1×10^{-6}	1.0×10^{-9}
Aqueous Solubility	mol/L	5.4×10^{-4}	1.9×10^{-4}
	mg/L	123	42.2
Henry's Law Constant	(L-torr)/mol	2.0×10^{-3}	5.0×10^{-6}
Octanol/Water Partition Coefficient	log K_{ow}	1.60 - 1.84	0.87
OC Partition Coefficient	log K_{OC}	2.67	1.78
Dipole Moment(b)	debye	1.37	—

a) Data from Layton et al. 1987

b) Data from Merck 1983

2.0 MATERIALS AND METHODS

2.1 CHEMICALS AND STANDARDS

A set of stock materials of both 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were obtained from Chem Service (West Chester, Pennsylvania), U.S. Army Toxic and Hazardous Materials Agency SARM Repository. Purity was >98% for each compound. All solvents used for extractions or analyses were either HPLC- or GC-grade; all other chemicals (e.g., $CaCl_2$) used in the present studies were reagent grade.

The 2,4,6-Trinitrotoluene [ring-^{14}C(U)] on hand required purification. The radiolabelled TNT was purified by semi-preparative HPLC on a Beckman Ultrasphere column (25 cm x 10 mm i.d., dp = 5 µm). Isocratic mobile phase, consisting of equal volumes of acetonitrile and water, was delivered to the column at a flow rate of 5.0 ml/min by a Waters Model 590 pump. Injections of TNT (150 µL) were accomplished by a Waters U6K injector. Eluting components were detected by UV absorbance at 254 nm (Schoeffel Model SF770 detector). Tracings of the chromatographic runs were performed on a Hewlett-Packard Model 3390A recording integrator. Approximately 500 µCi of TNT radiolabel was purified under the above chromatographic conditions. The column eluate corresponding to TNT was collected during a total of 9 repetitive chromatographic runs. The pooled TNT fraction (140 mL) was reduced to approximately 80 mL with a stream of nitrogen, frozen, and lyophilized. After lyophilization, the dry ^{14}C-TNT was dissolved in 3.0 mL of methanol. The purified radiolabel was assayed by analytical HPLC and liquid scintillation spectrometry. Of the initial 500 µCi of radiolabel, 447 µCi of TNT was recovered after purification. The specific activity of the radiolabel was determined to be 4.0 mCi/mmole. The radiopurity of ^{14}C-TNT was assayed by radiochromatographic analysis and was found to be 98.86%.

Uniformly ring-labeled ^{14}C-RDX was obtained from Sigma Chemical Co. (St. Louis, MO). A total of 1.0 mCi of this material was available for soil sorption studies. In preparation for these studies, the purity of the ^{14}C-RDX was determined by radiochromatography. Detection was accomplished by collecting successive 0.5 mL fractions of the column eluate with subsequent assay of each individual fraction for radiocarbon by liquid scintillation spectrometry. The radiopurity of the ^{14}C-RDX was calculated to be 93.2%. Therefore, the ^{14}C-RDX was purified by semi-preparative HPLC under the same conditions as previously noted for TNT except eluting components were detected by UV absorbance at 243 nm. The column eluate corresponding to RDX (5.25 min) was repetitively collected for a total of 10 consecutive semi-preparative chromatographic runs. The pooled eluate (100 mL) was evaporated to dryness using a stream of nitrogen and then dissolved in 3.0 mL of acetone. A total of 260 µCi of RDX radiolabel was purified by this methodology. Prior to purification, chromatography with UV detection verified the presence of the 2 polar radiolysis products that eluted before RDX, however, the ultraviolet absorption trace (234 nm) showed the presence of only RDX (retention time of 16.73 min) after purification. The purified ^{14}C-RDX was assayed by radiochromatography using the same techniques and equipment as described for ^{14}C-TNT. The peak corresponding to RDX accounted for 99.6 % of the activity eluted during the chromatographic run. The specific activity of the purified radiolabel was determined to be 17.1 mCi/mmol.

2.1.1 Preparation of aqueous TNT and RDX solutions

A known mass (± 0.1 mg) of vacuum desiccated TNT or RDX was dissolved in 2.0 L of 0.01 M $CaCl_2$ previously prepared using deionized water. A stock solution at ≤ 50% of the compounds' aqueous solubility was produced and dilutions for other stock concentrations were made from this stock; the solubilities of TNT and RDX are approximately 123 and 60 µg/mL, respectively. For experiments requiring radiotracer, approximately 200 - 250 µL of ^{14}C-labelled material was added to the cold stock solutions yielding a solution with about 50,000 dpm/mL. All solutions were filter sterilized (0.2-µm filter system) and collected in a sterile receiver flask. HPLC and liquid scintillation analysis of the filtered solutions were determined.

2.2 SOIL CHARACTERIZATION AND SELECTION

The problem is to select a group of soils in which the selected properties are not, or only minimally related. Further, the soils are required to represent a range of soil properties so that when the models are developed, they can be used to predict the behavior of TNT and RDX over a range of soil properties likely to be encountered in the field.

Thirty-six soil horizons from 14 soil pedons (distinct soil profiles) were initially selected as potential candidates for the present studies. The soils had been previously characterized with respect to cation exchange capacity (CEC), pH, inorganic and organic carbon, particle size distribution (sand, silt, and clay), and extractable Fe by dithionate/citrate/bicarbonate (DCB) (Ainsworth and Zachara 1988). The goal was to find a group of about 12 to 15 soil horizons from the major soil groups (i.e., Alfisol, Mollisol, Ultisol, Inceptisol) whose soil properties covered the broadest possible range but were not highly correlated. All soil analyses and sorption studies were performed with air-dried, sieved materials (<2.0 mm). Particle-size distribution was determined by sedimentation following sonic dispersion, with noncalcareous soils receiving a prior DCB treatment (Kittrick and Hope 1963). The CEC was determined by $^{22}Na^+$ exchange (Babcock and Schultz 1970). Organic carbon content (OC) was determined by a modified Pregl procedure by Schwarzkopf Microanalytical Lab., Woodside, NY. The DCB extraction was performed according to Jackson et al. (1986), and Fe analysis done by inductively coupled argon plasma emission spectroscopy (ICP).

In the initial correlation analysis with all 36 soil horizons, iron content was significantly correlated with percent clay, CEC and pH. Additionally, pH and CEC were also significantly correlated at the 5% level of significance. In selecting 15 soils, attention was paid to minimizing these relationships, while maximizing the ranges of the five soil properties. The 15 selected soils and their properties are listed in Table 2-1. For the final 15 soils, significant ($p = 0.05$) correlations still existed between iron content and percent clay and pH, as well as between pH and CEC. However, at the 1% significance level, only iron and percent clay were correlated. The effect of significant correlations on the regression analysis is to make the regressions unstable. That is, removal of a single data set from a stable regression analysis does not markedly affect the analysis results; however, if the regression is unstable, the removal of the same data set would result in very different regression coefficients. This instability also means that the variances are inflated. Needless to say, inflated variances are quite harmful to the use of the regression as a basis for hypothesis testing, estimation and forecasting (Belsley et al. 1980). A measure of the stability of the regression is called the condition number and is obtained by a mathematical manipulation of the correlation matrix. For the set of 15 soils selected the matrix condition number is 26 which is borderline but within acceptable limits (Belsley et al. 1980) with regard to the stability of a regression model. Therefore, sorption data generated from experimentation using the 15 selected soils will have a greater probability of producing a viable predictive model than a model generated from studies with soils whose important physicochemical properties exhibit a larger matrix condition number.

The 15 soil horizons listed in Table 2-1 were collected from various parts of the United States and exhibit varied physicochemical properties. The Kenoma and Norborne soils are from the midwest, the Elk, Watson, and Westmoreland soils were collected from the Ohio basin and Appalachian coal regions, the Cecil and Cloudland soils are from the southeast and the Haggerstown and Ocala soils are from Pennsylvania and Nevada respectively. The Burbank Ap soil horizon is from the mod-columbia basin in Washington state. The clay mineralogy of the Kenoma, Norborne, and Hagerstown Saprolite horizons is dominated by smectite. The clay mineralogy of the Ocala soil horizon, which is from a calcareous inceptisol of pyroclastic origin, is dominated by illite, and vermiculite. The clay mineralogy of the Cecil and Cloudland soil horizons is dominated by oxides of Fe and Al, and kaolinite. The other three soil materials (Elk, Watson, and Westmoreland) exhibit clay mineralogies dominated by vermiculite, mica, and kaolinite.

2.3 SOIL STUDIES

2.3.1 Method of sterilization

All sorption and column studies were performed using sterilized soils and glass corex centrifuge tubes. Soils were typically weighed out into centrifuge tubes (about 6.0 g), mass recorded, and then both the tube and soil sterilized; soils for column studies were first sterilized and then packed into sterile steel columns in an aseptic manner. Three sterilization techniques were investigated for possible use. Steam sterilization (autoclaving) at 121 ^{0}C and 0.1 MPa was carried out for about 20 to 30 min/day on three successive days. Soils and tubes were irradiated (^{60}Co gamma irradiation) in a 1.67×10^5 rad/hr field for 30 h resulting in a total dose to the soil of 5.0 ± 10% Mrad; the exposure rate was measured with a Capintec PROC ion chamber that has a NIST traceable calibration. The third technique was the use of $HgCl_2$ additions of 1.84mmole/kg soil as a concentrated solution added to the soil with the solute of interest. Each of these techniques has potential problems associated with them (Wolf et al. 1989). The three sterilization techniques were evaluated during the initial part of the project (kinetics of sorption); steam sterilization was used exclusively after this initial phase.

2.3.2 Sorption time dependence

Two soils (the Norborne C and Cloudland Ap) with diverse mineralogies and physicochemical properties were used to determine the time dependence of TNT and RDX sorption. These studies were performed at two initial concentrations of TNT (60 and 10 µg/mL) and RDX (30 and 3 µg/mL). The TNT or RDX stock solutions (25 g) were added to a known mass (approximately 6 g) of steam-sterilized soil in sterilized 50-ml Corex centrifuge tubes. Duplicate samples were prepared for each incubation period and solute concentration. The samples were then agitated for periods ranging from 1 hr to 24 d using an end-over-end rotator at 29±5 rpm. Light was excluded from tubes during the incubation periods by wrapping the tubes with aluminum foil. At prescribed times (0.17, 0.33, 0.67, 1.0, 4, 8, 16, and 24 days), samples were centrifuged and the supernatant decanted. The supernatant was subsequently analyzed by HPLC and liquid scintillation spectrometry. An accurate weight of the moist soil was obtained to determine the amount of residual solute solution remaining in the soil; occluded solute mass was determined by difference between the initial and post-centifuged soil mass. Soil from the duplicate samples were then extracted either by washing repetitively with methanol (MeOH) or by exhaustive Soxhlet extraction. The sorbed concentration was determined by HPLC analysis of the extract solutions (discussed below) and an accounting for the occluded solute mass. Mass balance was determined by comparison of HPLC analysis of the aqueous supernatant and the extract solutions and compared with ^{14}C analysis of the same solutions.

2.3.3 Soil extraction

The MeOH rinse procedure (after Ainsworth et al. 1991) for extracting adsorbed TNT from soils involved 3 successive washes with 15 mL portions of MeOH. The samples were agitated on a wrist-action shaker for 15 min at which time the sample was centrifuged and the MeOH decanted. The three rinses were pooled and brought to a final volume of 50 mL. MeOH extracts were filtered through 0.45-μm nylon filters, and analyzed by either or both liquid scintillation spectrometry and HPLC.

For the exhaustive Soxhlet extraction studies, soils were transferred to glass extraction thimbles (24 mm i.d. x 70 mm) that contained coarse frits (ASTM 20-40 mesh). Extractions were performed with 150 mL of MeOH for periods ranging from 48 to 96 h. At the conclusion of the extraction, the final volume of the MeOH extract was brought to 100 mL with MeOH. This final extract was then filtered through a 0.45-μm nylon filter prior to HPLC and LSC analyses. Both extraction techniques were evaluated during the initial part of the project (kinetics of sorption); the MeOH method was used exclusively after this initial phase.

2.3.4 Batch sorption studies

1. All soils were steam sterilized (20 min at 121 °C and 0.2 MPa) for three consecutive days and the sorbate solutions were filter sterilized (0.2 μm pore diameter filter). The maximum sorbate concentration was $\leq$ 50% of its solubility dissolved in a background electrolyte of 0.01 M $CaCl_2$. Solutions and suspensions were protected from exposure to light by wrapping the containers with aluminum foil.

2. Five concentrations of TNT (0.74 to 50 μg/mL) and RDX (0.9 to 26 μg/mL) were employed for each soil and sorbate or set of sorbates and were carried out in duplicate; a complete set of no soil blanks were carried through the entire procedure.

3. Soil and sorbate were contacted at a 1:4 solid-to-solution ratio using 25-mL glass centrifuge tubes sealed with teflon-lined caps; the mass of solid and solution was such that head space was minimized (i.e., < 1.5 mL).

4. Soil suspensions and blanks were agitated via an end-over-end rotator at 29 ± 5 rpm at 23 ± 2 ^{0}C for an appropriate period of time (4 days and 24 hours for TNT and RDX, respectively).

5. After agitation, the suspensions were centrifuged at about 8000 rpm for 30 min to separate the aqueous and solid phases. A 4-mL aliquot of the supernatant was removed to an amber HPLC vial for HPLC analysis. The remaining supernatant was carefully decanted and discarded and the occluded solution mass determined.

6. The soil was then washed with 15 mL of 100% HPLC-grade MeOH; MeOH was added to the soil, the tube sealed, and the mixture aggressively agitated on a wrist shaker for 15 min. After agitation, the MeOH suspension was centrifuged as before and the supernatant decanted and saved. The MeOH wash procedure was repeated three times with each of the supernatants being combined in an amber volumetric flask; after the 3x MeOH washes the final volume was brought to 50 mL with MeOH. The MeOH wash solution was then analyzed via HPLC.

7. The quantity of solute sorbed was calculated from the MeOH wash analysis and an accounting of the occluded solute mass, and from the difference between the initial and final aqueous concentrations.

8. Selected samples and blanks were tested for sterility; agar plates were streaked and incubated at 25 ^{0}C for 4 days.

2.3.5 Desorption studies

Desorption studies with TNT and RDX were carried out using the Norborne C and Cloudland Ap soil horizons in duplicate over the same range of solute concentrations, and the using the same procedure noted above. However, after the supernatant was separated (step 5 above) one of the duplicate samples (for each soil, solute, and concentration level) had the decanted solution mass replaced with the same mass of 0.01 M $CaCl_2$ while the other duplicate sample and both supernatants continued to be treated as a regular sorption study. The duplicate whose solution mass was replaced was resealed and rotator mixed for an additional 24 h; this constituted the desorption step. After 24 h, the desorption step samples were treated in the same manner as all batch sorption samples (i.e., samples followed steps 5 through 8 above).

2.3.6 Cosolute Studies

Cosolute sorption isotherm studies, where TNT and RDX were present in equal concentrations (up to about 15 µg/mL each), were performed on the Cloudland Ap and Norborne C soil horizons; except for the presence of cosolute these studies where carried out in the same manner as all sorption studies.

2.3.7 Temperature studies

A series of batch sorption studies (using the above sorption procedure) were performed at three temperatures for both the TNT and RDX. Temperature studies were carried out at 10, 20, and 50 ^{0}C for TNT and RDX sorption to the Cloudland Ap, Norborne C, and Kenoma BC soil horizons; the exception to this was that the RDX studies on the Kenoma BC soil were performed at 10 and 20 ^{0}C only. The temperature was held at the appropriate level ± 2.0 ^{0}C by placing the mixing apparatus inside a constant temperature incubator.

2.3.8 Column studies

A series of 1-D laboratory-scale solute transport experiments (column experiments) were conducted with TNT and RDX to assess any change in sorption behavior that might occur in a flowing system compared to a batch system. Column experiments were conducted with the following soils: Norborne C, Westmoreland B1, Ocala C4, Cloudland C, and Burbank Ap. The soils used for these experiments were chosen because of differences in the amount of organic matter, iron oxide, and clay content, all of which were believed to be important contributors to solute sorption. All soils were sterilized, and all solutions were filter sterilized. The column experiments took two forms: 1) The standard breakthrough studies, which involved pumping a solute-laden solution (and other tracers) through a column until solute breakthrough occurred, and then pumping a solute-free solution into the column until effluent concentrations decreased to below detectable concentrations, and 2) Small-pulse column experiments were performed and differed only by the repeated injection of a small volume of solute-laden solution (1.885 mL) into the column, rather than a single large volume injection.

The columns were 0.5-cm-diameter by 5-cm-long stainless steel. All materials in contact with the fluid (fig. 2-1) were 316L stainless steel, Teflon, or glass. A column heater was used to maintain the temperature (±0.5°C) in all column experiments. At the column inlet, a 4-way HPLC valve enabled switching between solute-laden and solute-free solutions without interrupting flow in the column. Separate pumps and pulse dampers (Gilson Medical Electronics, Lincoln, Nb. and Scientific Systems Incorporated, Boston, Ma.) were used for the two solutions to maintain a sharp solute boundary at the column inlet. A third pump attached to the two feed solutions was used to calibrate standards during the experiment. The use of unsealed reservoirs did not produce any mass losses because the volatilization of TNT or RDX is relatively small (vapor pressure is $< 10^{-6}$ mm Hg at 25 ^{0}C) over the 1- to 44-h experiments. In-line detectors were used to measure the concentrations of $CaCl_2$ (by electrical conductivity), and TNT or RDX (by UV absorbance; 243 nm and 234 nm, respectively). In some experiments, water samples were collected at the column outlet for analysis of TNT or RDX and associated degradation products. The average interstitial water velocity was calculated from the effluent weight and elapsed time. To achieve boundary and initial conditions in reactive transport models, the volumes at the inlet and in detectors were accounted for. The volume between the inlet valve and the column and the column outlet to detector was measured at 0.482 mL, based on 8 tracer breakthrough experiments with no column. This lag was corrected for in column experimental data. Solute concentrations were typically 4.35 µg/mL and 4.18 µg/mL for TNT and RDX, respectively.

Columns were packed dry using the "tap-fill" method, weighed, saturated with 10 to 50 pore volumes of water, and reweighed. Monitoring effluent during this process insured attainment of chemical stability, as unbound clay was washed out of the column. There was some variation in packing different columns, as seen by the variation in calculated porosity and dry bulk density, so measurement of the bulk density and porosity for each packed column was essential to accurately calculate a sorption K_d (see appendix A). In general, two column experiments were conducted with each soil/solute pair, with one experiment conducted at a specific velocity (v = 0.01 cm/sec) for direct comparison of results between soils. The second experiment was conducted at a different velocity, which was chosen to quantify the kinetics of the adsorption or transformation reaction. Interstitial velocities were varied from 2.6 x 10^{-5} cm/sec to about 0.015 cm/sec. Because the Ocala C4 soil had the highest percent clay (33%), flow through this soil was difficult to achieve without some of the clay clogging the column outlet filter. Therefore, a 50/50 mixture of this soil and alumina particles (inert with respect to TNT and RDX sorption) was used in all experiments.

Additional column experiments were conducted with two soils to further identify the mass loss reaction(s) and in an attempt to quantify transformation rates. Because previous experiments showed that the mass loss is relatively small, these experiments consisted of consecutive injections of a small mass (8.2 µg) of TNT into a column of either Norborne C soil or Cloudland C soil. Three to six injections were made at 25, 45, 65, and 85 °C.

2.4 CHEMICAL/ANALYTICAL PROCEDURES

An HPLC system was utilized for the routine analysis of TNT, RDX, and their possible soil transformation products. This system consists of a pair of Waters 510 pumps, a WISP 712 automatic injector, and a Waters Lambda Max Model 481 variable wavelength detector. A Macintosh SE computer with Rainin Dynamax HPLC software (version 1.1) was used for data collection. This data collection system allows for convenient post-run data manipulation and file storage for future reference.

Gradient elution chromatography was employed to allow for the analysis of a broad range of potential transformation products. The gradient elution runs utilized a water/acetonitrile gradient delivered to an Ultrasphere 25 x 0.46 cm column containing 5-µm octadecyl silica packing (Beckman, San Ramone, CA) at a flow rate of 1.0 mL/min as described elsewhere (Cataldo et al. 1989, 1990). Typically, sample injection volumes of 20 µL were analyzed. Detection wavelengths for TNT and RDX were 254 and 243 nm, respectively. For RDX, a biphasic linear gradient was generated. The solvent ramp progressed from 20 to 60%

acetonitrile in 20 minutes, and continue to 100% acetonitrile in an additional 10 minutes. The final mobile phase composition was held for 10 min prior to a 20 min column equilibration at 20% acetonitrile. Analysis of TNT utilized a linear gradient ramp from 40 to 100% acetonitrile over 20 min. The final mobile phase composition was held for 15 min followed by a 20 min column equilibration period at the initial mobile phase composition.

Methanol standards of TNT and RDX were accurately prepared using vacuum desiccated stocks. TNT shows a linear response within the range of 0.2 to 80 µg/mL, RDX has a linear response for the range of our standards of 0.25 to 50 µg/mL. The approximate detection limit is 0.2 µg/mL and 0.25 µg/mL for TNT and RDX, respectively. Comparison of peak areas to standard curves formed the basis for quantification in the present studies. Standard curves were developed for each set of samples generated throughout the soil adsorption studies.

Gas chromatography-mass spectrometry (GC/MS) was utilized to determine transformation products when mass loss of TNT was substantial and HPLC analysis suggested the presence of possible transformation products; GC/MS analysis was not performed on a routine basis. GC/MS analyses utilized a Hewlett-Packard 5970 mass-selective detector interfaced to a Hewlett-Packard 5990A gas chromatograph.

In accordance with the protocol developed for the present studies, soils were extracted 3x with methanol (15-mL/extraction) and brought to 50 mL volume. Typically, the volume of methanol was subsequently reduced to approximately 1 mL by rotary evaporation and further reduced to 100 µL with a gentle flow of nitrogen in preparation of GC/MS analysis. Direct analysis of the concentrated extracts by GC-MS gave total ion current (TIC) chromatograms that contained severe interferences arising from compounds extracted from the soil matrix. Examination of spectra obtained in the expected retention window of the aminodinitrotoluene isomers indicated that the major fragments (197 and 180 a.m.u.) characteristic of the compounds were present; however, the spectral features were not sufficiently robust to allow unambiguous identification.

Therefore, aminodinitrotoluene isomers were isolated by HPLC prior to GC-MS analysis. The initial HPLC isolation removed the majority of soil matrix interferences that were responsible for obscuring the aminodinitrotoluene isomers in the GC-MS experiments described above. Therefore, the 50-mL methanol extracts were taken to dryness and reconstituted with acetonitrile, and HPLC separations performed using the previously described system. The column eluant corresponding to non-TNT HPLC peaks were manually collected. HPLC-purified samples were evaporated to dryness, reconstituted with toluene, and introduced to the gas-chromatographic system by cold on-column injection. Components were separated on a 30 m x 250 µm i.d. DB-5 column (df = 0.25 mm). The column was temperature programmed from 50 to 260 °C at 16 °C/min and the final temperature maintained for 15 min. During the separation, mass spectra were collected over the mass range of 45 to 500 a.m.u. Under the separation conditions, the retention time of TNT was 12.0 min, whereas 4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene eluted at 13.7 and 14.0 min, respectively. The elution order of the aminodinitrotoluene isomers on a DB-5 stationary phase has been previously established (Harvey et al. 1990). Toluene injection blanks were run between each of the samples as an extra precaution to ensure that cross contamination between gas-chromatographic runs had not occurred.

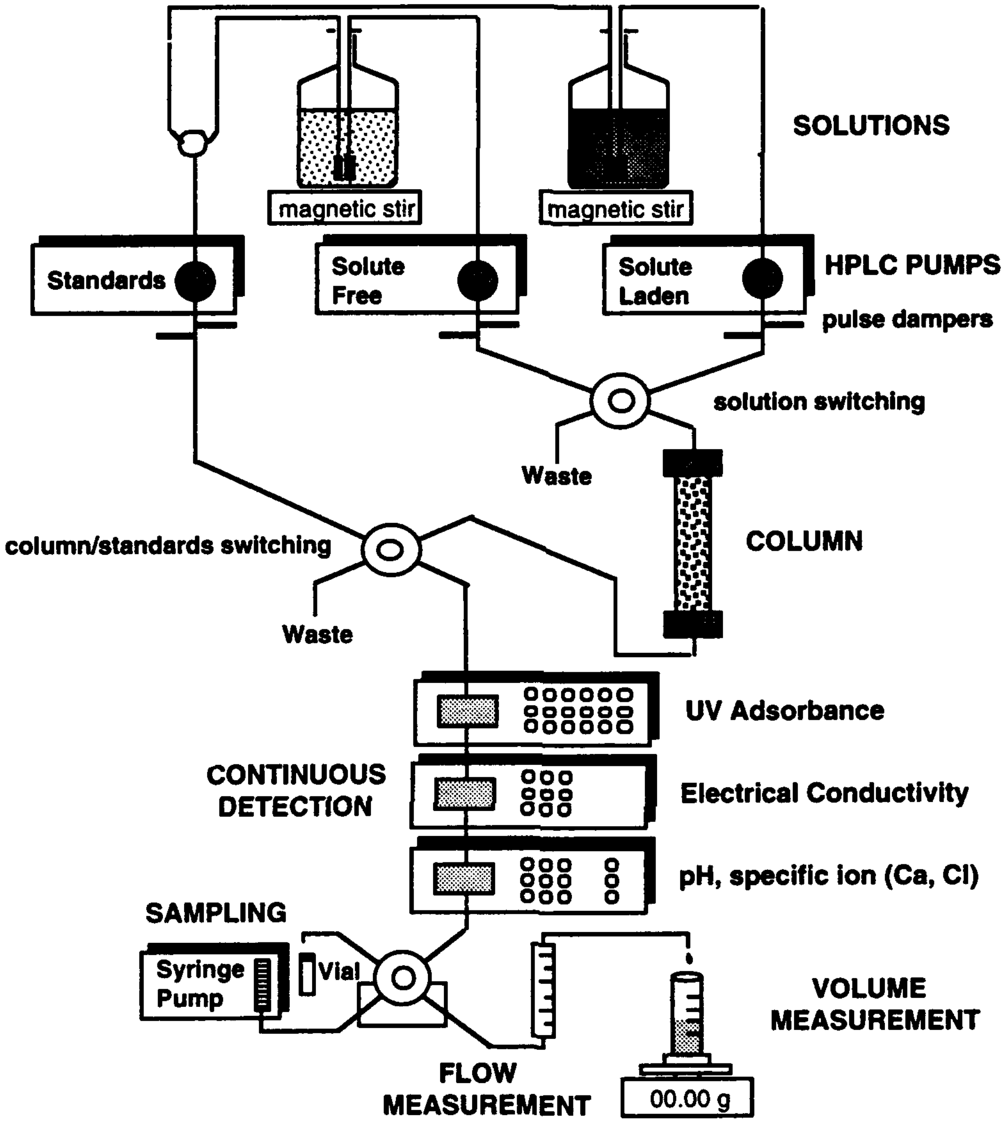


Figure 2-1. Experimental column apparatus.

Table 2-1. Selected physical-chemical properties of soils selected for study.

	Soil	Horizon	pH	OC (a) %	Clay %	Silt %	Sand %	DCB - Fe (b) µmole/g	CEC (c) meq/100g
1	Burbank (Xeric Torriorthent)	Ap	7.0	0.50	4.0	51.0	45.0	110.3	5.50
2	Cecil (Typic Hapludult)	Ap	5.1	0.59	62.0	24.0	14.0	631.2	4.88
3		Bt	5.3	0.32	53.0	29.0	18.0	551.0	2.92
4	Cloudland (Typic Fragiudult)	Ap	5.3	1.19	11.0	53.0	36.0	89.9	2.49
5		C	4.2	0.05	30.0	7.0	63.0	345.0	5.58
6	Elk (Ultic Hapludalf)	Ap	4.7	1.66	10.5	59.1	30.3	147.0	5.51
7		B1	4.7	0.45	16.5	62.0	21.4	245.0	6.92
8	Hagerstown (Typic Hapludalf)	Saprolite	8.6	0.03	5.0	89.0	6.0	104.4	2.00
9	Kenoma (Vertic Argiudoll)	Bt1	5.6	1.43	44.0	51.0	5.0	163.0	26.00
10		BC	6.7	0.50	44.0	51.0	5.0	162.0	31.40
11	Norborne (Typic Argiudoll)	C	7.1	0.23	13.0	72.2	14.8	55.0	9.14
12	Ocala (Aeric Halaquept)	C4	10.7	0.08	33.0	43.0	24.0	6.1	33.50
13	Watson (Aquic Fragiudult)	2Bxg	4.1	0.40	47.0	44.0	9.0	388.0	10.30
14		BE	5.3	1.10	37.0	55.0	8.0	312.0	6.06
15	Westmoreland (Ultic Hapludalf)	A1	4.9	2.03	14.4	60.7	23.9	172.0	6.91
16		B1	5.2	0.98	13.6	64.0	22.3	173.0	5.56

a) OC - organic carbon determined by a modified Pregl procedure Schwarzkopf Microanalytical Lab; Woodside NY.

b) DCB-Fe - dithionate/citrate/bicarbonate dissolution of whole soils and Fe determined on the extract by ICP.

c) CEC - cation exchange capacity determined by 22-Na isotopic exchange.

3.0 RESULTS OF BATCH SORPTION STUDIES

3.1 SORPTION KINETICS, EXTRACTION METHODS, AND TRANSFORMATION OF TNT AND RDX

Initial studies in this project were directed at addressing several questions concerning sorption time dependence (sorption kinetics), extraction methodology, and abiotic transformation. Information concerning these questions was necessary to ensure that the sorption data collected later were reasonable and accurate. However, time did not permit these questions to be addressed for each soil that was to be used over the course of the project. Therefore, two soils were selected that reflected the variation in clay content, mineralogy, pH, OC, and iron content of all the soils; the soils chosen were the Norborne C and Cloudland Ap soil horizons. In addition, time dependence studies were used as a way of answering the above questions while performing the least number of individual experiments as possible. Hence, the sorption kinetics of RDX and TNT were determined in duplicate. The duplicate samples were extracted either by 3X methanol washes, or Soxhlet extraction, and a sorbate mass balance performed for each sample.

3.1.1 Sorption kinetics and extraction technique

Based on published data suggesting that RDX did not undergo aerobic biotransformation (McCormick et al. 1981; Spanggord et al. 1980) time dependent RDX sorption studies were initially carried out without sterilization. RDX was observed to reach aqueous steady-state conditions after about 8h and did not vary over a 24 d period for the Norborne C soil at 30 and 3 µg/mL initial RDX concentration. However, RDX sorption to the Cloudland Ap soil reached a maximum sorbed concentration in about 8h but then began to decrease with time over the remaining 24 d study; in addition, the aqueous phase RDX concentration reached what appeared to be steady-state conditions after about 8 h but also decreased from then on (Fig. 3-1). Interestingly, depending on the analysis (HPLC vs ^{14}C), different aqueous concentrations of RDX were calculated and this difference increased with time; aqueous concentrations determined by

HPLC were always lower than by ^{14}C liquid scintillation counting (LSC; Fig. 3-1). In addition, the solid phase RDX concentration (HPLC) decreased with time suggesting that RDX was being rapidly transformed by microorganisms after as few as 8 h lag time. These findings are vastly different than those observed by Spanggord et al. (1980a; see section 1.1.1). By steam sterilizing the Cloudland Ap soil, RDX reached and maintained steady-state conditions both in the aqueous and solid phases after about 6 h (Fig. 3-1).

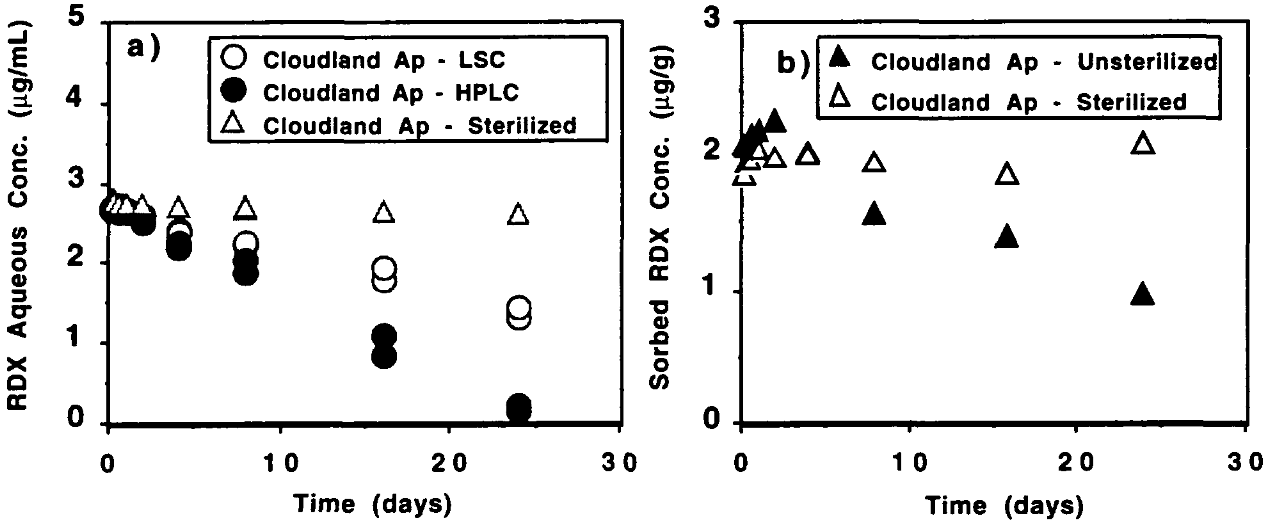


Figure 3-1. Behavior of 3µg/mL RDX in contact with steam sterilized or unsterilized Cloudland Ap soil horizon over a 24 d period a) aqueous concentration, and b) sorbed concentration.

TNT, on the other hand, appears to come to aqueous phase steady-state conditions with time under sterile conditions; however, the time needed to approach steady-state conditions varies slightly with soil and initial sorbate concentration (Fig. 3-2a). However, depending on how the solid phase concentration is determined, one obtains different solid phase TNT densities; that is, if it is calculated from the change in the aqueous phase concentration a larger solid phase density (µg TNT/g soil) is obtained compared to that determined from direct analysis via extraction (Fig. 3-2b). Additionally, the solid phase density (as determined by extraction) is greater from LSC than form HPLC analysis. This suggests that there is a small but significant abiotic transformation component to sorption that is not accounted for by determining sorption from the change in the aqueous phase solution concentration. Further, this phenomenon, shown in figure 3-2b for the sorption of 10 µg/mL TNT on the Norborne C soil, was evident for both soils and at both initial concentrations. After approximately 50 h the extracted concentration of TNT (as determined by HPLC) appeared to have reached a steady-state condition.

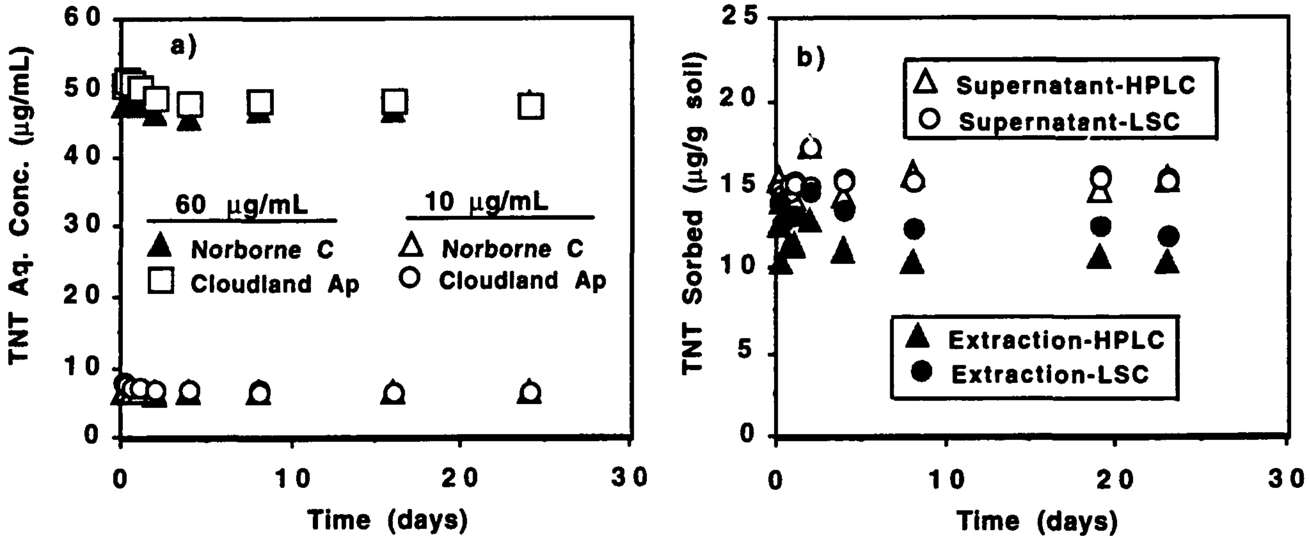


Fig. 3-2. Affect of time on TNT aqueous and solid phase concentrations: a) aqueous concentration of TNT in the presence of *Norborne C and Cloudland Ap soils* at initial concentrations of 10 and 60 µg/mL TNT, and b) the solid phase concentration of TNT at an initial TNT concentration of 10 µg/mL as a function of analysis (HPLC or LSC) and extraction versus aqueous calculation of sorbed concentration on the Norborne C soil horizon.

Throughout the above time dependency studies, duplicate samples were extracted using the Soxhlet technique or 3 MeOH washes. The MeOH wash technique proved to be faster (about 2 hr) than the Soxhlet extraction (24 hr) and more reproducible. For instance, the recovery of TNT for both the Cloudland Ap and Norborne C soils ranged from 90 to 107% and from 81 to 105% for the MeOH wash and Soxhlet extractions, respectively (Fig. 3-3). The soils sorbed between 20 to 30% of the TNT in the 60 µg/mL equilibration experiments, and as can be seen from the comparisons presented in Figure 3-3 equivalent extraction results for both the Soxhlet and MeOH rinse procedures were not always obtained. In addition, the recovery efficiency of the Soxhlet extraction was considerably less than the MeOH wash particularly for the Cloudland Ap soil. During the Soxhlet extractions, the extraction thimbles often remained filled with MeOH during the solvent cycling process; the resulting inefficient percolation through the soil may have given rise to the low recovery values. The reason for the solvent impermeability is not clear but may be related to a combination of the small particle size of the soils, the specific mineralogy, and the high moisture content.

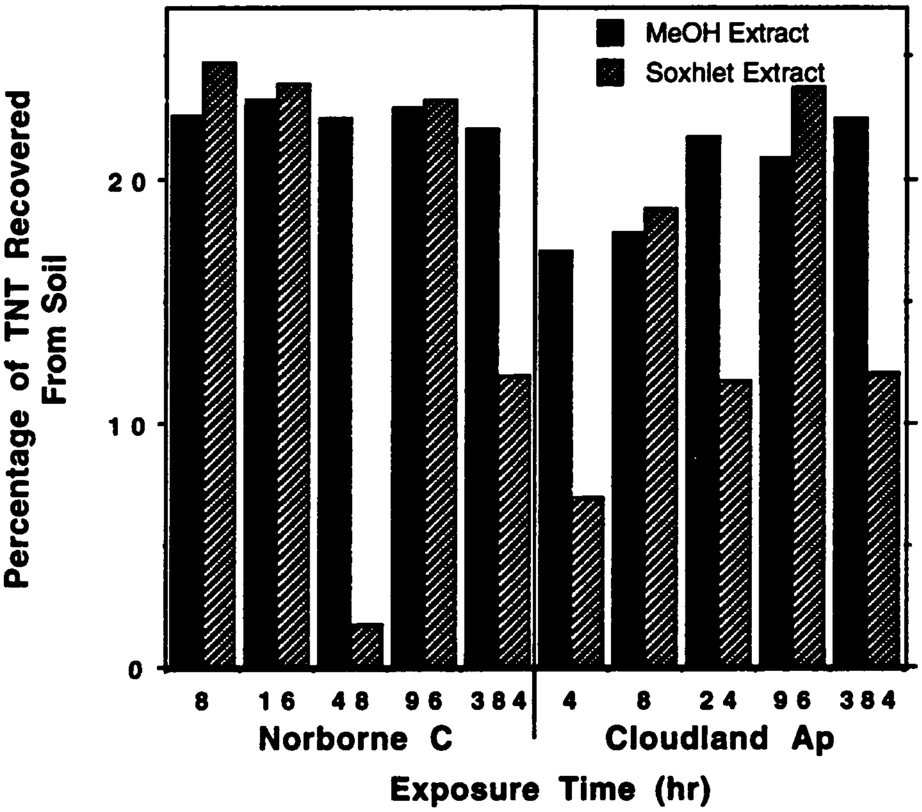


Figure 3-3. Comparison between the Soxhlet and repetitive MeOH wash extractions; 60 µg/mL initial TNT concentration.

The inconsistency of the Soxhlet extraction translated into variable mass balances of TNT for both the Norborne C and Cloudland Ap soils (98.5 ± 9 and 93 ± 12%). In comparison, the MeOH wash yielded mass balance results for both soils that were remarkably good; 98±6 and 100±6% for the Cloudland Ap and Norborne C soil horizons, respectively. However, the MeOH extraction for both soils, exhibited a trend towards an increasing TNT mass balance deficit as sorption times became longer (Fig. 3-4). It is considered likely that TNT is becoming irreversibly bound to the soils. The irreversible binding of TNT, however, is believed to be the result of an abiotic transformation since no microorganism could be cultured from the soils after the studies had been completed. To determine if the unaccounted for TNT is in fact irreversibly bound, the

24 d soils that had been extracted were oxidized (by total combustion using a Packard Model 306 oxidizer) and the gases ($^{14}CO_2$) collected for LSC. The total amount of ^{14}C accounted for by ignition and subsequent LSC was between 2 and 9% of the total TNT added. Therefore, at the worst 94% of the initial TNT could be accounted for after 24 d.

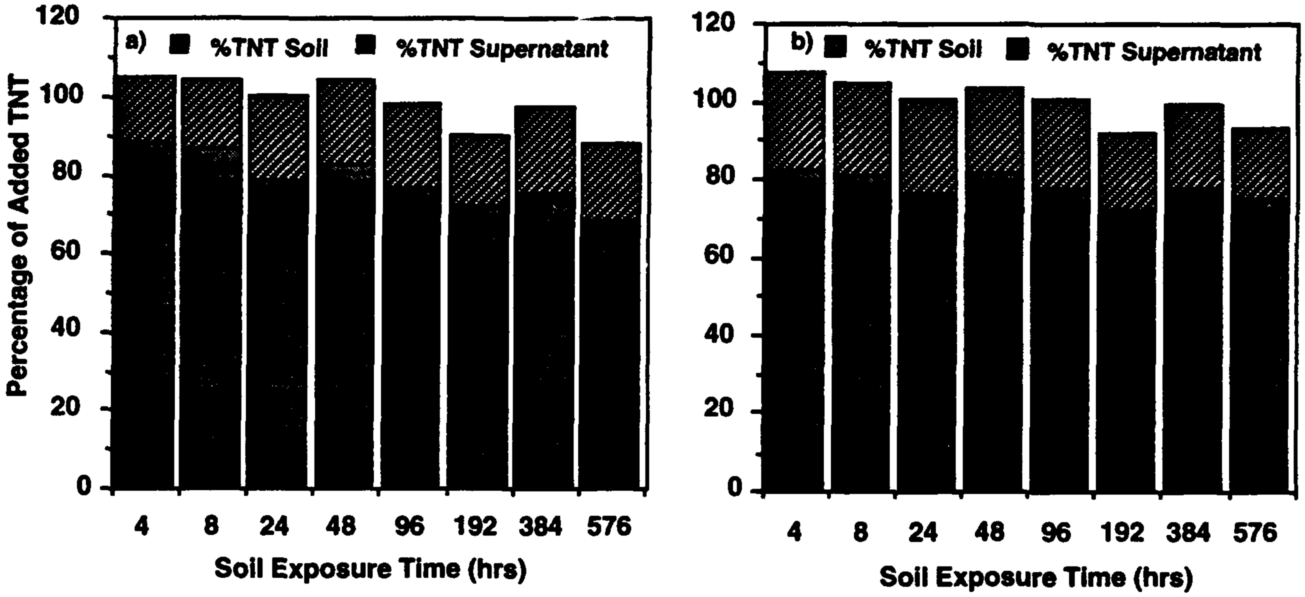


Figure 3-4. Mass balance based on HPLC analyses of TNT in the a) Cloudland Ap, and b) Norborne C soil horizons; 60 µg/mL initial TNT concentration.

3.1.2 TNT mass loss

As discussed above, the mass balance of TNT recovered from soil sorption experiments exhibits a decrease in percentage of TNT recovered over time. Reductive transformations have been observed in previous studies utilizing TNT amended soils (Cataldo et al. 1990; Harvey et al. 1990). To confirm this, a soil known to yield reductive transformations of TNT (Burbank Ap; Cataldo et al. 1990; Harvey et al. 1990) was treated in the same manner as described above. Chromatographic profiles of the methanol extracts of the three soils aged with aqueous TNT solutions were found to contain an HPLC peak which corresponded to the retention time of aminodinitrotoluenes (retention time of 10.9 min; Fig. 3-5). Proof that this peak was due to the aminodinitrotoluene isomers involved analysis by combined GC/MS. For this, the 50-mL methanol extracts were taken to dryness and reconstituted with acetonitrile. HPLC separations proceeded as described previously. The column eluant corresponding to the small peak that eluted immediately before TNT (Fig. 3-5) was manually collected. Injection of a 2-amino-4,6-dinitrotoluene standard indicated a HPLC retention time match between the standard material and the suspect TNT transformation product.

To determine whether the aminodinitrotoluene isomers were present as trace impurities in the TNT used for these experiments, both the bulk TNT and the 60 µg/mL aqueous solutions were examined by GC/MS. For this experiment, the aqueous solution was evaporated to dryness and dissolved in toluene to give a concentration of TNT that was comparable to that in the concentrated soil extracts. The center panel of Figure 3-6 is the total ion current chromatogram for the 6 µg/mL TNT stock solution concentrate. The mass spectra of TNT is shown in the top panel of Figure 3-6. The bottom panel of Figure 3-6 presents the extracted ion current chromatogram for the 197 a.m.u. ion. This ion is diagnostic for the aminodinitrotoluene isomers. The absence of the 197 ion demonstrates the lack of detectable aminodinitrotoluene isomers in this sample. Similar results, indicating the absence of aminodinitrotoluene isomers, were obtained from concentrated toluene solutions of the bulk TNT.

GC/MS analysis of the HPLC separated MeOH extracts from the Burbank Ap (Fig. 3-7) and Cloudland Ap (Fig. 3-8) soil horizons provides unequivocal evidence for the presence of the aminodinitrotoluene isomers in both samples. The full scan mass spectra of these TNT transformation products are presented in the center and top panels of Figures 3-7 and 3-8. The sample prepared from Norborne C horizon indicated possible traces of the aminodinitrotoluene isomers, as evidenced by the presence of ions at 180 and 197 a.m.u.; however, because of the very small quantities of material, the results were not conclusive. Additionally, a peak eluting well before the aminodinitrotoluene isomers (8.22 minutes for the unknown, 10.95 for the aminodinitrotoluenes) was observed in HPLC runs of extracts from Norborne C soil horizon. This tentative transformation product was manually collected,

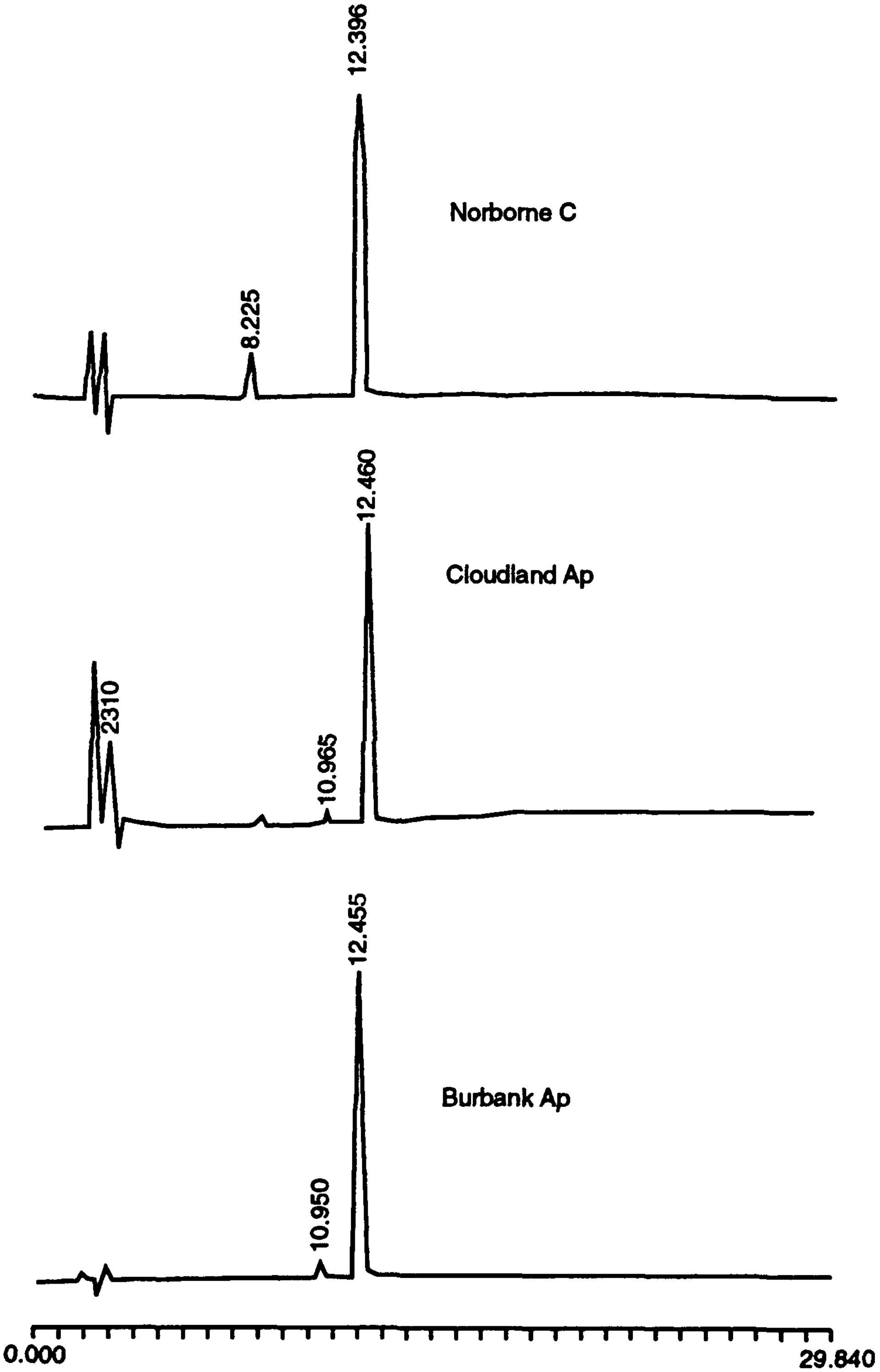
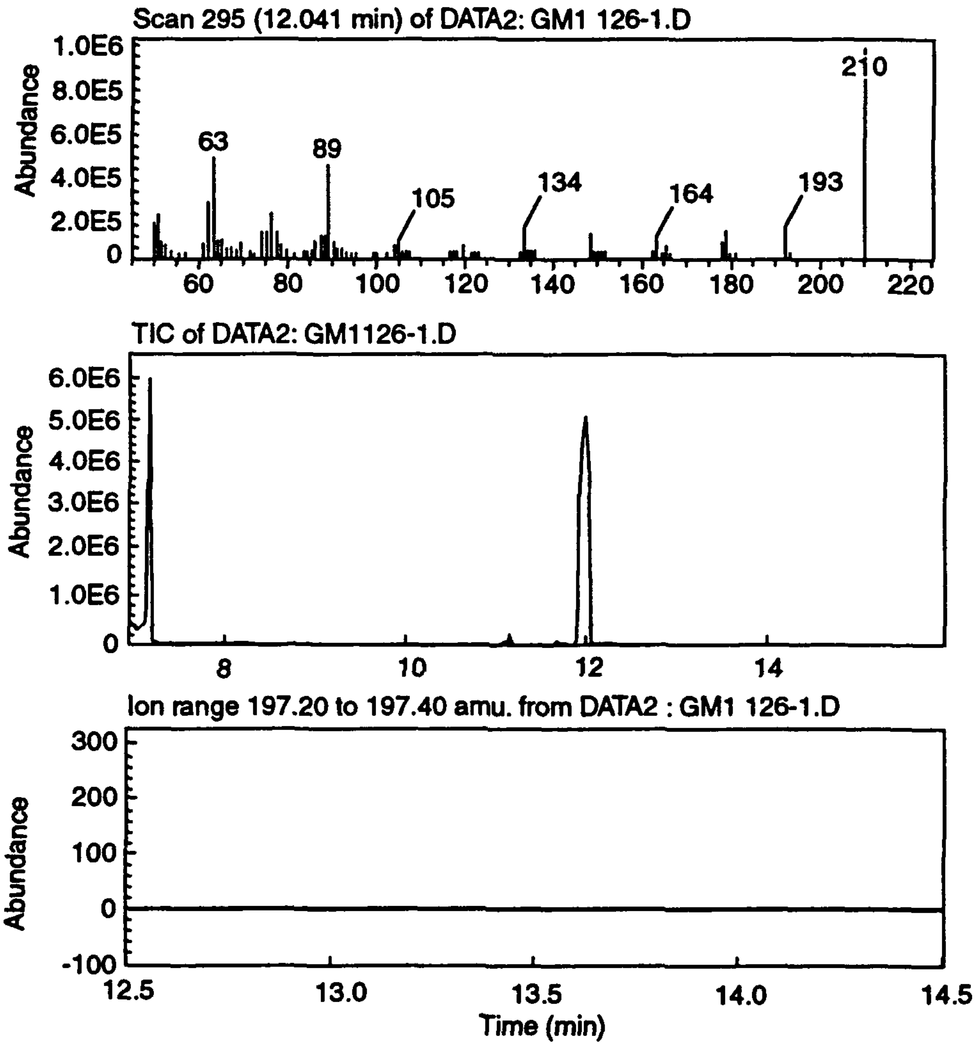


Figure 3-5. HPLC chromatograms illustrating the concentrated MeOH extractables from three different soils after 24 h of incubation under sterile conditions.



R9305065.2

Figure 3-6. GC/MS total ion current chromatogram of a concentrate from the 6 µg/mL aqueous TNT solution used to amend the soils (center), the mass spectrum of TNT (top), and the 197 a.m.u. extracted ion plot.

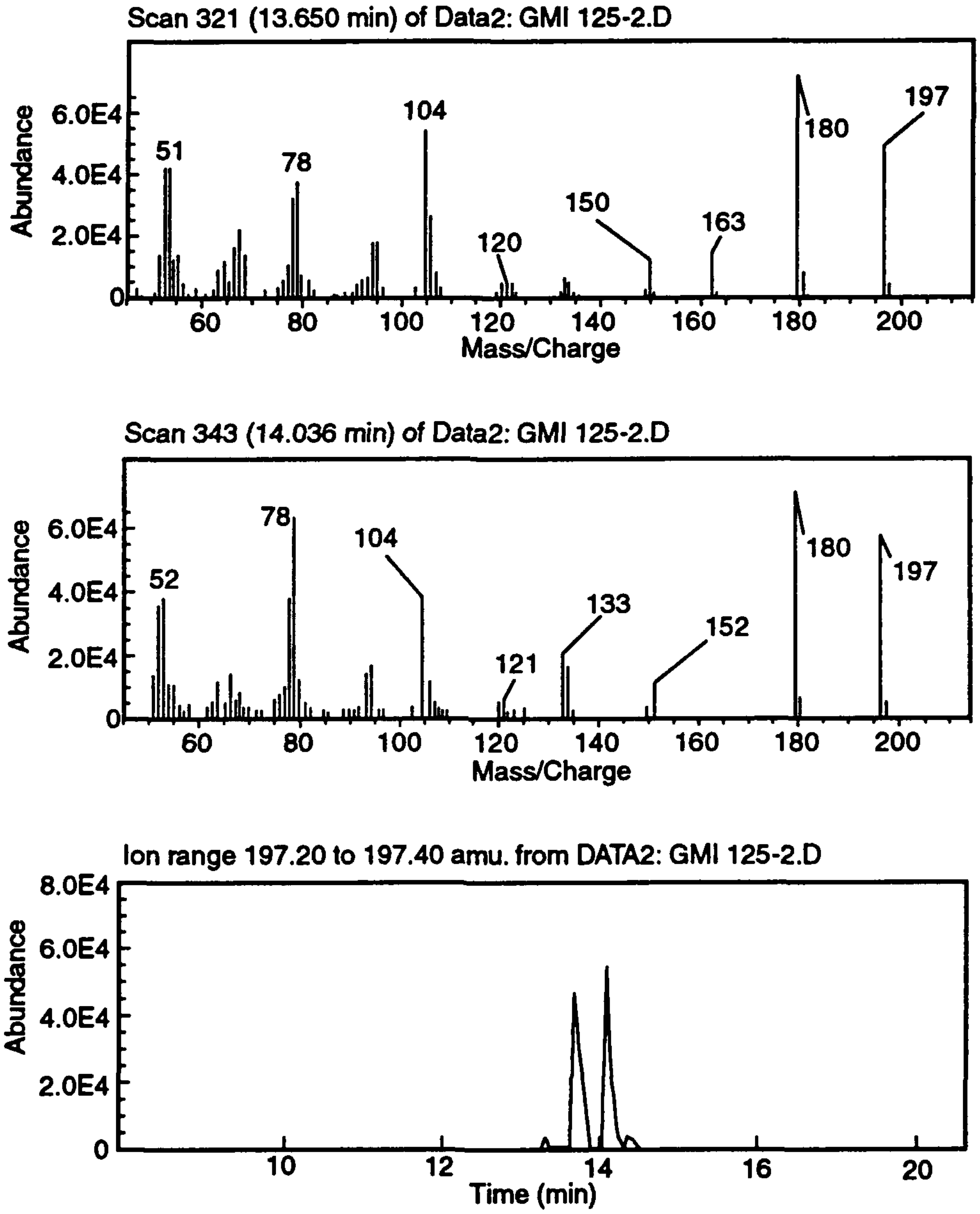


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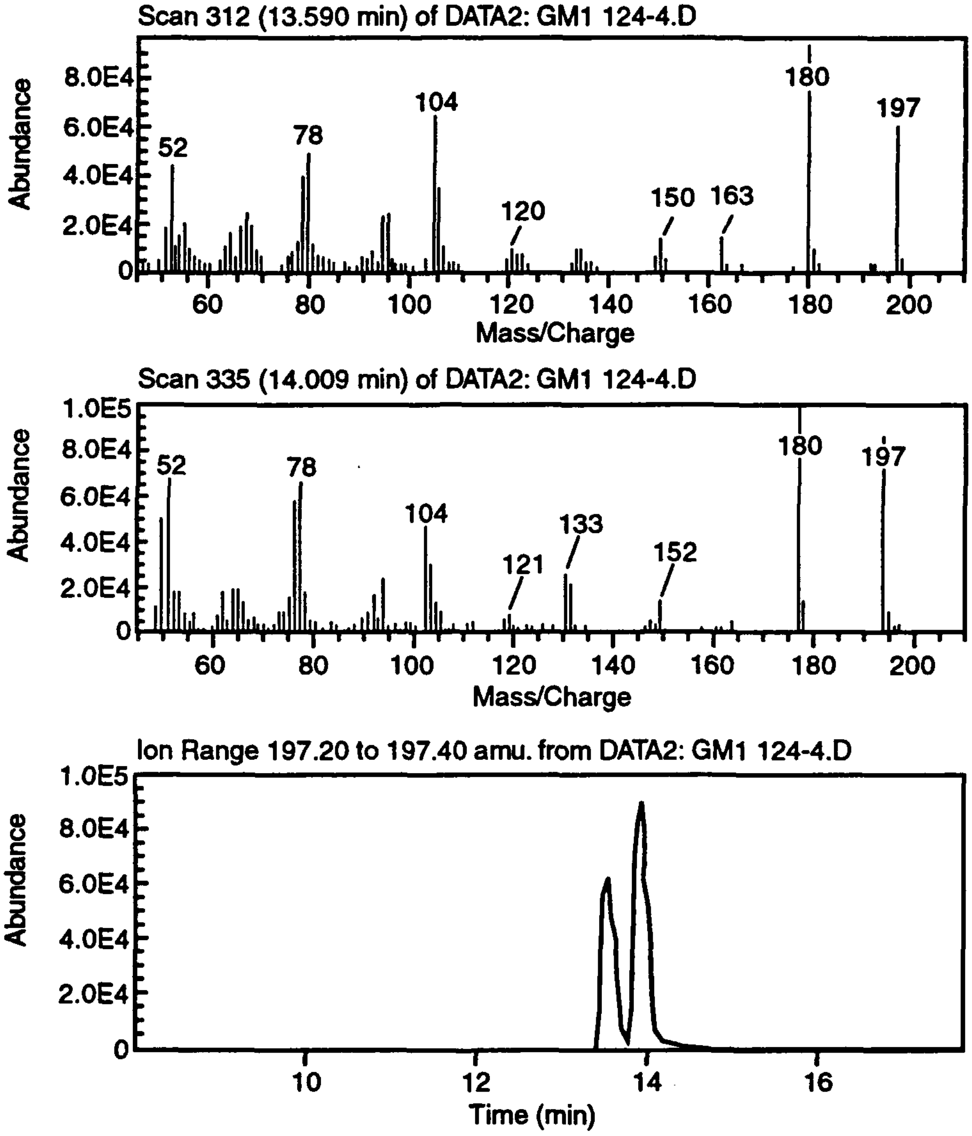
Figure 3-7. Extracted ion plot of a concentrated extract from the Burbank Ap soil (bottom), and the mass spectra of the aminodinitrotoluene isomers (top and center).



Scan 312 (13.590 min) of DATA2: GM1 124-4.D

Scan 335 (14.009 min) of DATA2: GM1 124-4.D

Ion Range 197.20 to 197.40 amu. from DATA2: GM1 124-4.D

R9305065.4

Figure 3-8. Extracted ion plot of a concentrated extract from the Cloudland Ap soil (bottom), and the mass spectra of the aminodinitrotoluene isomers (top and center).

concentrated, and analyzed by GC/MS in a manner similar as described above for the aminodinitrotoluene isomers. The GC/MS data from this experiment did not yield evidence of an additional transformation product. It is possible that the compound contained in Norborne C soil is a polar nonvolatile transformation product that is not amenable to GC/MS analysis. Among the many possibilities, this transformation product could be a diaminonitrotoluene isomer.

It must be emphasized that the levels of aminodinitrotoluene isomers identified in the present experiment are extremely low. Assuming that the aminodinitrotoluene isomers have a similar molar extinction coefficient as TNT, approximate concentrations can be calculated from the HPLC chromatograms shown in Figure 3-5. Also significant error is introduced by the 500-fold concentration of the methanol extract. Concentration estimates of the aminodinitrotoluene isomers in the 50 mL extracts prior to concentration are calculated to be 5.5, 4.5, and <1.0 ppb for Burbank Ap, Cloudland Ap, and Norborne C soil horizons, respectively.

The presence of aminodinitrotoluene isomers in the soil extracts confirms that a reductive transformation of TNT is occurring in all soils studied. Further, the above results suggest that the irreversible binding noted previously may be the result of catalytic reactions involving aminodinitrotoluene isomers. This conclusion is reached based on the fact that the aminodinitrotoluene isomers concentrations are low but that the irreversibly bond materials account for up to 10% of the TNT mass after 24 days. If the binding is the result of catalytic reactions involving aminodinitrotoluene isomers then one would not expect a build up of the aminodinitrotoluene isomers but would observe a steady increase of irreversibly bound material; the latter appears to be observed. Catalytic reactions utilizing the aminodinitrotoluene isomers is supported by investigations of aniline, and several of its ethyl- and chloro- substituted analogs that have shown that they can undergo biotic and abiotic transformations in soils resulting in 1) colored-clay complexes, 2) formation of multiring compounds such as azobenzene, and azoxybenzene (Pillai et al. 1982; Barta and Pramer 1967; Parris 1980), and 3) other higher molecular weight products from chemical interactions with soil organic matter (Hsu and Barta 1974; Bollag et al. 1978, 1987). Aniline undergoes oxidation at the surface of smectite clays in the presence of adsorbed Fe^{3+} or Cu^{2+} resulting in the formation of near humic-like materials (Cloos et al. 1979; Cloos et al. 1981) as well as clays that have Fe^{3+} isomorphically substituted into the lattice structure (Furukawa and Brindley 1973); these reactions have been characterized as clay surface catalyzed radical cation polymerizations of the aniline substrate.

The results of these studies suggest that transformation of TNT does occur, and may be the reason for the slow (2-3 d) approach to steady-state conditions (fig. 3-2) for both the aqueous and solid phase TNT concentrations. Hence, sorption data collected for isotherm construction needs to be collected after at least three day equilibration periods and the sorbed phase concentration determined directly by HPLC analysis of the MeOH extraction solution. RDX, on the other hand, requires only a 24 h equilibration. However, because of these preliminary studies, HPLC analysis and mass balance determinations were used throughout the remaining studies for both RDX and TNT.

3.2 BATCH SOIL SORPTION STUDIES

Batch sorption experiments were conducted per the protocol described previously (section 2.2.2) on the soils listed in Table 2.1. The relationships of the independent variables of the concentration of TNT and RDX (µg/mL solution) and the dependent variables of the concentration of TNT and RDX (µg/g soil) respectively were evaluated with three competing models. The three models, one linear and two nonlinear models, are commonly used to relate solid and aqueous phase contaminant concentration in soils (Pennington and Patrick 1990). The linear model is a regression through the origin, and the two nonlinear models are the Langmuir Isotherm Model and the Freundlich Isotherm Model. The equations for each relationship are

$$\text{Linear} \quad q = K_d C \qquad (1)$$

$$\text{Langmuir} \quad q = (QbC)/(1+bC) \qquad (2)$$

and

$$\text{Freundlich} \quad q = K_f C^{1/n} \qquad (3)$$

where q is the solid phase concentration of contaminant (µg/g); K_d and K_f are sorption coefficients for the linear and Freundlich equations, respectively; C is the equilibrium solution concentration (µg/mL); *Q* is the monolayer sorption capacity; *b* is the Langmuir constant and has been related to sorption entropy, and *1/n* is the Freundlich characteristic constant.

Determining which model fit best was conducted in a step-wise fashion. Since all three models were fit to the data for each soil independently, the first step was to select the model which generated the smallest mean squared error (MSE). Small MSEs signify that a large amount of the variation is being explained by the model. Both the Freundlich and Langmuir model fits were determined using a nonlinear fitting routine [JMP, SAS Institute, Inc. (1989; version 2)]. If the Freundlich model produced the smallest MSE, then the second step was to examine the approximate 95% confidence interval about the parameter 1/n. If the confidence interval overlapped 1, then the model was considered not significantly different from the linear model and the simpler model was chosen. If either the linear or the Langmuir model produced the smallest MSE, then the latter step was ignored.

3.2.1 RDX soil sorption/desorption at 23 ^{0}C

RDX was poorly sorbed to all soils; the maximum amount sorbed for any given initial concentration was approximately 36%. Examples of six sorption isotherms are presented in Figure 3-9. A total of 4 out 14 soils sorbed as much or greater than 20% of any given initial concentration, and the Hagerstown saprolite sorbed only 0.64% RDX at a maximum. Because of the very low sorption on the Hagerstown saprolite, its sorption data was excluded from consideration in model development. The mass balance for RDX was excellent; typically > 90% of the initial concentration of RDX could be accounted for after the 24 h experiment duration. In addition, HPLC traces showed no evidence of any peaks other than that attributable to RDX.

Both the linear (Eq. 1) and the Freundlich Isotherm Model (Eq. 3) produced the smallest MSEs for roughly half of the soils when used to fit the RDX sorption data (Table 3-1). The Langmuir Isotherm Model gave, in every case, the largest MSE. Tables 3-2 and 3-3 presents the estimated Freundlich and Linear Isotherm Model parameters and approximate 95% confidence limits for each soil.

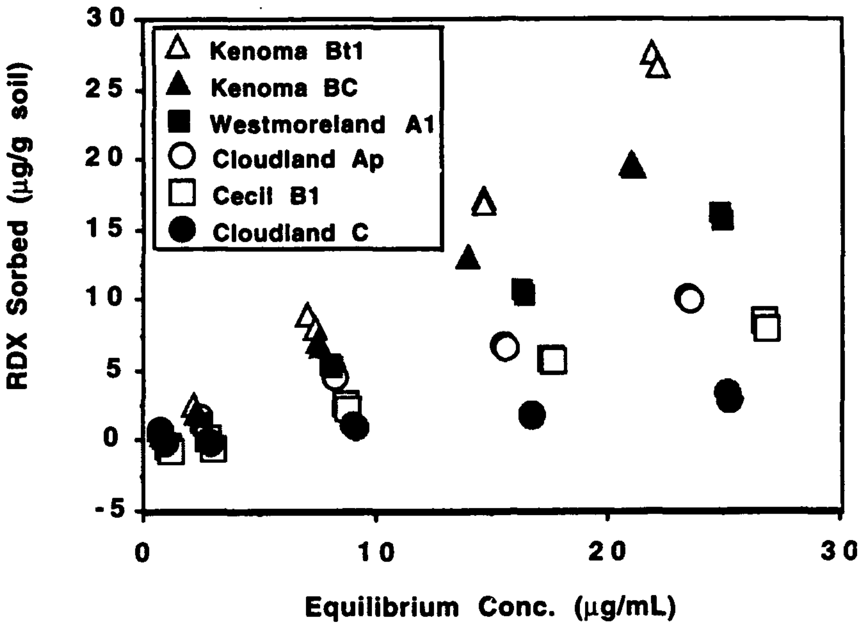


Figure 3-9. RDX sorption isotherms for six selected soils.

Table 3-1. The resulting mean squared error from fitting each model (Eq. 1 - 3) to the independent variable of the concentration of RDX (µg/mL solution) and the dependent variable of the concentration of RDX (µg/g soil).

Soil	Linear Model	Langmuir Model	Freundlich Model
Burbank AP	0.07	0.17	0.41
Cecil AP	3.17	18.03	3.52
Cecil Bt	0.15	8.61	0.18
Cloudland Ap	0.54	7.06	0.14
Cloudland C	0.05	1.14	0.05
Elk-B1	0.38	5.99	0.40
Kenoma BC	0.05	37.04	0.05
Kenoma Bt1	0.35	69.77	0.30
Norborne C	0.52	5.46	0.08
Ocala C4	6.29	138.87	4.76
Watson 2Bxg	0.34	19.44	0.22
Watson BE	0.70	9.99	0.17
Westmoreland A1	0.08	26.40	0.09
Westmoreland B1	0.56	6.29	0.08

Table 3-2. Parameter estimates (K_f and 1/n) and approximate 95% confidence limits (CL) for the soils best fit by the Freundlich Isotherm Model (Eq. 3) for RDX phase concentration data.

Soil	K_f	Lower CL	Upper CL	1/n	Lower CL	Upper CL
Cloudland Ap	0.95	0.70	1.23	0.744	0.652	0.847
Kenoma Bt1	1.00	0.81	1.30	1.050	0.975	1.140
Norborne C	0.91	0.71	1.10	0.718	0.642	0.802
Ocala C4	1.30	0.57	2.60	1.220	0.967	1.550
Watson 2Bxg	0.30	0.17	0.48	1.140	0.983	1.320
Watson BE	1.10	0.83	1.40	0.754	0.666	0.853
Westmoreland B1	0.98	0.79	1.20	0.721	0.652	0.796

Table 3-3. Parameter (K_d) estimate and approximate 95% confidence limits (CL) for RDX sorption to those soil horizons best described by the Linear Model (Eq.1) and those soils whose Freundlich 1/n value where statistically no different from 1.

Soil	K_d	Lower CL	Upper CL
Burbank AP	0.16	0.12	0.20
Cecil AP	0.43	0.34	0.52
Cecil Bt	0.31	0.29	0.33
Cloudland C	0.12	0.11	0.13
Elk-B1	0.27	0.24	0.30
Kenoma BC	0.93	0.92	0.94
Kenoma Bt1	1.21	1.18	1.24
Ocala C4	2.37	2.18	2.56
Watson 2Bxg	0.45	0.42	0.48
Westmoreland A1	0.65	0.63	0.67

Of the seven soils whose sorption data produced the smallest MSEs (Table 3-1) with the Freundlich model, three of these (i.e., Kenoma Bt1, Ocala C4, and Watson 2Bxg) had confidence intervals about the parameter 1/n which overlapped 1 (Table 3-2) and therefore reduce to the linear model. In addition, except for the Cloudland Ap, Norborne C, Watson BE, and Westmoreland B1 soils, the difference in the MSE's between the Freundlich and Langmuir models was fairly small. There is no discernable relationship between these soils' physical-chemical properties (pH, OC, percent clay, CEC, and DCB-Fe) and the fact that they are better represented by the Freundlich Isotherm Model rather than the Linear model. Interestingly, these four soils' sorption data are very tightly grouped and could be described equally well by a single set of Freundlich parameters.

The sorption of RDX to the Norborne C and Cloudland Ap soil horizons was completely reversible (fig. 3-10) within the 24 h time frame of this study. The sorption part of this study was performed in duplicate, but after the sorption phase was complete (24 h) one set of samples was extracted with MeOH and the other set had the fluid replaced with non-RDX ladened background electrolyte; in this manner a mass balance could be performed. Almost 97% of the initial RDX concentrations were accounted for based on HPLC analysis of the supernatant, sorption phase MeOH extract, and a likewise analysis at the end of the desorption phase.

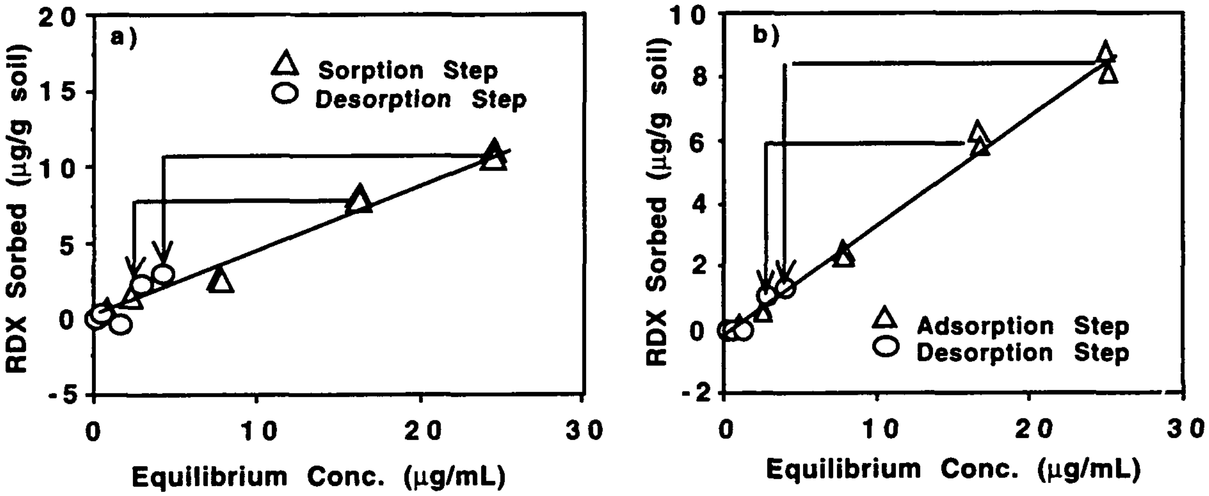


Figure 3-10. RDX sorption/desorption for the a) Cloudland Ap, and b) Norborne C soils.

Since RDX sorption for all but four soils could be statistically described by a linear isotherm and the sorption reaction appears to be totally reversible, carbon-referenced sorption (Karickoff 1984; Chiou et al. 1983, 1989) might be considered as an adequate estimate of solute partitioning between the aqueous and solid phase. However, K_{OC} values calculated from the linear sorption coefficient [$K_{OC} = K_d/(f_{OC})$] range from 2962 to 32; with the high and the low K_{OC} values attributed to the Ocala C4 and Westmoreland A1 soil horizons. Even excluding those soils with low f_{OC} due to possible inorganic solid phase participation in RDX sorption (Karickoff 1981), the range in K_{OC} is about factor of 6; with the high and low values being 186 and 32 for the Kenoma BC and Westmoreland A1, respectively. It seems clear that RDX does not follow carbon-referenced partitioning to the exclusion of other sorption mechanisms.

3.2.2 TNT soil sorption/desorption at 23°C

TNT sorption to all soils is somewhat stronger than RDX; examples of TNT isotherm curves are presented in Figure 3-11. While RDX isotherms may be characterized as C-type sorption curves (linear to slightly curvilinear), TNT sorption is more demonstrative of the L-type isotherm (Sposito 1984) with the soil having relatively higher affinity for TNT, and a greater degree of curvilinearity. However, the best isotherm model fit is dependent on whether the solid phase concentration is based on direct HPLC analysis of the MeOH extracts, or calculated by the difference between initial and final aqueous concentrations.

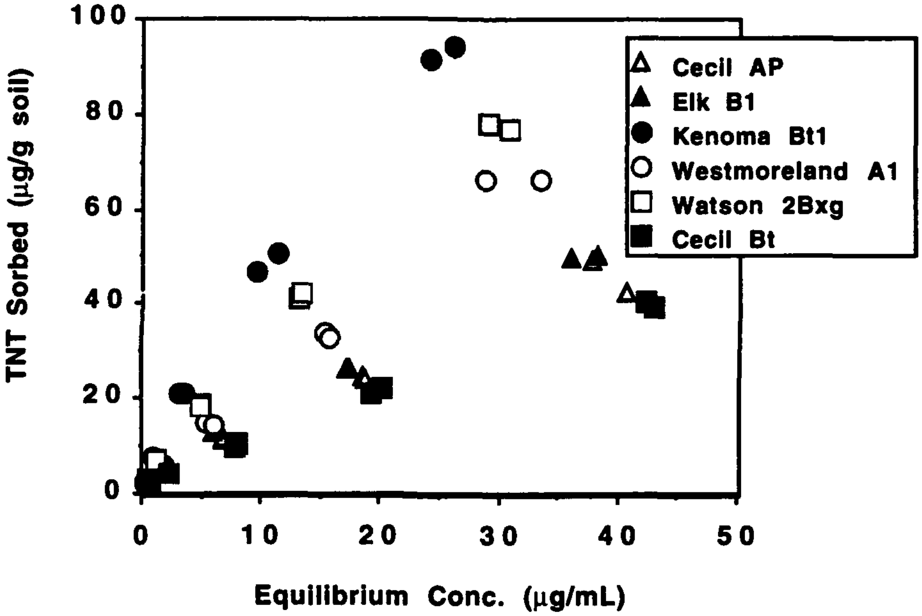


Figure 3-11. TNT sorption isotherms for six selected soils.

If the solid phase concentration is determined by direct HPLC analysis of the MeOH extracts, the Freundlich Isotherm Model produces the smallest MSEs for all the soils isotherm data except the Ocala C4 soil horizon (Table 3-4). The Langmuir Isotherm Model (Eq. 2) produced the second smallest MSEs for all soils except Kenoma BC and Ocala C4 for which they were the largest and smallest MSEs respectively. All confidence intervals about the parameter 1/n did not overlap 1 except for the Westmoreland A1 soil (Table 3-5). As previously stated, the direct analysis of sorbed TNT is used to negate any effect abiotic transformation of TNT could have on determining the sorbed TNT concentration.

Table 3-4. The resulting mean squared error from fitting each model (Eq. 1 - 3) to the independent variable of the concentration of TNT (μg/mL solution) and the dependent variable of the concentration of TNT (μg/g soil).

Soil	Linear Model	Langmuir Model	Freundlich Model
Burbank AP	8.27	1.83	0.93
Cecil AP	10.96	5.53	5.45
Cecil Bt	4.58	0.79	0.12
Cloudland Ap	7.47	1.55	0.39
Cloudland C	14.26	1.50	0.37
Hagerstown Sap	5.04	0.66	0.08
Kenoma BC	27.00	926.75	2.92
Kenoma Bt1	43.10	4.27	1.02
Norborne C	19.16	4.02	0.53
Ocala C4	168.40	5.58	10.22
Watson 2Bxg	23.28	3.19	1.29
Watson BE	14.46	1.31	0.18
Westmoreland A1	9.89	7.22	6.71
Westmoreland B1	8.19	1.73	0.24

Table 3-5. Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Freundlich Isotherm Model (Eq. 3) for TNT phase concentration data.

Soil	K_f	Lower CL	Upper CL	1/n	Lower CL	Upper CL
Burbank AP	2.96	2.41	3.51	0.740	0.660	0.820
Cecil AP	2.23	1.00	3.97	0.656	0.481	0.889
Cecil Bt	1.87	1.62	2.13	0.555	0.516	0.597
Cloudland Ap	3.04	2.70	3.40	0.772	0.737	0.808
Cloudland C	3.65	3.09	4.24	0.455	0.410	0.505
Hagerstown Sap.	2.04	1.81	2.28	0.465	0.430	0.501
Kenoma BC	7.85	6.11	9.80	0.654	0.582	0.733
Kenoma Bt1	8.49	7.76	9.24	0.698	0.670	0.729
Norborne C	4.46	3.96	4.98	0.657	0.623	0.694
Ocala C4	27.9	24.9	31.0	0.647	0.595	0.702
Watson 2Bxg	5.39	4.65	6.17	0.706	0.662	0.752
Watson BE	4.21	3.94	4.48	0.727	0.707	0.747
Westmoreland A1	2.80	1.64	4.33	0.837	0.700	1.00
Westmoreland B1	3.00	2.71	3.31	0.732	0.702	0.763

The TNT data were also modeled based on the assumption that there was no TNT transformation (called NL-TNT). This was undertaken to provide a direct comparison to TNT sorption study results performed with selected Army Ammunition Plant soils by Pennington and Patrick (1990). Phase data used in the NL-TNT modeling consists of 1) the aqueous concentration of TNT (as described earlier) and 2) the solid phase concentration calculated as the initial minus the final aqueous concentrations expressed on a soil mass basis (μg TNT sorbed/ g soil); this type of analysis assumes no transformation (hence no loss) of TNT. Both the Langmuir Isotherm Model (Eq. 2) and the Freundlich Isotherm Model (Eq. 3) produce the smallest MSEs for roughly two thirds and one third of the soils, respectively (Table 3-6). None of the soils, for which the smallest MSEs are produced with the Freundlich model have confidence intervals about the 1/n parameter that overlapped 1; the 1/n value ranged from 0.236 to 0.880 (Table 3-7). It is interesting to note, however, that for the Westmoreland B1 and Watson BE soils', the Freundlich parameters are statistically the same regardless of the manner in which the sorbed concentration is determined. Table 3-8 shows the Langmuir sorption parameters for those soils that were described best by Equation 2.

Table 3-6. The resulting mean squared error (MSE) from fitting each model (Eq. 1 - 3) to the NL-TNT independent variable of the concentration of TNT (μg/mL solution) and the dependent variable of the concentration of NL-TNT (μg/g soil).

Soil	Linear Model	Langmuir Model	Freundlich Model
Cecil AP	25.83	9.54	10.52
Cecil Bt	19.45	3.94	7.05
Cloudland Ap	2.40	0.64	0.47
Cloudland C	41.71	2.97	8.19
Elk-B1	34.60	6.58	7.12
Hagerstown Sap	12.21	2.03	3.74
Kenoma BC	356.30	84.29	19.12
Kenoma Bt1	128.20	18.93	22.89
Norborne C	8.63	1.66	0.19
Ocala C4	160.10	4.78	12.63
Watson 2Bxg	56.20	5.96	9.39
Watson BE	13.94	0.64	0.49
Westmoreland A1	55.07	43.84	46.74
Westmoreland B1	7.16	0.24	0.21

Table 3-7. Parameter estimates and approximate 95% confidence limits (CL) for each soil that was best fit by the Freundlich Isotherm Model (Eq. 3) using NL-TNT phase concentration data.

Soil	K_f	Lower CL	Upper CL	1/n	Lower CL	Upper CL
Cloudland Ap	2.26	1.96	2.58	0.880	0.839	0.923
Kenoma BC	31.5	26.6	35.9	0.236	0.191	0.293
Norborne C	3.25	3.00	3.51	0.755	0.731	0.779
Watson BE	4.24	3.85	4.66	0.761	0.732	0.792
Westmoreland B1	2.94	2.70	3.19	0.781	0.757	0.807

Table 3-8. Parameter estimates and approximate 95% confidence limits (CL) for each soil that was best fit by the Langmuir Isotherm Model (Equation 2)using NL-TNT phase concentration data.

Soil	Q	Lower CL	Upper CL	b	Lower CL	Upper CL
Cecil AP	40.2	27.6	80.1	0.05	0.02	0.14
Cecil Bt	20.1	15.1	28.9	0.09	0.04	0.21
Cloudland C	23.0	19.6	27.5	0.17	0.10	0.31
Elk B1	51.2	39.7	73.8	0.06	0.03	0.11
Hagerstown Sap.	15.4	12.0	21.1	0.10	0.05	0.22
Kenoma Bt1	132	106	179	0.07	0.04	0.11
Ocala C4	287	259	322	0.10	0.08	0.12
Watson 2Bxg	117	96.9	151	0.04	0.03	0.06
Westmoreland A1	153	73.5		0.02	0.00	0.07

In the Pennington and Patrick (1990) study, the Langmuir Isotherm Model proved to best describe the sorption data. However, they assumed that a 2 h equilibration time was sufficient to reach steady-state conditions using a solid-to-solution ration of 1:20. Importantly, their preliminary kinetic studies did show a slow loss of TNT with time over the 24 h study duration. Under the *conditions* use by Pennington and Patrick (1990), reductive transformation of TNT would be expected to be less than that observed under the conditions used in the present studies if the soil has only a limited capacity for abiotic reductive TNT transformation. Assuming a limited capacity for TNT transformation, the greatest loss of TNT by transformation would be expected to be at the lower initial concentrations regardless of the conditions the data was collected. However, TNT transformation at the lower initial concentrations would tend to cause an over estimation of TNT sorption (if the sorbed concentration is determined using only the aqueous phase concentration), and perhaps yield a langmuirian type curve. Unfortunately, when there is not substantial sorption (as was often the case in the present study) over- or underestimation of the sorbed phase concentration at the lower initial concentrations (1 and 3 µg/mL) may result from extraction determinations and cumulative error.

Greater than 100% mass balance of TNT occurs at the lowest initial TNT levels and is a result of the low concentrations involved (both in the aqueous phase and the solid phase) and the error introduced by the MeOH washing and the calculation of the sorbed concentration. This causes an overestimation of the sorbed concentration by about 3 to 15% at the lower concentrations. This phenomenon was exhibited in eight soils (Norborne C, Cloudland Ap, Westmoreland A1 and B1, Watson 2Bxg and BE, Cecil Bt, and Hagerstown saprolite) for the lowest initial concentration, and at the two lowest concentrations for the Norborne C, Cloudland Ap, and Hagerstown saprolite. At all other concentrations recovery was ≤ 100%; recovery varied from 100% to 25%.

A second set of isotherm data was collected on the Norborne C and Cloudland Ap and in this data set recovery was well below 100% but recovery increased as the initial concentration increased (Table 3-9). This second set of data was collected using ^{14}C-TNT and determinations were done by both LSC and HPLC on the aqueous and extracted solutions, and only about 4 % difference was observed between the two determinations; in addition, post-experiment culture growth was nonexistent. Even though the two sets of isotherm data yielded quiet different mass balances (the first data set was between 110 and 98% of the TNT recovered compared to the results in Table 3-9), it is important to note that the Freundlich model described both sets of data best and that the K_f and 1/n values were statistically identical ($p = 0.05$). These results, in conjunction with the results from the Kenoma BC soil (discussed below), would suggest that 1) the capacity of different soils for abiotic transformation of TNT is not the same, and 2) the transformation capacity of a single soil is not a constant from one sample to the next. When sorbed TNT is determined directly, however, the same model fits the sorption data best, and modeling results appears to be independent of TNT mass transformed. Therefore, it is believed that the data collected from the MeOH extractions are the better estimate of TNT sorption.

Table 3-9. Percent recovery of TNT added to the Norborne C and Cloudland Ap soil horizons after a 4 day sorption period as a function of initial TNT concentration.

Norborne C	Initial Conc. (mg/L)	Recovery (%)	Cloudland Ap	Initial Conc. (mg/L)	Recovery (%)
	0.74	42.9		0.74	82.0
	1.40	59.1		1.40	84.6
	11.4	93.0		11.4	90.7
	26.3	95.0		26.3	93.2
	52.3	96.9		52.3	96.1

While all soils demonstrated a deficit in mass balance of TNT over some range in initial concentration that the isotherm data was collected, the Kenoma BC and, to a lesser extent, the Kenoma Bt1 exhibited the greatest capacity for TNT transformation. The recovery of TNT from the Kenoma BC soil was 50, 25, 28, 86, and 98 % for initial concentrations of 1, 2.9, 9.36, 23.61, and 46.2 µg/mL, respectively. Aside from the lowest concentration (which may have suffered from overestimation as discussed above), it is interesting that TNT recovery increases with increasing total TNT added to the systems. This trend is observed in most of the soils used in the current study and would suggest that the capacity of a soil for abiotic reductive TNT transformation is limited but soil dependent. None of the other soils used in the current batch studies were as capable of TNT transformation as the Kenoma BC.

Methanol extracts from the Kenoma BC soils' lowest three initial concentrations were analyzed by GC/MS. Both the 2-, and 4-amino-2,6-dinitrotoluene (2ADNT and 4ADNT, respectively) transformation products were found in all three samples and their duplicates. In an attempt to quantify the two isomers present in the extracts, known concentrations of TNT and 2ADNT were prepared. The quantification was performed by integrating on a single ion for each material, 210 amu for TNT and 197 amu for 2ADNT. The response of 4ADNT was assumed to be similar to 2ADNT since no readily available standard was available; however, the 4ADNT has been adequately characterized (Harvey et al. 1990). Significant amounts of both isomers were found (0.35 to 4.8 µg/mL, and 1.1 to 8.4 µg/mL of 2ADNT and 4ADNT, respectively). In all cases the quantity of 4ADNT was found to be larger than 2ADNT. These results are based on the relative intensity of the parent ion at 197 amu; however the relative stability and fragmentation pathways of the 197 ion in the two species may be significantly different. In addition, the actual values were determined via a single calibration value and extensive concentration and laboratory manipulation, therefore a quantitative interpretation of these results must be approached with caution.

Desorption of TNT sorbed to the Cloudland Ap soil horizon (as determined by MeOH extraction of duplicate samples) was essentially as predicted assuming a reversible reaction (fig. 3-12a). It is interesting that the TNT desorption step was so well behaved; that is, the predicted and observed values agreed and fell on or below the sorption isotherm line. Since TNT has been shown to undergo an abiotic transformation it was felt that desorption of the sorbate would exhibit some hysteresis (i.e., desorb less than that predicted and yield a desorption isotherm that would be above that of the predicted line) due to the extra 24 h needed for the desorption step.

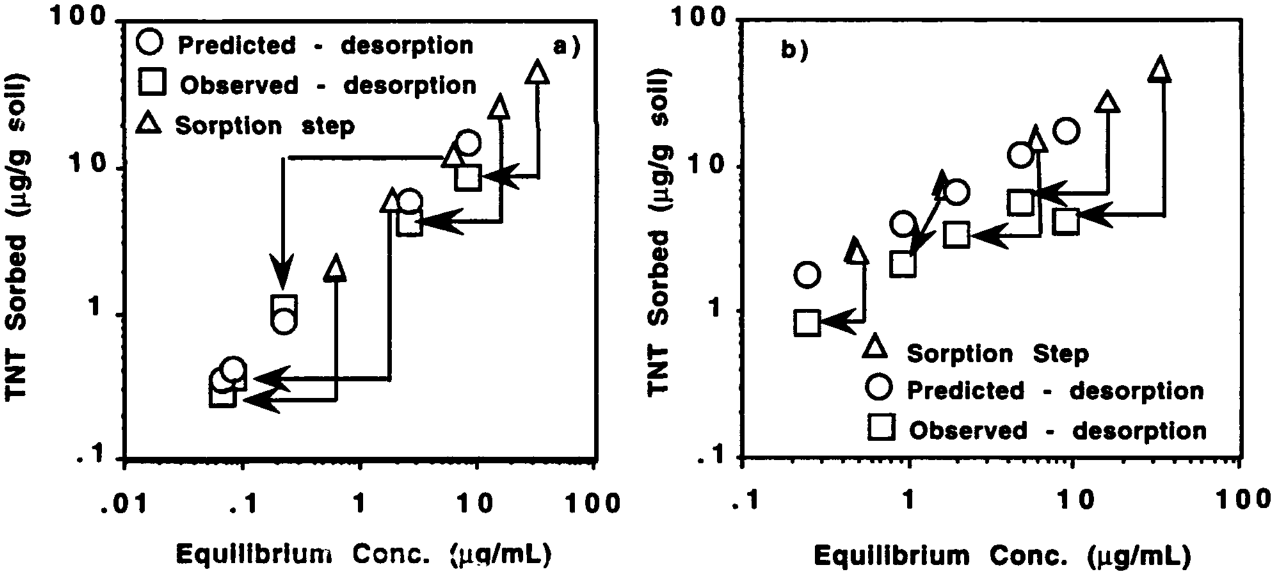


Figure 3-12. TNT sorption/desorption isotherms on the a) Cloudland Ap, and b) Norborne C soils.

Desorption from the Norborne C soil was also reversible (Fig. 3-12b), but was not as well predicted. It is important to note, however, that the soil phase concentration is less than that predicted, but the aqueous phase concentrations are well predicted. This discrepancy between the observed and predicted concentrations of the sorbed TNT could be caused by continued TNT transformation during the desorption step. However, this is not believed to be the case because 1) transformation would have to be greater during the desorption step than during the initial sorption process (this is contrary to the results discussed in 3.1), 2) transformation products were not observed during the HPLC analyses of the supernatants and MeOH extracts, and 3) the aqueous phase concentrations would have been less than that observed due to equilibration between the sorbed and aqueous TNT phases. Further, the desorption isotherm falls below the sorption isotherm rather than above it (the latter would indicate desorption hysteresis). The above discussion suggests analytical error rather than transformation during desorption. While this data is not as definitive as the results from the Cloudland Ap soil, it is believed that the desorption of TNT from both of these soils is reversible and predictable if TNT loss is taken into account.

When the sorption step was competed (96 h sorption time) the percent recovery of TNT (based on MeOH extraction of duplicate samples) increased with increasing initial concentrations of TNT for the Cloudland Ap soil. However, the data for the desorption step suggests that the TNT determined to be on the surface after the initial sorption step was *reversible* and totally *recoverable* as TNT. This suggests that the TNT transformation ability of a given soil is limited. That is, there are a limited number of abiotic transformation "sites" and that reaction with these sites is rapid enough to have been completed within the sorption step time frame. Therefore, a reversible and predictable desorption process is observed. This hypotheses is further supported by a series of pulsed column studies where small individual TNT pulses are repeatedly put through a soil column and mass balance of each pulse is determined. The pulsed column data and results are discussed in section 5.3 of this report.

3.2.3 TNT and RDX cosolute studies

The presence of a cosolute affects the sorption of both TNT and RDX to the Norborne C and Cloudland Ap soil horizons (fig. 3-13). However, the sorption of RDX is affected to a greater degree by the presence of an equal mass of TNT compared to the affect of RDX on the sorption of TNT. While the observed decrease in TNT sorption K_f values is statistically significant, the 1/n values for both soils are not significantly different from the single solute values (Table 3-10).

These data suggest that both solutes utilize the same set of sorption sites and competition for those sites between TNT and RDX when present as cosolutes decreases the sorption of the other solute. TNT, however, is less effected by the presence of RDX. The change in the RDX K_f and particularly 1/n due to the presence of cosolute suggest that the sorption of RDX to both the Cloudland Ap and Norborne C soils may benefit from the presence of the cosolute, at higher cosolute TNT levels; that is, RDX sorption appears to be enhanced through some type of cooperative interaction.

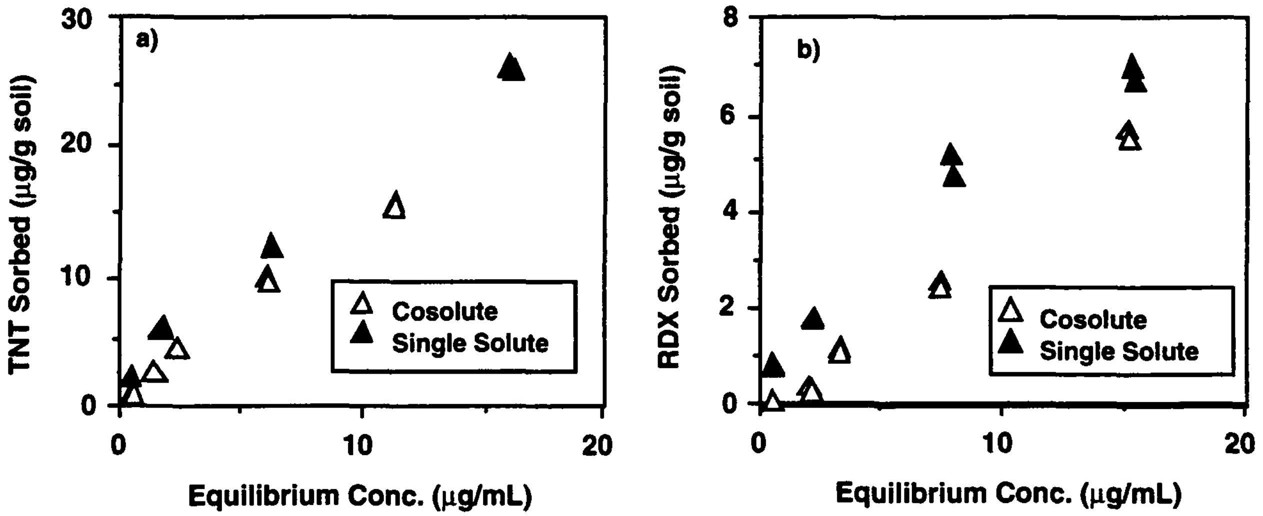


Figure 3-13. The effect of equal cosolute mass concentrations of TNT and RDX on the sorption of TNT or RDX to the a) Cloudland Ap, and b) Norborne C soils.

Table 3-10. Parameter estimates and approximate 95% confidence limits (CL) for each isotherm and soil using the Freundlich Isotherm Model (Eq. 3) and the cosolute (CoS) or single solute (S) phase concentration data.

Isotherm	Soil	K_f	Lower CL	Upper CL	1 / n	Lower CL	Upper CL
TNT-CoS	Cloudland Ap	1.86	1.56	2.18	0.874	0.803	0.951
TNT-CoS	Norborne C	3.14	2.78	3.51	0.732	0.679	0.789
RDX-CoS	Cloudland Ap	0.19	0.13	0.27	1.238	1.108	1.387
RDX-CoS	Norborne C	0.20	0.11	0.32	1.179	0.998	1.399
TNT-S	Cloudland Ap	3.04	2.70	3.40	0.772	0.737	0.808
TNT-S	Norborne C	4.46	3.96	4.98	0.657	0.623	0.694
RDX-S	Cloudland Ap	0.95	0.70	1.23	0.744	0.652	0.847
RDX-S	Norborne C	0.91	0.71	1.10	0.718	0.642	0.802

The > 1 value for 1/n observed for RDX for both soils in the presence of TNT is indicative of an S-curve isotherm (Sposito 1984) and suggests that the relative affinity of RDX for the soil increases with sorption of both cosolutes; this is may be due to cooperative interactions among sorbed molecules. It is interesting, however, that the data would suggest that only RDX sorption appears to benefit from this proposed interaction. While this type of phenomenon has been observed with ionizable compounds, and mixtures of ionizable and hydrophobic compounds (Serratosa 1968; Zachara et al. 1987; Ainsworth et al. 1989; Traina and Onken 1991), it must be contrasted with published data suggesting that nonionic mixtures sorb independently to soil materials (Schwarzenbach and Westall 1981; Chiou et al. 1983). The sorption of binary mixtures of organic compounds to activated carbon with hydrophobic/neutral and ionizable compounds has been accomplished using a simplified model based on ideal adsorbed solution (IAS) theory (Zachara et al. 1987). In the simplified version, single solute isotherm equations are used to predict sorbed concentrations of binary solutes at equilibrium based on initial concentrations. While this approach may be applicable to the solutes TNT and RDX more in depth cosolute investigations will have to be conducted before this type of model can be evaluated.

3.2.4 TNT and RDX temperature studies

RDX and TNT sorption isotherm data were collected at 10, 20, and 50 ^{0}C for the Norborne C, Cloudland Ap, and Kenoma BC soils; data were collected in the same manner as all other isotherm data except for the temperature. Temperature affected the sorption of both TNT and RDX on all three soils indicating enthalpy (ΔH) contributions to the free energy of sorption. A reduction in temperature to 10 ^{0}C increased sorption of both compounds for all soils (Fig. 3-14; 3-15). In contrast to these findings, entropy is expected to dominate the free energy of sorption of hydrophobic organic compounds on mineral surfaces (Chiou and Stroup 1985). Also, interactions between soil OC and hydrophobic compounds are typically observed to be endothermic rather than exothermic as observed in the present study; however, small and nearly constant exothermic heats of sorption for nonionic organic solutes may be observed and has been suggested to be the result of the differences between the heats of solution in water (ΔH_w) and solvent (ΔH_{Org}) (Chiou 1989).

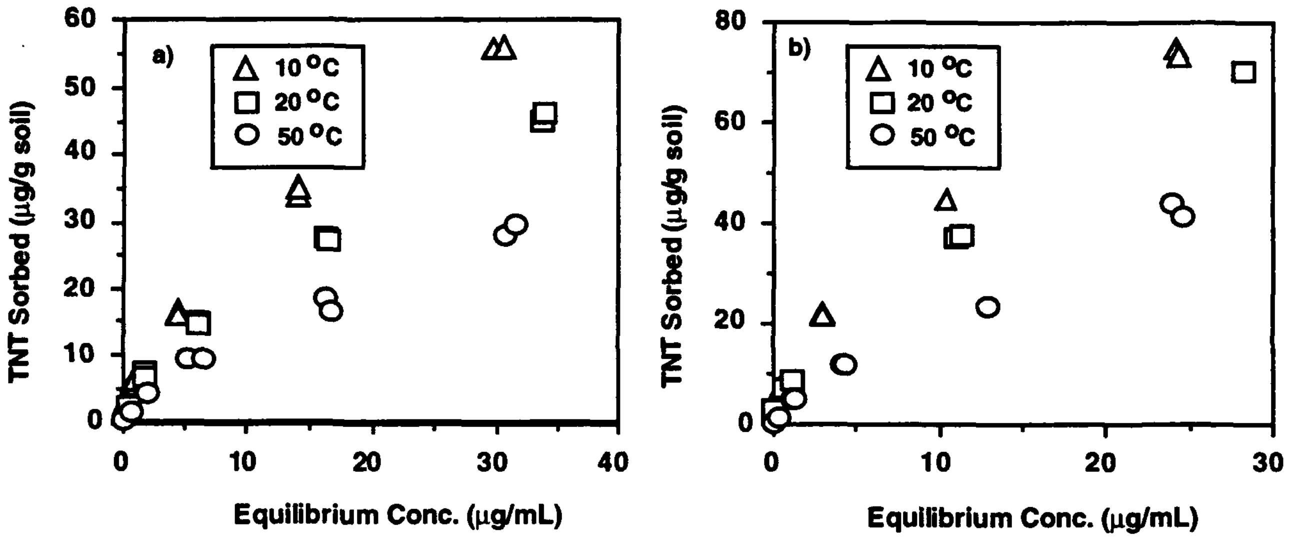


Figure 3-14. Sorption of TNT to the Norborne C, and b) Kenoma BC soils at 10, 20, and 50 ^{0}C.

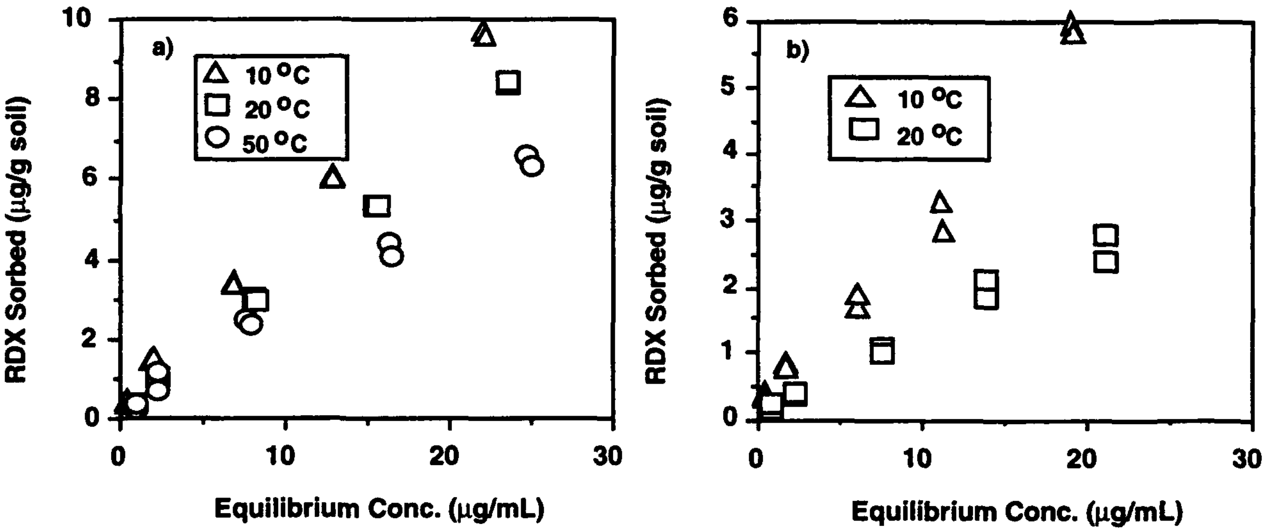


Figure 3-15. Sorption of RDX to a) the Cloudland Ap soil at 10, 20, and 50 ^{0}C, and b) the Kenoma BC soil at 10 and 20 ^{0}C.

The isosteric heats of sorption (ΔH_Γ) for TNT and RDX to the three soils were calculated as a function of sorption density (Γ; mol sorbate/g soil) by the use of the Clausuis-Clapeyron equation (Chiou and Shoup 1985; Zachara et al. 1990):

$$\Delta H_\Gamma = R \ln (C_2/C_1)/(1/T_2 - 1/T_1) \qquad (4)$$

where R is the gas constant (8.3143 $J \bullet mol^{-1} \bullet K^{-1}$), C_2 is the equilibrium concentration of the solute (mol/L) at T_2 (degrees K) at the specified Γ, and C_1 is the equilibrium concentration of the solute at T_1 at the same Γ. The ΔH_Γ calculations were performed over three sorption densities that incorporated the full range of the adsorption isotherms and ranged from 10^{-9} to 5 $\times 10^{-7}$ mol/g soil and 5 x 10^{-9} to 10^{-7} mol/g soil for TNT and RDX, respectively. The isosteric heat of sorption is a macroscopic measurement incorporating the effects of solute-surface, solute-solvent, and solvent-surface interactions and their changes that accompany sorption (Burchill et al. 1981).

The ΔH_Γ of TNT for the Kenoma BC and Norborne C soils ranged from -18.4 to -38.5 kJ/mol. These calculated enthalpies are within the range, albeit the low end, reported for van der Waals forces and hydrogen bonding (-20 to -60 kJ/mol; Burchill et al. 1981). It is not unexpected that these two soils would yield comparable ΔH_Γ since the clay mineralogy of both is dominated by virtually identical smectite clays, and the pH, OC, and type of Fe oxides are similar. For the Cloudland Ap soil, on the other hand, both isotherm parameters (K_f and 1/n) were affected by changing temperature and the ΔH_Γ went from an endothermic reaction at low sorption densities to exothermic at elevated sorption densities. This crossover is believed to be the result of variations in TNT recovery rather than a change in the sorption reaction since the ΔH_Γ varied dependent on which temperature range was used (i.e., 10 to 20 ^{0}C, or 10 to 50 ^{0}C), and that the ΔH_Γ at the higher (and more accurately measured) surface densities was comparable to the other two soils (about -18.8 kJ/mol). Similar to TNT, RDX sorption to the Norborne C and Kenoma BC exhibited a ΔH_Γ that was negative (-16.8 and -19.9 kJ/mol, respectively) and close to the lower end of the enthalpy range cited for van der Waals forces and hydrogen bonding. Sorption of RDX to the Cloudland Ap soil yielded a ΔH_Γ that was always negative (in contrast to TNT), slightly less than for the other soils, and dependent on the temperature range used in the calculation; The ΔH_Γ ranged between -20.8 and -10.9 kJ/mol for the range of 10 to 20 ^{0}C and 10 to 50 ^{0}C, respectively.

None of the soil exhibited significant trends with surface loading; that is, a statistically observable increase or decrease in ΔH_Γ as the surface concentration increased. However, using the 10 to 50 ^{0}C range as the best measure of the ΔH_r, both RDX and TNT shows a consistent trend of increasing ΔH_r with increasing surface densities. These trends, however, should not be taken as absolutes since 1) statistically there is no difference between the measured values for a given soil (this includes TNT ΔH_r for the Cloudland Ap), and 2) these measurements were determined on whole soils and are meant to convey a qualitative sense of the ΔH_r for the sorption process and not a definitive value. Rather, the exothermic nature of the sorption reaction, and the trend toward increasing ΔH_r with increasing surface coverage observed for both compounds suggests that nonhydrophobic sorption (i.e., sorption other than OC partitioning) is an important sorption component and there may be significant "sorption site" specificity. However, the "sorption sites" responsible for the nonhydrophobic sorption can not as yet be identified.

All three of the soils used in the temperature study exhibited the capacity to transform TNT at all temperatures examined. In these studies, decreased recovery of TNT was considered to be evidence of transformation; selected analysis by GC/MS showed transformation had occurred but, as discussed previously, quantification is difficult. At 10 ^{0}C, transformation was evident at only the lower initial concentrations (Table 3-11). *At higher temperatures transformation* was more evident and, in the case of the Cloudland Ap soil, dramatic. As would be expected, the Kenoma BC and Norborne C soils exhibited similar increases in TNT transformation with temperature. The reason for the observed difference transformation with temperature between the Cloudland Ap and the other two soils is not currently known. However, in most cases it would appear that while sorption is an exothermic process (Cloudland Ap soil may be an exception), transformation would seem to be an endothermic reaction. In addition, these temperature studies would suggest that the capacity of a soil to facilitate TNT nitro group reduction is variable and, at present, does not appear to be linked to bulk soil properties. This may not be surprising in that their is a considerable number of natural reductants that could play a role in TNT transformation, and these reductants may, or may not be related to bulk soil properties (Schwarzenbach et al. 1990; Macalady et al. 1986).

Table 3-11. The percentage of TNT recovered[a] from the Kenoma BC, Cloudland Ap, and Norborne C soils as a function of initial concentration and temperature.

Initial Concentration	Kenoma BC		Cloudland Ap		Norborne C	
	°C					
(µg/mL)	10	50	10	50	10	50
1.0	52.5	37.5	59.7	15.8	57.3	52.8
2.9	85.1	84.7	91.5	6.1	91.0	55.4
9.6	99.1	80.9	96.9	2.3[b]	100	90.5
23.6	98.4	86.3	102	2.4	103	96.8
46.2	99.5	85.2	101	19.1[c]	102	93.6

[a] Recovered TNT is the aqueous plus extracted concentrations as determined by HPLC.

[b] Recoveries of TNT from duplicate samples were 2.3 and 82.0%.

[c] Recoveries of TNT from duplicate samples were 19.1 and 64.8%.

4.0 STATISTICAL ANALYSIS AND MODEL DEVELOPMENT

4.1 STATISTICAL ANALYSIS

The relationships of the independent variables of the concentration of TNT and RDX (µg/mL solution) and the dependent variables of the concentration of TNT and RDX (µg/g soil) respectively were evaluated with three competing models as previously discussed. The linear model is a regression through the origin, and the two nonlinear models are the Langmuir Isotherm Model and the Freundlich Isotherm Model. The equations for each relationship are

Linear $q = KdC$ (1)

Langmuir $q = (QbC)/(1+bC)$ (2)

and

Freundlich $q = K_f C^{1/n}$ (3)

where q is the solid phase concentration of contaminant (µg/g); K_d and K_f are adsorption coefficients for the linear and Freundlich equations, respectively; C is the equilibrium solution concentration (µg/mL); Q is the monolayer sorption capacity; b is the Langmuir constant, and n is the Freundlich characteristic constant.

Determining which model fit best was conducted in a step-wise fashion. Since all three models were fit to the data for each soil independently, the first step was to select the model which generated the smallest mean squared error (MSE). Small MSEs signify that a large amount of the variation is being explained by the model. If the Freundlich model produced the smallest MSE, then the second step was to examine the approximate 95% confidence interval about the parameter 1/n. If the confidence interval overlapped 1, then the model was considered not significantly different from the linear model and the simpler model was chosen.

If either the linear or the Langmuir model produced the smallest MSE, then this step was ignored. The results of the above analyses were reported in section 3.0. To promote consistency between soils and ease of predictive model development, the isotherm model with the greatest number of minimum MSE's was chosen as best for that solute and was used in the predictive model development. For RDX, the best model was the linear, for TNT, the Fruendlich.

Soil properties including the content of organic carbon, clay, iron, pH, and CEC (see table 2-1) were used to generate a predictive model for the parameters of the best fit isotherm model to the phase (i.e., solid and aqueous phases) concentration data. The total number of different soils being used to generate the predictive model is relatively small for the potential number of parameters to be estimated (5 parameters and 13 soils). Since each parameter utilizes a single degree of freedom, there are less available for the error term. Fewer degrees of freedom in the error term generally implies larger confidence intervals about parameter estimates. The number of parameters in the model, then, must be balanced with the size of the resulting confidence intervals and the predictive capability of the resulting model. Thus, principal component analysis was used to reduce the number of variables describing the soil components from five to two or three. The intent of this analysis was to explain as much of the variation in the soil characteristics as possible with a minimum number of components. Decreasing the number of explanatory soil property vectors by this method reduces the number of parameters to be estimated in the later regression analysis and increases the degrees of freedom available for the error term. Thus, the confidence intervals about the parameters in the predictive model are expected to be smaller.

Regression analysis was used to determine the relationship between the resulting parameters from the best fit isotherm model and the principal components from the soil characteristics data. If only one or two of the soil characteristics showed a relationship with the model parameters, then a regression against those soil properties was also conducted. The intent of this analysis was to find the best predictive linear model for the phase concentration parameters using all or some of the soil characteristics. The criteria for choosing between models was that all parameters had to be significantly different from zero, and the resulting model must have a small MSE and a large multiple correlation coefficient (R^2). The value of R^2 was considered last because the number of parameters in the model increases the value of R^2

regardless of how well the model fits and despite possible insignificant parameters. Deviations from the estimated parameters (O) and the predicted values (P) from the regression model were measured as the fraction (O-P)/P.

All soils had approximately ten observations on both the concentration of TNT and RDX (µg/mL solution) and the concentration of TNT and RDX (µg/g soil) except Elk B1 which had no observations of TNT in solution (this occurred due to a mix up in the analysis and hence the ELk data was not used) and Hagerstown Saprolite which had only four observations of RDX in solution and soil (the Hagerstown Saprolite adsorption at the lowest concentrations was so low no sorption could be discerned). Elk B1 and Hagerstown Saprolite were eliminated from further analysis for TNT and RDX, respectively. The Elk B1 soil property data was not used in the principal components analysis since there was no associated phase concentration data for the TNT isotherm; however, it was used as a check of the model building process to predict the best fit phase model parameters for the RDX isotherm.

The individual soil properties were relatively uncorrelated except for clay content and DCB iron which had a correlation of 0.724 (Table 4-1). Because this correlation is not exceedingly high, all soil variables remained in the analysis. Principal component analysis on the soil data was successful in reducing the number of variables from five to three. The cumulative variation in soil properties explained by the first three principal components was 94% (Table 4-2). The first principal component can be characterized as a function of DCB iron and pH (as noted by the large absolute values of the eigenvector elements for these properties). The second principal component can be characterized as a function of organic carbon and clay content. The third principal component can be characterized as a function of organic carbon and CEC. Since the eigenvalue of the third principal component is less than one, this component may not be adding a significant amount of information beyond the first two components. However, since the cumulative percent of variation explained by the first two components is less than 80%, all three components were used for further regression analysis.

Table 4-1. Correlation matrix of the average soil properties.

	Organic Carbon	Clay	DCB Iron	pH	CEC
Organic Carbon	1.000	-0.138	-0.103	-0.425	-0.70
Clay	-0.138	1.000	0.724	-0.253	0.284
DCB Iron	-0.103	0.724	1.000	-0.591	-0.407
pH	-0.425	-0.253	-0.591	1.000	0.513
CEC	-0.70	0.284	-0.407	0.513	1.000

Table 4-2. First three principal components (P_1 - P_3) for the average soil properties. The principal components are linear combinations of the standardized soil properties [i.e., $(X_i - X_{ave})/S_x$; where X_{ave} is the mean X, S_x=standard deviation of X and X_i the individual values of X].

	Principal Component		
	1[a]	2[b]	3[c]
Eigenvalue	2.17	1.65	0.89
Percent of Variation Explained	43.3	33.0	17.8
Cumulative Percent of Variation Explained	43.3	76.3	94.1
Eigenvectors			
Organic Carbon (X_1)	0.085	-0.573	0.658
Clay Content (X_2)	0.342	0.613	0.325
DCB iron (X_3)	0.630	0.259	0.016
pH (X_4)	-0.557	0.327	-0.167
CEC (X_5)	-0.410	0.348	0.658

Descriptive Statistics	Mean	Standard Deviation
Organic Carbon (X_1)	0.687	0.615
Clay Content (X_2)	31.308	18.387
DCB iron(X_3)	242.508	191.217
pH(X_4)	6.012	1.862
CEC(X_5)	11.288	11.205

---

[a] $P_1 = 0.606 + 0.196 X_1 + 0.0214 X_2 + 0.00323 X_3 - 0.305 X_4 - 0.0319 X_5$

[b] $P_2 = -2.217 - 0.819 X_1 + 0.0330 X_2 + 0.00134 X_3 + 0.157 X_4 + 0.0426 X_5$

[c] $P_3 = -1.180 + 1.19 X_1 + 0.0156 X_2 - 0.00073 X_3 - 0.0885 X_4 + 0.0519 X_5$

4.2 TNT MODEL DEVELOPMENT

For all soils except Ocala C4, the Freundlich Isotherm Model (Eq. 3) produced the smallest MSEs when used to fit the phase concentration data (see section 3.2.2, Table 3-4). The Langmuir Isotherm Model (Eq. 2) produced the second smallest MSEs for all soils except Kenoma BC and Ocala C4 for which they were the largest and smallest MSEs, respectively. All confidence intervals about the parameter 1/n did not overlap 1 except for the Westmoreland A1 soil (see section 3.2.2 Table 3-5). Thus, for consistency among soils, the Freundlich model was chosen as the best fitting model to the phase concentration data. Figure 4-1a presents the predicted line using the Freundlich model and observed phase concentration data for the Cecil AP soil. Table 3-5 (see section 3.2.2) presents the estimated Freundlich parameters and approximate 95% confidence limits for each soil.

As discussed previously, regression analysis was used to determine the relationship between the resulting parameters from the best fit isotherm model and the principal components from the soil characteristics data. If only one or two of the soil characteristics showed a relationship with the model parameters, then a regression against those soil properties was also conducted. Statistical analysis of the TNT sorption parameter, K_f, exhibited just such a case and therefore, two competing predictive models were developed.

Regression analysis with the first three principal components from the soil data and the estimated Freundlich parameter, K_f, for each soil showed that the third principal component was not significant and thus it was dropped from the regression. Therefore, the model contained an intercept and the first two principal components (P_1 and P_2),

$$K_{fp} = 5.92 - 2.96P_1 + 3.02P_2 \qquad (4)$$

where K_{fp} is the predicted Freundlich constant. The R^2 for this model was 0.70 (Table 4-3). A measure of the deviation between the estimated parameter (K_f) from the Freundlich model and the predicted (K_{fp}) values from the regression model (Eq. 4; Table 4-4) is presented in Table 4-5 and Figure 4-1b.

A strong correlation (R) between K_f and several of the soil characteristics was found during the statistical analysis (R = -0.33, -0.02, -0.406, 0.74, and 0.69 for OC, Clay content, DCB-Fe, pH, and CEC). Therefore, the second model was constructed that contained the soil properties pH and CEC,

$$K_{fp} = -7.69 + 1.6X_4 + 0.35X_5 \qquad (5)$$

where X_4 and X_5 are pH and CEC, respectively. The R^2 for this model was 0.77 (Table 4-6). Deviations from the estimated parameter and the predicted values using Equation 5 (Table 4-7) are presented in Table 4-8 and Figure 4-2a.

Predictive models for the estimated Freundlich parameter, 1/n, where unsuccessful when constructed from the principal components. R^2 values were less than 0.35 and the first principal component was not significant. The best predictive model contained only the single soil property of organic carbon content (Table 4-9). The prediction equation is

$$1/n_p = 0.56 + 0.15X_1 \qquad (6)$$

where X_1 is organic carbon content (Table 4-10). Table 4-11 and Figure 4-2b present a measure of the deviation from the estimated parameter and the predicted values from Equation 6.

From the analysis of the TNT data here and in section 3.2.2 it is clear that the Fruendlich model is the best for TNT sorption. The criteria for selecting the better of the two K_f predictive models (Eq. 4 and Eq. 5) are that all parameters had to be significantly different from zero, and the resulting model must have a small MSE and a large multiple correlation coefficient (R^2). On these bases, Equation 5 is the better of the two competing K_f predictive models. The 1/n value is best represented by Eq. 6. It should be noted, however, the models developed for TNT are statistical in nature, and the mechanistic basis for them are not currently understood.

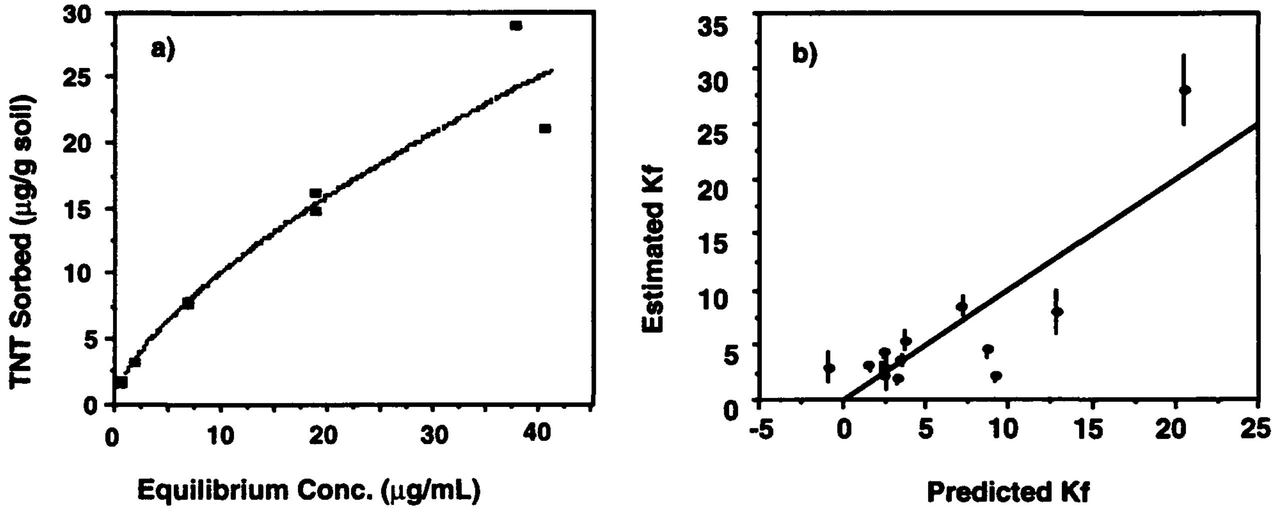


Figure 4-1. Plots of a) TNT sorption isotherm for the Cecil Ap soil showing the Freundlich model fit, and b) predicted K_{f_p} from Eq. 4 versus the estimated K_f from the Freundlich model; bars represent the 95% confidence limits and the line represents x=y.

Table 4-3. Analysis of variance of the regression of the estimated K_f for TNT against the first two principal components.

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	*Probability* of a > F	R^2
Model	2	401.46	200.73	11.41	0.0026	0.70
P_1	1	234.21		13.32	0.0045	
P_2	1	167.25		9.51	0.0116	
Error	10	175.87	17.59			
Corrected Total	12	577.33				

Table 4-4. Parameter estimates for the predictive model for K_f for TNT (Eq. 4).

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	5.92	1.16	5.09	< 0.001
P_1	-2.96	0.81	-3.65	0.005
P_2	3.02	0.98	3.08	0.012

Table 4-5. Estimated (O) and Predicted (P) K_f values for TNT using Eq. 4 and a measure of their deviation.

Soil	Estimated K_f	Predicted K_f	Deviation (O-P)/P
Cecil Ap	2.23	2.55	-0.13
Cecil Bt	1.87	3.29	-0.43
Cloudland Ap	3.04	1.58	0.93
Cloudland C	3.65	3.53	0.03
Hagerstown Sap	2.04	9.19	-0.78
Kenoma BC	7.85	12.87	-0.39
Kenoma Bt1	8.49	7.19	0.18
Norborne C	4.46	8.70	-0.49
Ocala C4	27.94	20.53	0.36
Watson 2Bxg	5.39	3.66	0.47
Watson BE	4.21	2.40	0.76
Westmoreland A1	2.80	-0.94	-3.98
Westmoreland B1	3.00	2.41	-0.02

Table 4-6. Analysis of variance of the regression of the estimated K_f for TNT against pH (X_4) and CEC (X_5) (Eq. 5).

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Probability of a > F	R^2
Model	2	442.09	221.04	16.34	0.0007	0.77
X_4	1	78.03		5.77	0.0372	
X_5	1	140.12		10.36	0.0092	
Error	10	135.24	13.52			
Corrected Total	12	577.33				

Table 4-7. Parameter estimates for the TNT K_f predictive model (Eq. 5); X_4 is pH, X_5 is CEC.

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	-7.69	3.67	-2.10	0.062
X_4	1.60	0.66	2.40	0.037
X_5	0.35	0.11	3.22	0.009

Table 4-8. Estimated (O) and Predicted (P) K_f values for TNT using Eq. 5 and a measure of their deviation.

Soil	Estimated K_f	Predicted K_f	Deviation (O-P)/P
Cecil Ap	2.23	2.23	-0.00
Cecil Bt	1.87	1.81	0.03
Cloudland Ap	3.04	1.69	0.80
Cloudland C	3.65	1.05	2.48
Hagerstown Sap	2.04	6.72	-0.70
Kenoma BC	7.85	14.23	-0.45
Kenoma Bt1	8.49	10.41	-0.18
Norborne C	4.46	6.89	-0.35
Ocala C4	27.94	21.30	0.31
Watson 2Bxg	5.39	2.45	1.20
Watson BE	4.21	2.99	0.41
Westmoreland A1	2.80	2.56	0.09
Westmoreland B1	3.00	2.64	0.14

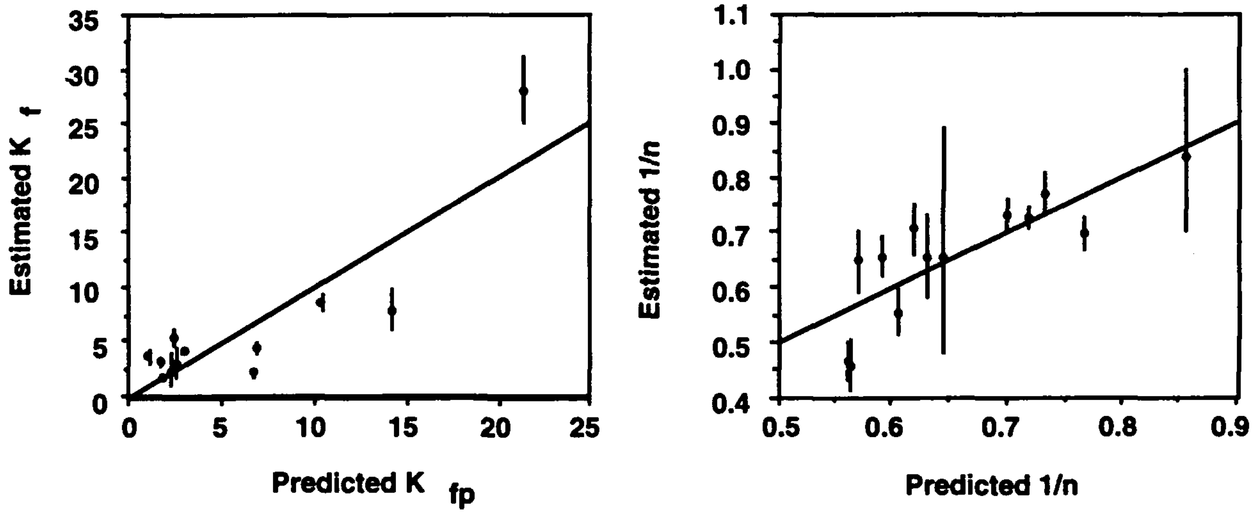


Figure 4-2. Plots of a) predicted K_{fp} from Eq. 5 versus estimated K_f from the Fruendlich model, and b) predicted 1/n values from Eq. 6 versus estimated 1/n values from the Freundlich model; bars represent 95% confidence limits and the lines depict x = y.

Table 4-9. Analysis of variance of the regression of the estimated 1/n for TNT against organic carbon (X_1) (Eq. 6).

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Probability of a > F	R^2
Model	1	0.10	0.10	21.16	0.0008	0.66
X_1	1	0.10		21.16	0.0008	
Error	11	0.05	0.005			
Corrected Total	12	0.15				

Table 4-10. Parameter estimates for the predictive model for 1/n for TNT (Eq. 6).

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	0.56	0.03	19.31	< 0.001
X_1	0.15	0.03	4.60	< 0.001

Table 4-11. Estimated (O) and Predicted (P) 1/n values for TNT using Eq. 6 and a measure of their deviation.

Soil	Estimated 1/n	Predicted 1/n	Deviation (O-P)/P
Cecil Ap	0.656	0.644	0.02
Cecil Bt	0.555	0.605	-0.08
Cloudland Ap	0.772	0.732	0.05
Cloudland C	0.455	0.565	-0.19
Hagerstown Sap	0.465	0.562	-0.17
Kenoma BC	0.654	0.631	0.04
Kenoma Bt1	0.699	0.768	-0.09
Norborne C	0.657	0.592	0.11
Ocala C4	0.647	0.570	0.14
Watson 2Bxg	0.706	0.616	0.15
Watson BE	0.727	0.719	0.01
Westmoreland A1	0.837	0.856	-0.02
Westmoreland B1	0.732	0.702	0.04

4.3 RDX MODEL DEVELOPMENT

As discussed previously, both the linear (Eq. 1) and the Freundlich Isotherm Model (Eq. 3) produced the smallest MSEs for roughly half of the soils when used to fit the phase concentration data (see section 3.2.1, Table 3-1). Three of the soils, for which the smallest MSEs were produced with the Freundlich model (i.e., Kenoma Bt1, Ocala C4, and Watson 2Bxg), had confidence intervals about the parameter 1/n which overlapped 1 (see section 3.2.1, Table 3-2) and were reduced to linear models. Thus, for consistency among soils, the linear model was chosen as the best fitting model to the phase concentration data. In addition, the difference between the MSE's for those soils (i.e.; Cecil Ap, Cecil Bt, Elk B1, Westmoreland A1) that fit the linear model best and the MSE's for the Freundlich model, for the same soils, was extremely small and hence there is not much difference between the models ability to explain the observed variability. Figure 4-3a presents the predicted line using the linear model and observed phase concentration data for the Cecil AP soil. Table 4-12 presents the estimated linear parameter and approximate 95% confidence limits for each soil.

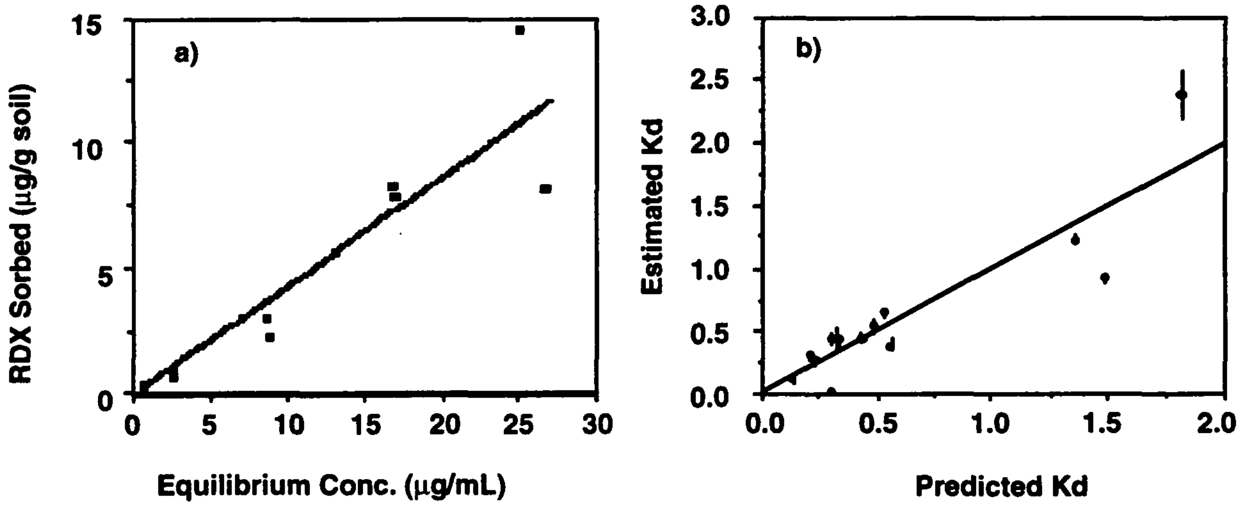


Figure 4-3. Plots of a) RDX sorption isotherm for the Cecil Ap soil showing the linear model fit, and b) the predicted Kd from Eq. 7 versus the estimated Kd from the linear isotherm model (Eq. 1); the bars represent the 95% confidence limits and the line represents x = y.

Regression analysis with the first three principal components (P_1, P_2, and P_3) from the soil data and the estimated linear parameter, K_d, for each soil produced the best predictive model. The equation can be expressed as

$$K_{dp} = 0.64 - 0.22P_1 + 0.23P_2 + 0.32P_3 \qquad (7)$$

where K_{dp} is the model predicted K_d. The R^2 for this model was 0.82 (Table 4-13). A measure of the deviation between the estimated parameter (K_d) from the Linear model and the predicted values from the regression model (Eq. 7; Table 4-14) is presented in Table 4-15 and Figure 4-3b.

Table 4-12. Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Linear Model (Eq. 1) and RDX phase concentration data.

Soil	K_d	Lower CL	Upper CL
Cecil AP	0.43	0.34	0.52
Cecil Bt	0.31	0.29	0.33
Cloudland Ap	0.45	0.41	0.49
Cloudland C	0.12	0.11	0.13
Kenoma BC	0.93	0.92	0.94
Kenoma Bt1	1.21	1.18	1.24
Norborne C	0.39	0.35	0.43
Ocala C4	2.37	2.18	2.56
Watson 2Bxg	0.45	0.42	0.48
Watson BE	0.54	0.49	0.59
Westmoreland A1	0.65	0.63	0.67
Westmoreland B1	0.43	0.39	0.47

Table 4-13. Analysis of variance of the regression of the estimated K_d for RDX against the first three principal components.

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Probability of a > F	R^2
Model	3	3.70	1.23	14.88	0.0001	0.82
P_1	1	1.34		16.25	0.0024	
P_2	1	0.96		11.66	0.0066	
P_3	1	1.30		15.66	0.0027	
Error	10	0.83	0.08			
Corrected Total	13	4.52				

Table 4-14. Parameter estimates for the predictive model for K_d for RDX (Eq. 7).

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	0.64	0.08	8.32	< 0.001
P_1	- 0.22	0.06	-4.03	0.002
P_2	0.23	0.07	3.41	0.007
P_3	0.32	0.08	3.96	0.003

Table 4-15. Estimated (O) and Predicted (P) K_d values for RDX using Eq. 7 and a measure of their deviation.

Soil	Estimated K_d	Predicted K_d	Deviation (O-P)/P
Cecil Ap	0.43	0.33	0.32
Cecil Bt	0.31	0.22	0.44
Cloudland Ap	0.45	0.31	0.43
Cloudland C	0.12	0.14	-0.14
Elk-B1	0.27	0.24	0.13
Hagerstown Sap	0.02	0.31	-0.94
Kenoma BC	0.93	1.49	-0.38
Kenoma Bt1	1.21	1.36	-0.11
Norborne C	0.39	0.56	-0.31
Ocala C4	2.37	1.81	0.31
Watson 2Bxg	0.45	0.44	0.02
Watson BE	0.54	0.48	0.13
Westmoreland A1	0.65	0.53	0.23
Westmoreland B1	0.43	0.34	0.25

4.4 NL-TNT MODEL DEVELOPMENT

NL-TNT (no loss-TNT) was analyzed in the same fashion as TNT and RDX in order to make comparisons with the results obtained by Pennington and Patrick (1990). In this analysis, the phase data consisted of 1) the aqueous concentration of TNT (as described earlier), and 2) the solid phase concentration calculated as the initial minus the final aqueous concentrations expressed on a soil mass basis (µg TNT sorbed/ g soil); this type of analysis assumes no transformation (hence loss) of TNT. As discussed previously (see section 3.2.2) both the Langmuir Isotherm Model (Eq. 2) and the Freundlich Isotherm Model (Eq. 3) produced the smallest MSEs for roughly two thirds and one third of the soils, respectively, when used to fit the phase concentration data calculated as described above (see section 3.2.2, Table 3-6). None of the soils, for which the smallest MSEs were produced with the Freundlich model had confidence intervals about the parameter 1/n which overlapped 1 (see section 3.2.2, Table 3-7). Thus, for consistency among soils, the Langmuir model was chosen as the best fitting model to the phase concentration data. Figure 4-4a presents the predicted line using the Langmuir model and observed phase concentration data for the Cecil AP soil. Table 4-16 presents the estimated Langmuir parameters and approximate 95% confidence limits for each soil.

Regression analysis with the first three principal components (P_1, P_2, and P_3) from the soil data and the estimated Langmuir parameter, *Q*, for each soil was not successful. The best predictive model for this parameter was a regression against the iron content in the soil (X_3). The equation can be expressed as

$$Q_p = 175.69 - 0.26X_3 \quad . \qquad (8)$$

where Q_p is the predicted Langmuir parameter, and X_3 is the DCB iron content. The R^2 for this model was 0.34 (Table 4-17). A measure of the deviation between the estimated parameter from the Langmuir model and the predicted values from the regression model (Eq, 8; Table 4-18) is presented in Table 4-19 and Figure 4-4b.

The best predictive model for the Langmuir parameter, b, was a regression against the soil CEC (X_5). The equation can be expressed as

$$b_p = - 0.05 + 0.02X_5 \quad . \qquad (9)$$

where X_5 is CEC. The R^2 for this model was 0.31 (Table 4-20). A measure of the deviation between the estimated parameter from the Langmuir model and the predicted values from the regression model (Eq. 9; Table 4-21) is presented in Table 4-22 and Figure 4-5.

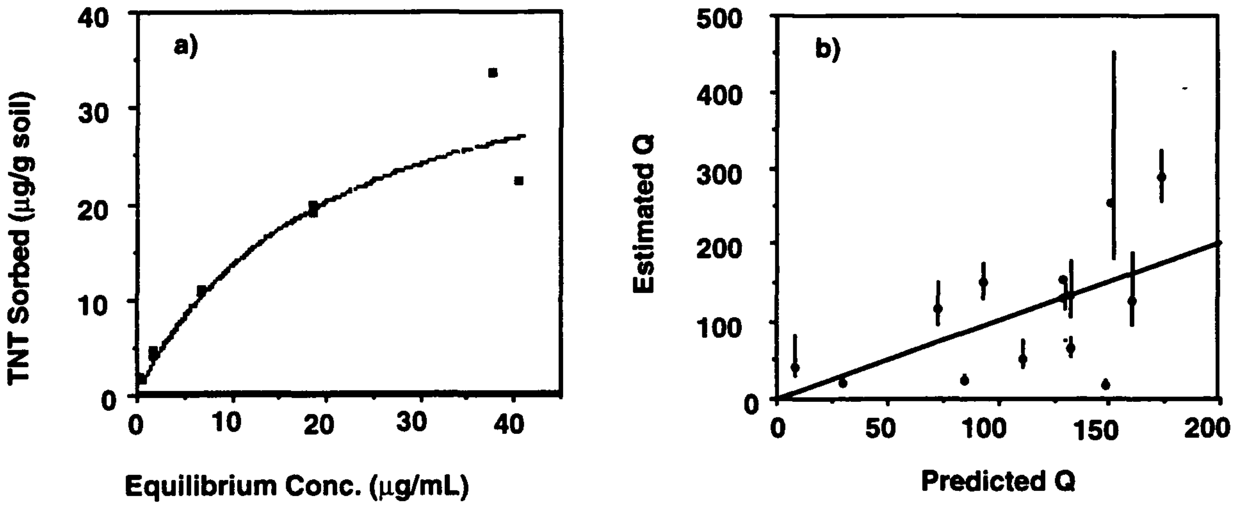


Figure 4-4. Plots of a) TNT sorption on the Cecil Ap soil using the NL-TNT solid phase concentration data (the curved line depicts the fit for the Langmuir model, and b) predicted Langmuir Q parameter from the Langmuir model; bars represent 95% confidence limits and the solid line represents x = y.

Table 4-16. Parameter estimates and approximate 95% confidence limits (CL) for each soil using the Langmuir Isotherm Model (Eq. 2) and NL- TNT phase concentration data.

Soil	Q	Lower CL	Upper CL	b	Lower CL	Upper CL
Cecil AP	40.2	27.6	80.1	0.05	0.02	0.14
Cecil Bt	20.1	15.1	28.9	0.09	0.04	0.21
Cloudland Ap	256	182	451	0.01	0.00	0.01
Cloudland C	23.0	19.6	27.5	0.17	0.10	0.31
Elk B1	51.2	39.7	73.8	0.06	0.03	0.11
Hagerstown Sap.	15.4	12.0	21.1	0.10	0.05	0.22
Kenoma BC	64.1	51.5	78.4	1.39	0.37	11.7
Kenoma Bt1	132	106	179	0.07	0.04	0.11
Norborne C	124	94.7	188	0.02	0.01	0.03
Ocala C4	287	259	322	0.10	0.08	0.12
Watson 2Bxg	117	96.9	151	0.04	0.03	0.06
Watson BE	149	130	174	0.02	0.02	0.03
Westmoreland A1	153	73.5		0.02	-0.00	0.07
Westmoreland B1	129	115	147	0.02	0.01	0.02

Table 4-17. Analysis of variance of the regression of the estimated Q for NL-TNT against the iron content of the soil (X_3) (Eq. 8).

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Probability of a > F	R^2
Model	1	30739	30739	6.04	0.0301	0.335
X_3	1	30739		6.04	0.0301	
Error	12	61053	5087.7			
Corrected Total	13	91792				

Table 4-18. Parameter estimates for the predictive model for Q for NL-TNT (Eq. 8); X_3 is DCB iron content.

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	176	32.35	5.43	< 0.001
X_3	-0.26	0.11	-2.46	0.030

Table 4-19. Estimated (O) and Predicted (P) Q values for NL-TNT using Eq. 8 and a measure of their deviation.

Soil	Estimated Q	Predicted Q	Deviation (O-P)/P
Cecil Ap	40.2	8.6	3.67
Cecil Bt	20.1	29.9	-0.33
Cloudland Ap	255.5	151.9	0.68
Cloudland C	23.0	84.4	-0.73
Elk-B1	51.2	110.9	-0.54
Hagerstown Sap	15.5	148.1	-0.90
Kenoma BC	64.1	132.8	-0.52
Kenoma Bt1	132.1	132.6	-0.00
Norborne C	124.4	161.1	-0.23
Ocala C4	286.6	174.1	0.65
Watson 2Bxg	117.4	73.0	0.61
Watson BE	148.6	93.1	0.60
Westmoreland A1	152.9	130.2	0.17
Westmoreland B1	128.8	129.9	-0.01

Table 4-20. Analysis of variance of the regression of the estimated b for NL-TNT against the soil CEC (X_5) (Eq. 9).

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Probability of a > F	R^2
Model	1	0.52	0.52	5.45	0.0377	0.312
X_5	1	0.52		5.45	0.0377	
Error	12	1.15	0.10			
Corrected Total	13	1.67				

Table 4-21. Parameter estimates for the predictive model for b for NL-TNT (Eq. 9); where X_5 is CEC.

Term	Estimate	Standard Error	t Ratio	Probability of a > |t|
Intercept	-0.05	0.12	-0.41	0.691
X_5	0.02	0.01	2.33	0.038

Table 4-22. Estimated (O) and Predicted (P) b values for NL-TNT using Eq. 9 and a measure of their deviation.

Soil	Estimated b	Predicted b	Deviation (O-P)/P
Cecil Ap	0.05	0.04	0.28
Cecil Bt	0.09	0.01	17.15
Cloudland Ap	0.01	-0.004	-3.42
Cloudland C	0.17	0.05	2.15
Hagerstown Sap	0.10	-0.01	-9.44
Kenoma BC	1.39	0.53	1.61
Kenoma Bt1	0.07	0.43	-0.84
Norborne C	0.02	0.12	-0.86
Ocala C4	0.10	0.57	-0.82
Watson 2Bxg	0.04	0.14	-0.70
Watson BE	0.02	0.06	-0.68
Westmoreland A1	0.02	0.08	-0.75
Westmoreland B1	0.02	0.05	-0.70

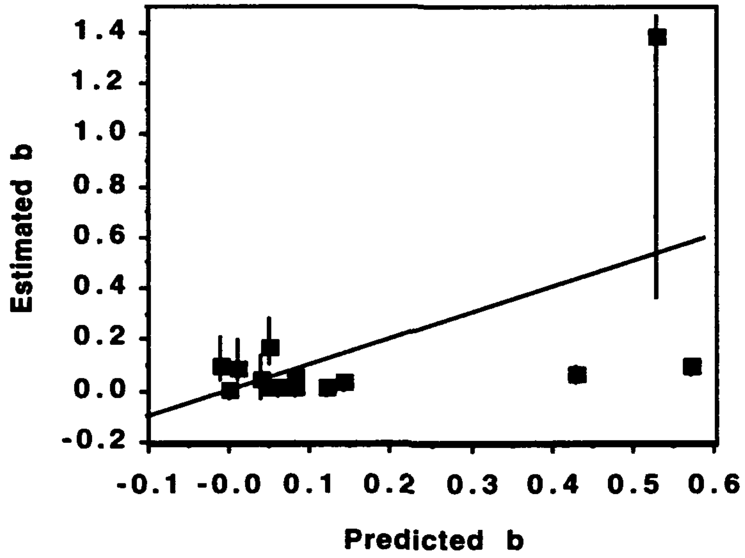


Figure 4-5. Predicted b parameter from Eq. 9 for NL-TNT versus the estimated parameter from the Langmuir isotherm; bars depict the 95% confidence limits.

4.5 MODEL EFFECTIVENESS

From the above analyses of RDX data it is clear that the Linear model is best utilized for the predictive model and the sorption coefficient (K_d) is best modeled by the linear combination of the three principal components (Table 4-2) as expressed in Eq. 7. The three principal components are:

$$P_1 = 0.606 + 0.196\ X_1 + 0.0214\ X_2 + 0.00323\ X_3 - 0.305\ X_4\ -0.0319\ X_5 \qquad (10)$$

$$P_2 = -2.217 - 0.819\ X_1 + 0.0330\ X_2 + 0.00134\ X_3 + 0.157\ X_4 + 0.0426\ X_5 \qquad (11)$$

and,

$$P_3 = -1.180 + 1.19\ X_1 + 0.0156\ X_2 - 0.00073\ X_3 - 0.0885\ X_4 + 0.0519\ X_5 \qquad (12)$$

where X_1, X_2, X_3, X_4, and X_5 are the quantities of OC (%), clay (%), DCB-Fe (μmole/g soil), pH, and CEC (meq/100g soil), respectively. Since these equations are linear relations, equations P_1, P_2, and P_3 may be substituted into Eq. 7 and the terms combined to yield a single expression for K_{dp}:

$$K_{dp} = -0.38 + 0.149(\%OC) + 0.008(\%clay) - 0.0006(DCB\text{-}Fe) + 0.074(pH) + 0.033(CEC) \tag{13}$$

The K_{dp} for each of the soils used in the model development was calculated (Table 4-15). As can be seen from a comparison of the actual K_d and K_{dp}, the model predictions are well within a factor of 2 for all soils except for the Hagerstown saprolite. The Hagerstown saprolite soil, however, sorbed so little RDX over the range of initial concentrations that a reasonable K_d could not be estimated.

Two soils that were not included in the construction of the principal components or the predictive model were used as test soils; the Elk B1 and Burbank Ap soil horizons (see Table 2-1). Batch sorption isotherm data for these soils were collected in the same manner as the other soils. The Elk B1 horizon sorption data was fit to the linear isotherm model with a K_d of 0.27 ± 0.03 mL/g. The predicted value, calculated via Eq. 13, was $K_{dp} = 0.24$. The Burbank Ap had a measured $K_d = 0.16 \pm 0.04$ and a predicted $K_{dp} = 0.36$. The predicted value for the Elk B1 soil is almost equal to the measured value, but the predicted Burbank Ap value is a factor of 2.25 greater than that measured.

As stated earlier, the best isotherm model for TNT is the Freundlich Isotherm Model and the Eq. 5 is the better predictive model for calculating the sorption coefficient K_f; the Fruendlich parameter 1/n is best calculated via Eq. 6. A comparison of the estimated and predicted values for K_f and 1/n are presented in Tables 4-8 and 4-11, respectively. The ability to predict the K_f parameter was reasonable in that all of the measured K_f values were predicted to within a factor of 3.5 and most often better than a factor of 2. Again sorption to the Hagerstown Saprolite soil was poorly predicted by the model; this cannot be construed as a result of a low level of sorption since the Cecil Bt had about the same K_f value (1.87) and low level of sorption as the Hagerstown soil (2.04) but was well predicted. The other soil poorly predicted by the model was the Cloudland C; the high observed K_f may be the result of transformation not being fully accounted for and hence yielding a higher K_f than one would expect. Using the Burbank Ap soil horizon as a test soil the sorption isotherm data was best described by the Freundlich Isotherm Model whose sorption coefficients were $K_f = 2.96 \pm 0.55$ and $1/n = 0.74 \pm 0.08$. The predicted values for the Burbank Ap soil were $K_{f_p} = 5.43$ and $1/n = 0.64$.

As discussed earlier, Pennington and Patrick (1990) found that the Langmuir Isotherm Model described TNT sorption to a series soils best when compared to the Freundlich and Linear models. In the present study, the Langmuir model effectively described TNT sorption only when TNT transformation was not taken into account. Under these conditions a predictive model was constructed. This model (Eq. 8 and 9) were used to predict the Langmuir parameters, Q and b, for the soils used in the Pennington and Patrick (1990) study of TNT sorption by soils.

As can be seen from the results presented in Table 4-23 the experimentally determined Q values are adequately predicted by Eq. 8. These results are interesting in that Pennington and Patrick (1990) used oxalate extractable Fe as a measure of Fe content (this value was used as the input value in Eq. 8), but Eq. 8 was constructed utilizing a DCB extractable Fe value. While both extractants remove noncrystalline, paracrystalline oxides and short-ranged-ordered oxides and hydroxides of Al, Fe, and Mn, the DCB extractant also removes crystalline materials such as goethite and hematite (Jackson et al. 1986). This difference in extractant strength may have resulted in the frequent over estimation of the predicted Q value (Table 4-23). Despite the different extractants used in the two studies the results of the comparison are remarkably good.

On the other hand, however, the ability of Eq. 9 to predict the value of b determined by Pennington and Patrick (1990) is very poor (Table 4-23). While the reasons for the poor predictability are not totally clear, it is believed that part of the problem relates to the fact that the Langmuir model itself did not adequately represent the behavior of TNT in the soils used in the present study. That is, only two thirds of the soils in the NL-TNT sorption analysis were described best by the Langmuir model, and only when TNT transformation was ignored. In addition, Eq. 9 is a function of CEC only, and the worst predictions for the Pennington and Patrick (1990) data are for soils (i.e., Joliet and Kansas) whose CEC values are considerably outside the range of those used in the present study to construct Eq. 9.

Another consideration that must be taken into account in comparing the present study with those of Pennington and Patrick (1990) is that the latter study utilized a smaller solid-to-solution ratio (1:20 compared to 1:4) and allowed only 2 h for equilibration (the present study equilibrated samples for 96 h). These two differences in methodology translates into less TNT transformation during the batch sorption studies of Pennington and Patrick (1990). It is believed that the greater transformation in the present study is reflected in the NL-TNT data analysis for the Langmuir b parameter, hence prediction of b values for the Pennington and Patrick (1990) soils is substantially greater than that actually determined.

Table 4-23. Comparison between the predicted Langmuir parameters (Q_p and b_p; Eq. 8 and 9) and Q and b values determined by Pennington and Patrick (1990).

Soil	Q_p	Q	b_p	b
Cornhuskers	143	72	0.66	0.16
Crane	85	76	0.57	0.12
Holston A	117	88	0.53	0.13
Holston B	142	79	0.65	0.08
Iowa	86	86	0.84	0.18
Joliet	95	93	1.99	0.23
Kansas	107	107	2.55	0.12
Lonestar	133	55	0.26	0.12
Longhorn	150	73	0.37	0.14
Louisiana	132	67	0.27	0.09
Newport	136	65	0.22	0.08
Radford	153	68	0.38	0.12
Savanna	127	100	0.21	0.05
Volunteer	114	87	0.89	0.11

In addition to the Langmuir parameters discussed above, the Freundlich parameters, K_f and 1/n, were calculated (Eq. 5 and 6) for the Pennington and Patrick (1990) TNT sorption data. Comparison of the predicted TNT Freundlich constants and those determined by Pennington and Patrick (1990) were found to be very reasonable (Table 4-24). With the exception of one soil, all predicted K_f values were within about a factor of 2.5 of those listed by Pennington and Patrick (1990), and for all but three of the soils the predicted value was within a factor of two. The 1/n values varied over a greater range than one would hope, but still reasonable considering the calculated value is only dependent on OC; for soils with OC greater than the range of soils used in the model development, 1/n values >1 should be expected. In these cases it would probably be preferable to use the average 1/n value of the soils reported here in this model. It must be realized also, that for the Pennington and Patrick (1990) TNT data, the Langmuir model was considered best; although in many cases there was very little difference in the R^2 values used to select the best isotherm model fit. The former study considered transformation to be negligible. However, if a small amount of TNT transformation did occur, particularly at the lower initial concentrations, the impact would be to accentuate the steepness of the sorption isotherm and yield data better described by the Langmuir isotherm model. In the present study, TNT transformation was observed to be greatest at the lower initial concentrations (in terms of percent TNT transformed).

Table 4-24. Comparison of the predicted Freundlich parameters (K_{fp} and $1/n_p$; Eq. 5 and 6) and the k_f and 1/n values determined for soils used by Pennington and Patrick(1990).

Soil	K_{fp}	K_f	$1/n_p$	1/n
Cornhuskers	16.1	10.2	0.68	0.63
Crane	10.8	8.8	0.98	0.67
Holston A	13.9	10.3	0.96	0.67
Holston B	14.2	6.6	0.74	0.71
Iowa	17.3	13.0	0.77	0.63
Joliet	38.8	16.0	1.10	0.63
Kansas	49.3	12.0	0.95	0.71
Lonestar	5.1	6.5	0.64	0.63
Longhorn	6.5	9.4	0.64	0.63
Louisiana	5.1	6.1	0.62	0.67
Newport	9.3	5.7	1.08	0.67
Radford	11.3	7.9	0.73	0.67
Savanna	6.2	5.3	0.75	0.71
Volunteer	17.5	8.9	0.81	0.71

Clearly, the predictive model constructed around the Freundlich Isotherm Model simulated the Pennington and Patrick (1990) data better than the Langmuir based model. Probably the two most important reasons for this are that 1) the Freundlich model was superior in describing the sorption data and hence, the predictive model was superior, and 2) accounting for TNT transformation in the present study (the Freundlich based model) yielded data that represented sorption of TNT only and related more directly to the data of Pennington and Patrick (1990) as a result of the limited TNT transformation that occurred in their study.

5.0 COLUMN STUDIES WITH RDX AND TNT

To determine how significant the solute/soil reactions are on affecting the transport of TNT and RDX in field systems, a series of 1-D column experiments were conducted with five soils. The purpose of these experiments was to determine if chemical sorption parameters determined in batch systems are accurate enough to predict the movement of the solutes, or if additional processes need to be quantified. The movement of a solute front through soil, though driven by gravity and pressure gradients, is attenuated by physical spreading processes (i.e. hydrodynamic dispersion). With some soils, the effect of hydrodynamic dispersion can mask chemical effects such as a nonlinear isotherm or slow sorption, particularly if soil particles (or aggregates) are large (which leads to significant slow diffusion of solutes in immobile pore water). To apply results of batch experiments to the field scale, the effect of solute flow through soil must be examined, and 1-D column experiments represent the simplest system in which the chemical effects can be observed (and quantified) in a flowing system. Therefore an *additional purpose of 1-D flow experiments* is to determine if a simple transport code that assumes local equilibrium (i.e., fast, reversible reaction) and accounts for hydrodynamic dispersion can accurately predict TNT and RDX movement through soils or are more complex solute transport codes required.

From batch experiments, it was shown that RDX sorption is small, and appears to be linear. Given the rather small and rapid amount of sorption and linear isotherms, RDX transport in columns are likely described by a simple transport code that assumes local equilibrium (i.e., fast, reversible reaction; van Genuchten and Cleary 1979) and accounts for hydrodynamic dispersion. The partial differential equation describing solute movement with equilibrium sorption **(model 1)** is:

$$-\frac{q}{\theta}\frac{\partial c}{\partial x} + \frac{D}{\theta}\frac{\partial^2 c}{\partial x^2} - \frac{\rho_b K_d}{\theta}\frac{\partial c}{\partial t} = \frac{\partial c}{\partial t} \qquad (1)$$

where q is the hydraulic head, θ is the soil porosity, ρ_b is the bulk density, D is the hydrodynamic dispersion coefficient, and K_d is the sorption coefficient. This differential equation, with appropriate boundary conditions, can be solved analytically after independently determining K_d and D.

By placing the $\rho_b K_d$ term on the right side of Eq. 1, the solute concentration term then has a coefficient of $(\rho_b K_d/\theta + 1)$, which is commonly referred to as the retardation factor ($R_f = \rho_b K_d/\theta + 1$), because it describes how much slower solute moves compared to water as a result of sorption (for water Kd = 0; so $R_f = 1$). In this study, the R_f is calculated by integrating the area under the sorption or desorption limb (i.e., the area in front of the breakthrough curve as C/C_0 goes from 0 to 1, or the area behind the breakthrough curve as C/C_0 goes from 1 to 0); K_d's for sorption and desorption are calculated from the R_f values. The R_f is equivalent to the relative velocity of the solute compared to that of a conservative tracer (v_{solute}/v_{water}). The sorption and desorption K_d's for RDX should be equal to each other and the batch determined K_d; under these conditions, **model 1** should simulate the column breakthrough data.

The value of D in Eq. 1 is estimated by measuring tracer ($CaCl_2$) dispersion and using the theoretical ratio of solute to tracer dispersion (Szecsody and Bales 1989; Horvath and Lin 1976, 1978). To accurately predict RDX and TNT transport, a measure of the physical spreading of a solute plume (hydrodynamic dispersion) is needed. Three column experiments at different velocities were conducted using the Cloudland C soil (Appendix A). Velocities of the experiments (0.033, 0.015, 0.00011 cm/sec) covered over two orders of magnitude (and the range used in present solute experiments) in order to develop a dispersion versus velocity relationship for one of the current soils and to compared it to published data (Rose 1977). Relationships of this type have some theoretical basis and follow a general relationship such as $D = D_o + \alpha_L V^n$, where D is the coefficient of hydrodynamic dispersion, D_o is the molecular diffusion of the solute in the porous media, α_L is the longitudinal dispersivity, v is velocity, and n is an empirical power (usually 1.0 to 1.5). Calculation and measurement of tracer dispersion in a specific system (same porous media, same velocity, same solute) is necessary to determine what portion of a breakthrough curve's shape is caused by dispersion versus other processes such as diffusion or slow reactions. Tracer values determined in the present study were similar to calculated values, indicating no slow physical processes in the Cloudland C soil. The five soils in the present study have similar grain size distributions, and their calculated dispersivities show little difference in dispersion. Because larger molecules diffuse more slowly, they may exhibit greater dispersion compared to a small tracer. However, TNT and RDX molecular diffusion coefficients are only slightly smaller than that of the tracer used in the present study and hence, calculated dispersivities are only slightly larger (10% to 30%). This small difference in dispersion between the tracer and solutes can be ignored, and actual tracer and solute dispersivities directly compared at the same velocity.

If TNT transport in the 5 soils is well behaved (i.e., weak linearity, and no transformation), R_f determinations will produce a K_d that will be equal to the K_d value calculated from the Freundlich isotherm ($q = K_f C^{1/n}$; $K_d = q/C$) assuming an equilibrium concentration (C) equal to the TNT injection concentration for the column studies. In addition, **model 1** will adequately simulate solute breakthrough. However, TNT sorption has been shown to be nonlinear in soils, and undergo a transformation reaction. Hence, compared to RDX, there are three additional chemical effects that could affect TNT transport: 1) the slow sorption/desorption of TNT, 2) nonlinearity of the TNT sorption process, and 3) the slow transformation of TNT. Several parameters in the one-dimensional solute transport code (discussed above) may act as indicators of nonequilibrium and the presence of these additional chemical effects (van Genuchten and Cleary 1979; van Genuchten, 1981): 1) coefficient of hydrodynamic dispersion (D) and, 2) the solute's retardation factor (or K_d). When **model 1** is used to fit breakthrough data that does not exhibit linear equilibrium sorption, the dispersion coefficient can be used as an indicator (e.g., Valocchi 1985) because slow rate processes (or nonlinear sorption) increase the observed spreading of a breakthrough curve and the dispersion coefficient obtained by fitting an equilibrium model to nonlinear data is larger than could be caused by physical dispersion processes alone. In addition, the determination of a smaller desorption R_f (or K_d) compared to the sorption R_f would indicate mass loss (i.e., the area under the desorption limb is smaller than the area under the sorption limb). A slow (or fast), reversible sorption reaction would result in the sorption and desorption limbs being inversely symmetrical; that is, the area under the desorption limb would equal the area under the sorption limb, and the two R_f values would be the same.

There is currently no transport codes available that will describe all of these effects, although one of two transport codes could be modified for this purpose (PDREACT by A. Valocchi and others at University of Illinois; RICE code, C. Dawson and M. Wheeler at Rice University). Both codes have been used to describe the biodegradation kinetics of multiple reactions, and chemical kinetics of multiple reactions. Either code could be efficiently modified specifically for the TNT system, but additional batch and column experimentation would be required to cbtain additional sorption and rate parameters for each reaction. This problem is similar to the reactions of 1-aminonaphthalene with clay (Szecsody et al. 1993, based on the work of Ainsworth et al. 1991), where 3 rate parameters were approximated for 2 reactions.

Alternatively, however, three simpler transport codes will be used in an attempt to model TNT transport if any of the additional chemical effects are observed. These codes are: 1) an advective-dispersive solute transport code with a slow first-order reversible reaction and linear sorption (**model 2**), 2) an advective-dispersive solute transport code with a slow first-order reversible reaction and nonlinear sorption (**model 3**), and 3) a code describing solute transport with a first-order irreversible reaction (**model 4**) (van Genuchten and Cleary, 1979). In the absence of a transport code that describes the TNT/soil reactions and the equilibrium/kinetic parameters for those reactions, these simpler codes may be used to simulate chemical effects to show the relative magnitude of importance. In each case, however, some portion of the TNT breakthrough curve may fit better, but fit may be poorer in another portion.

5.1 RDX COLUMN STUDIES

A series of 2 to 3 RDX column experiments were conducted on each of 5 soils, where the same pore water velocity (about 0.01 cm/sec) was used for one experiment with each soil for direct comparison of the sorption behavior. Given the different chemical properties in the 5 soils (Table 5-1), and that sorption has been demonstrated to be related to OC, clay content, and iron content, any significant difference in RDX sorption between soils would have been observed. However, RDX breakthrough in the soils (Norborne C, Cloudland C, Westmoreland B1, and Ocala

C4) at the same velocity (Fig. 5-1) showed nearly identical behavior, with very limited or no RDX sorption. Based on the low K_d values determined in the batch studies (see section 4.3, Table 4-15), these column study findings were not totally unexpected. Individual RDX breakthrough curves for all the soils and column parameters are presented in appendix A.

Table 5-1. Chemical and physical properties of those soils used in the column studies[a].

Soil Name	Clay	Silt	Sand	OC	Fe	CEC	pH	θ^b	ρ_b
		%			μmol/g	meq/100g			g/cm3
Norborne C	13.0	72.2	14.8	0.23	55.0	9.14	7.1	0.485	1.24±.02
Westmoreland B1	13.6	64.0	22.3	0.98	173.0	5.56	5.2	0.459	1.24±.07
Ocala C4	33.0	43.0	24.0	0.08	6.1	33.5	10.7	0.537	1.27±.04
Ocala C4 + alumina								0.527	1.08±.02
alumina								0.517	0.89±.05
Cloudland C	30.0	7.0	63.0	0.05	345.0	5.58	4.2	0.478	1.23±.09
Burbank4.0	4.0	51.0	45.0	0.50	110.3	5.50	7.0	0.413	1.37±.02

[a] Soil chemical analysis and particle size analysis from Table 2-1 of this report.

[b] Soil porosity (θ) and bulk density (ρ_b) determined for each packed column.

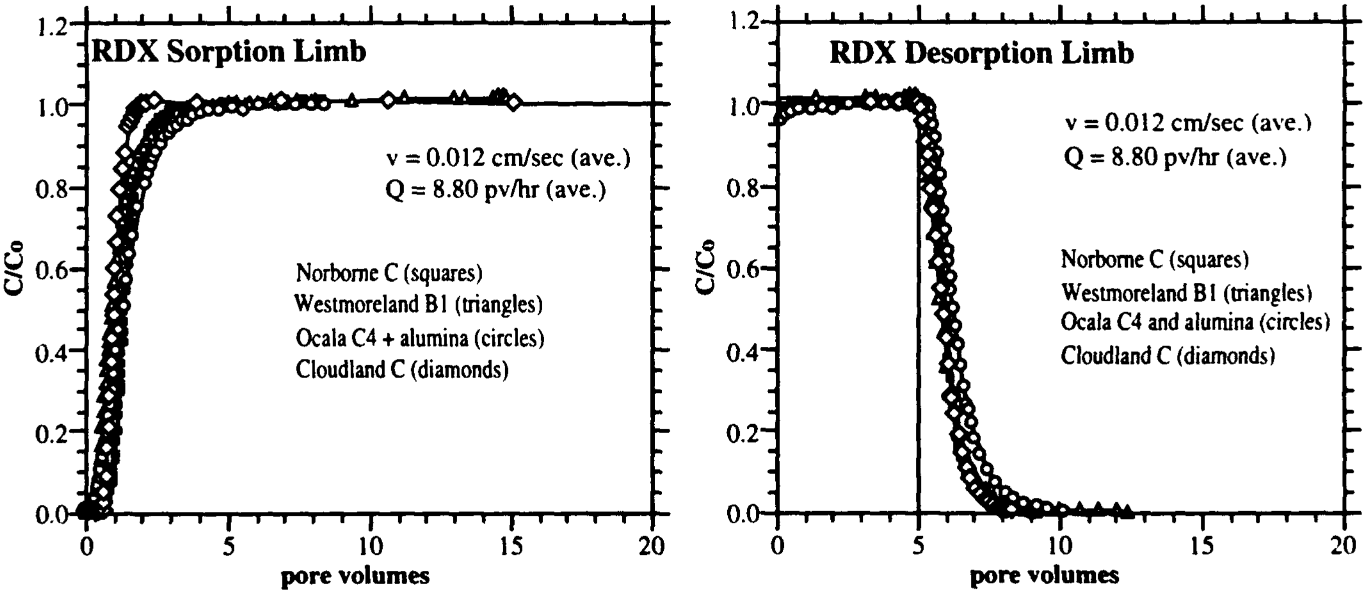


Figure 5-1. Comparison of the sorption and desorption limbs of RDX breakthrough curves for 4 different soils at the same velocity (0.012 cm/sec) and aqueous RDX concentration (4.18 μg/mL).

Three column experiments with RDX were conducted with the Norborne C soil (Fig. 5-1; Appendix A). All three breakthrough curves showed symmetrical sorption and desorption limbs with little tailing, and very little reversible sorption. The average sorption and desorption K_d's (0.12 mL/g and 0.16 mL/g) were similar, and nearly zero. The sorption isotherm for RDX with this soil (see section 3.2.1, Table 3.2) is slightly nonlinear ($1/n = 0.72$), which would be reflected in increased tailing of the breakthrough curves at lower RDX concentrations. However, tailing in the Norborne C soil was not noticeable due to the small mass of RDX sorbed in this column experiment. In fact, most (>95%) of the breakthrough curve behavior for RDX on the Norborne C soil could be accounted for by dispersion, but by including fast, reversible sorption with a linear isotherm (**model 1**) excellent breakthrough simulations were obtained at all three pore water velocities (model fits are shown in Appendix A). One experiment was conducted at a relatively high velocity ($v = 0.06$ cm/sec), and as little or no slow sorption was observed, reversible sorption appears to reach equilibrium in less than 6 minutes.

Two RDX column experiments conducted with the Westmoreland B1 soil also exhibited nearly zero sorption, with an average K_d of 0.03 mL/g (Fig. 5-1; Appendix A). Breakthrough was nearly identical to that observed with Norborne C soil (Fig. 5-1), although slightly more tailing in the sorption limb was observed. The slightly greater tailing in the breakthrough curve resulted from this soil's hydrodynamic dispersion which was determined to be slightly larger than in the Norborne C; like the Norborne C soil, solute breakthrough was well described by **model 1**. Given essentially no RDX sorption and no RDX mass loss for the Westmoreland B1, the transport of RDX through this soil can be completely described by only accounting for hydrodynamic dispersion.

Two column experiments with RDX were conducted with a 50/50 mix of Ocala C4 soil and porous alumina particles (Fig. 5-1; Appendix A), as flow through this soil alone was difficult to achieve. An additional RDX column experiment was conducted with alumina only to confirm that it exhibits no sorption ($K_d = 0.005$ mL/g). The Ocala C4 soil has a very low OC content (0.08%) and low iron (6.1 μmol/g) so any reactivity with RDX would be mainly related to the clay(s) present. These column experiments, as with previously reported soils, showed nearly zero sorption, with an average K_d of 0.12 mL/g. Breakthrough curve tailing was the greatest for these experiments compared to the other soils (Fig. 5-1), and may be due, in part, to slight additional dispersion caused by the presence of porous alumina particles. Time needed to reach diffusion equilibrium for the 200 µm porous alumina particles was about 2 min or less. **Model 1** yielded excellent fits to the breakthrough data at both pore water velocities, and hydrodynamic dispersion accounted for the observed breakthrough curve tailing associated with the presence of alumina.

Two column experiments with RDX conducted with the Cloudland C soil exhibited nearly zero sorption, with an average K_d of 0.06 mL/g and no observable mass loss over the 4 h or 16 h experiments (Fig. 5-1; Appendix A). As observed in the previously discussed soil column studies, RDX breakthrough in the Cloudland C soil was completely described by **model 1**. Two column experiments with RDX were also conducted with the Burbank soil. Similar to the other soils, it exhibited no, or limited sorption, with an average K_d of 0.08 mL/g (Appendix A). Breakthrough curve tailing was minimal, and RDX behavior was well described by **Model 1**.

In general, RDX transport through these soils exhibited essentially no, or limited sorption. In all cases, solute breakthrough could be well modeled by using a transport code that accounts for dispersion, but includes fast, reversible sorption that can be described by a linear sorption isotherm (**model 1**). The sorption/desorption K_d values calculated from the areas under the sorption and desorption limbs of the breakthrough curves were small, and in some cases almost nonexistent (i.e., equal to that of the tracer). The extremely small amount of RDX retardation compared to the water front made accurate calculation of the K_d values difficult. Essentially, the K_d values determined in these studies are at or below their discernable lower limit.

These column studies, however, are in agreement with the findings of the batch studies. First, sorption of RDX could be expressed as a linear sorption isotherm as suggested by the statistical analysis of the batch sorption data. Even the solute column breakthrough for the Norborne C soil, whose batch sorption data was best described by the Freundlich model (see section 3.2.1; Tables 3-1 and 3-2), could be well modeled by using a linear sorption model because the total mass of RDX sorbed was so small. Second, sorption in the column studies was fast and completely reversible as was observed in the batch studies. Third, the batch determined K_d's were all extremely low and of about the same magnitude as those determined in the column studies (i.e., $K_d < 1$). The results from the Ocala C4 soil column studies are difficult to compare to the batch study results due to the necessity of mixing alumina with the soil in order to achieve reasonable flow; although, the conclusions drawn from the column studies for the other soils due seem to describe the observations in the Ocala C4 column.

5.2 TNT COLUMN STUDIES

TNT column experiments were also conducted in each of the 5 soils (Table 5-1), but unlike RDX, there were differences in sorption behavior observed between the soils. TNT transport through 4 of the soils, all at the same velocity (Fig. 5-2), exhibit differences in the retardation factor (lag of the breakthrough curve; and hence K_d) and breakthrough curve tailing [due to sorption nonlinearity (nonlinear isotherm), sorption kinetics or mass loss].

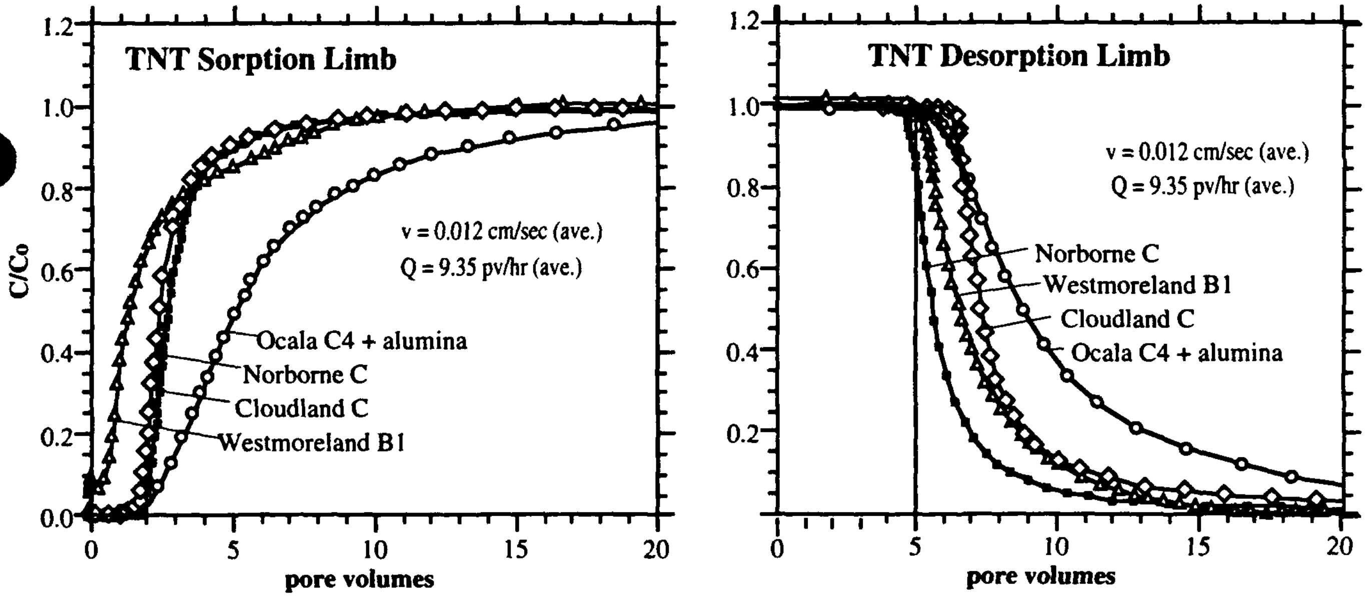


Figure 5-2. Comparison of the sorption and desorption limbs of TNT breakthrough curves for four different soils at the same velocity (v = 0.012 cm/sec) and TNT aqueous concentration (4.35 µg/mL).

Two column experiments with TNT were conducted with Norborne C soil at 25 °C. At the faster pore water velocity (Fig. 5-2), TNT behavior was reasonable and would appear to indicate reversible sorption. A similar TNT mass injection column experiment, conducted at a slow velocity (v = 0.0056 cm/sec), however, shows several prominent features of the reaction(s) exhibited by all the soils (Fig. 5-3). First, most of the breakthrough was relatively quick ($C/C_0 > 0.80$), occurring within 5 pore volumes. Importantly, however, the outlet concentration did not reach the inlet concentration even after 90 pore volumes (*i.e.*, 20 h), indicating either a very slow sorption/desorption process or continuous mass loss in the system. Second, during the desorption limb (Fig. 5-3), the TNT concentration decreased very rapidly, but then tailed before reaching zero outlet concentration. third, a smaller desorption R_f compared to the sorption R_f was observed (i.e., the area under the desorption limb was smaller than the area under the sorption limb); hence, the K_d from the sorption data (1.24 mL/g) is larger than the desorption K_d (0.10 mL/g), indicating some nonreversible component of the reaction. A reversible sorption reaction would result in the sorption and desorption limbs being inversely symmetrical, whereas, asymmetrical limbs is indicative of transformation or irreversible sorption. Comparison of the total mass between that eluting from the column and the mass injected shows a moderate mass loss (10.0 μg of 334 μg injected in 27 h).

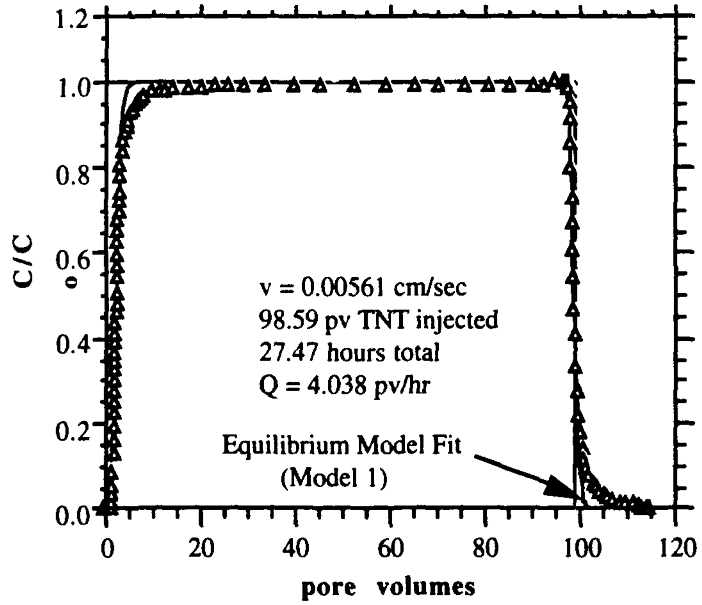


Figure 5-3. TNT breakthrough curve for the Norborne C soil horizon.

Mass loss in the context of these column experiments is not based on a true mass balance of TNT per se, but rather as the difference between the known concentration of TNT in solution injected into the column and the mass of TNT eluted from the column (the integrated area under the breakthrough curve) as determined by continuous TNT detection by UV/VIS at 254 nm. The difference between these two determinations is considered the mass loss. The accuracy of the "mass loss" is directly related to the accuracy of the pore water volume determination, and the area measurement error for a single pore volume may be considered a "mass loss detection limit". An estimate of the "detection limit" or area measurement error is about 2.3% of a pore volume based on the results of the RDX column studies. In these studies, the average variation in the difference between total RDX injected and that eluted was about ±2.3% of a pore volume. Assuming total reversibility of RDX sorption, 2.3 percent of a pore volume becomes the basis for mass loss detection limit. Taking this value as the "detection limit" for the TNT studies translates into approximately 0.3 μg TNT as a threshold detectable mass loss. It should be noted, however, that if mass loss is the result of TNT transformation, the products (e.g., 2-ADNT) associated with that transformation do absorb light in the same region as TNT. Hence the values for TNT mass loss reported here that are significantly above the "detection limit" should be considered a conservative estimate since the behavior of the transformation products under fluid flow are not well understood. In the case of the Burbank Ap and Cloudland C soil columns, HPLC analysis of the column effluent at selected times did not detect the presence of transformation products, which suggests that for these two soils continuous UV detection does represent TNT breakthrough.

Two column experiments with TNT were conducted with the Westmoreland B1 soil (Fig. 5-2; Appendix B). This soil has the highest OC of the group (0.98%), and moderate iron content (173 μmol/g). TNT breakthrough in both experiments ($v = 0.013$ and 0.0029 cm/sec) reached a steady state concentration after 15 pore volumes. The breakthrough data at the higher velocity appeared to indicate reversible sorption since the sorption and desorption limb K_d's were nearly identical (0.55 mL/g and 0.48 mL/g, respectively); very little tailing was observed and mass loss was within measurement error. The breakthrough data from the low velocity experiment, however, showed that C/C_0 was not attained even after 13 h, indicating either a slow reaction, or mass loss. However, TNT transformation in the Westmoreland B1 soil was small, and the column experiments could be reasonably simulated with **model 1**. While there is some additional desorption tailing not accounted for in this model fit [probably a result of the nonlinear sorption isotherm ($1/n \approx 0.73$)], the effect is minor (Appendix B).

Column effluent from the Westmoreland B1 soil was found to contain an iron precipitate (only with TNT, not with RDX), and it was affecting the detection of TNT by UV/VIS absorbance. The small peaks seen on the desorption limb of the low velocity breakthrough curve are probably from the precipitate (appendix B). The elution of an Fe precipitate was observed during the column experiments in 4 of the 5 soils studied, but only interfered with TNT detection in the Westmoreland B1 soil. While there was no way to quantify the mass of Fe precipitate, qualitatively the amount of precipitate eluted from the various soil columns follows as Westmoreland B1 >> Burbank Ap > Ocala C4 > Norborne C. Although the data is not conclusive, there appears to be a transformation reaction occurring in the Westmoreland B1 soil, but whether the Fe precipitate is present as a result of TNT transformation or another subsequent reaction such as that observed for the polymerization of aromatic amines in soils (Ainsworth et al. 1991) is not known.

As with the RDX column studies, TNT column experiments with the Ocala C4 soil utilized a 50/50 mixture of soil and alumina particles to achieve reasonable flow (alumina was inert with respect to TNT sorption). The Ocala C4 soil has a very low OC content (0.08%), low iron (6.1 µmol/g), high CEC (33.5 meq/100g) and the highest pH (10.7). Recalling that the predictive relationship developed for TNT sorption is a linear combination of pH and CEC (section 4-2; Eq. 5) it would not be surprising if this soil exhibited the highest TNT retardation.

The column experiment conducted at the high velocity showed fast breakthrough to 80% of inlet concentration (in 5 pore volumes), then somewhat slower breakthrough (i.e. tailing; Fig. 5-4). The TNT concentration did not reach $C/C_0 = 1$ even after 80 pore volumes (14 h), indicating continuous mass loss or slow sorption. The desorption limb of this curve reached $C/C_0 = 0$ within 20 pore volumes, and the desorption K_d (2.1 mL/g) was considerably smaller than the sorption limb K_d (3.10 mL/g). This suggests that the sorption tailing was caused by mass loss, as slow sorption would also produce slow desorption and equal K_d values. Calculation of the mass eluted confirmed that a moderate TNT mass of loss had occurred (5.2 µg of 285 µg injected) within the 21 h experiment.

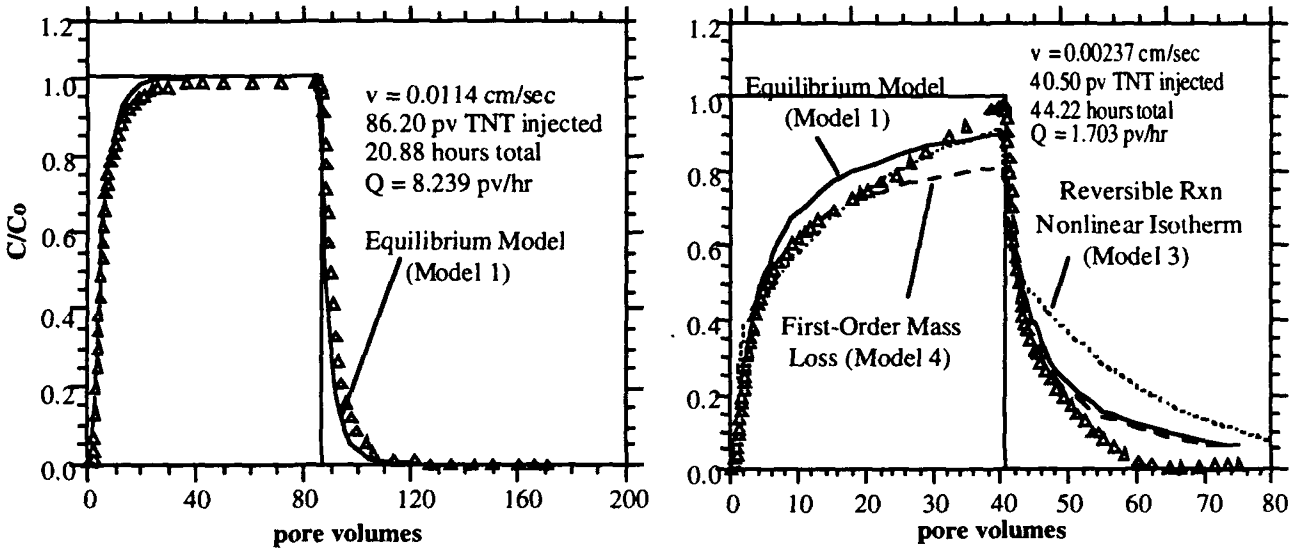


Figure 5-4. TNT breakthrough curves and model fits for the Ocala C4/alumina mixture at two different velocities.

In the second column experiment, the velocity was 5 times slower and over the 44 h experiment duration significantly more TNT mass was lost (25 µg of 132 µg injected), indicating that transformation is a slow process. The apparent K_d for this slower velocity experiment was approximately 5.5 mL/g for sorption and 1.7 mL/g for desorption; again, the difference in the two k_d values suggests mass loss. In addition, the higher sorption K_d value in slower velocity study compared to the high velocity experiment indicates the mass loss (transformation) reaction is likely a slow reaction. Given a 1.8% mass loss in 10 h at the higher velocity, and 19% mass loss in 25 h at lower velocity, the transformation half-life is roughly estimated to be in the 80 to 400 h range. A reaction this slow would be of little concern over less than a 10 h time period, but on the time scale of TNT transport in field soil systems mass loss could be expected to be substantial.

An additional feature of the Ocala C4 column experiment that indicates the presence of a slow reaction is the massive tailing apparent in both the sorption and desorption limbs of the low velocity study (fig. 5-4). The TNT nonlinear isotherm for this soil (1/n = 0.65; see section 3.2.2; Table 3-5) cannot account for this amount of breakthrough curve skewness. The mass loss and considerable skewness being less apparent at higher velocity probably indicates mass loss and considerable skewness being less apparent at higher velocity probably indicates that the reaction is so slow that very little of the reaction is occurring at this velocity. Three approaches were used in modeling high velocity data. Although **model 1** can be fit to this data (Fig 5-4), it can only be accomplished by increasing the dispersion coefficient to 15x that of the actual value, indicating significant nonequilibrium. Even with this unrealistic value, **model 1** does not fit the data well. A second modeling approach is to approximate the slow transformation reaction as a first-order mass loss from the sorbed phase (**model 4**). This provided a better fit on the first portion of the sorption limb, but removes too much mass at later times (Fig. 5-4). The third approach was to utilize a slow first-order reversible reaction with a nonlinear isotherm ($t_{1/2}$ = 5.2 h; **model 3**), which gave a good fit to the sorption limb, but could not fit the desorption limb (as mass is lost). Another approach that could be used to model this data is to actually simulate a third-order transformation reaction during transport, however, not enough information concerning the transformation process is currently known. These model fits plotted in Figure 5-4 demonstrate that in cases of considerable tailing due to the transformation reaction, simpler reactive transport codes do not provide adequate simulation of the process.

Two column experiments with TNT were conducted with the Cloudland C soil (Appendix B). The column experiment at higher velocity (Fig. 5-2) showed TNT breakthrough with little tailing, although the concentration did not reach C/C_0 =1 after the 3.8 h solute injection time. In the column experiment at 5 times slower velocity, the C/C_0 = 1 concentration appeared to be reached in about 8 h. Neither experiment showed appreciable tailing upon desorption. Both sets of data produced similar apparent K_d's (about 0.80 mL/g) for the sorption and desorption limbs. This small amount of sorption, however, was not completely reversible, as mass loss was observed in the low velocity experiment (3.7 μg of 109 μg injected); loss was suspected in the higher velocity experiment but the mass was at or below our detection limits. The mass loss over time in this case indicates a reaction half-life of 160 to 770 h. This half-life is similar to that observed with the Ocala C4 soil, although the mass loss is significantly smaller. The smaller mass loss could be caused by less transformation sites, which may be related to the type of clay (CEC is 6 times larger for the Ocala C4 although the percent clay is about the same). Efforts to model the breakthrough curve using **Model 1** simulated the overall process fairly well, but underestimated the desorption tailing (Appendix B). Simulations conducted assuming reversible sorption with nonlinear sorption (**model 3**) exhibited additional skewness in the breakthrough curves desorption limb compared to **Model 1** simulations, indicating that slow, reversible sorption with a nonlinear isotherm can account for almost all of the behavior observed.

The Burbank Ap soil was used as a test with properties intermediate to the other soils. Column experiments were conducted at two velocities (Appendix B). At the higher pore water velocity, the two limbs of the breakthrough curve were symmetrical with no measurable mass loss, and hence the sorption and desorption limb calculated k_d values were identical (0.88 and 0.89 mL/g, respectively). Two equilibrium model simulations of this experiment (**model 1** and **3**) showed that the small amount of apparent reversible sorption was predictable, and that use of the nonlinear isotherm increased the desorption tailing of the simulation (Fig. 5-5). The experiment conducted at a much slower velocity (a factor of 5) exhibited greater tailing, and a much poorer fit with the nonlinear isotherm equilibrium model (**model 3**). The sorption and desorption limbs of the breakthrough curve exhibited considerable asymmetry which was reflected in their K_d values (1.20 and 0.49 mL/g, respectively). In addition, there was approximately 11.3 μg TNT mass loss from a total of 110 μg injected.

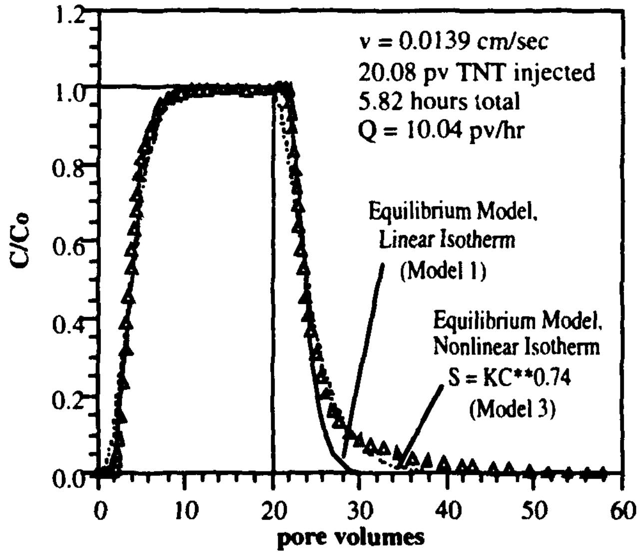


Figure 5-5. TNT breakthrough curve and model fits for the Burbank Ap soil.

In general, TNT transport through these soils exhibited reversible TNT sorption with at least some TNT mass loss suspected in every soil. At the higher pore water velocities, 95% of TNT behavior could be adequately described with reversible nonlinear sorption (**model 3**) and knowledge of the hydrodynamic dispersion in the soil. A small amount of reversible sorption (with little slow desorption) means that most of the TNT mass can be flushed out of the soil in a relatively short time. This fact is observed in the low K_d values calculated from the sorption limb of the breakthrough curve (Table 5-2). These column derived K_d values are somewhat smaller than those calculated from the batch sorption data (within a factor of 4), and may suffer from the same problem as the RDX; that is, the areas under the breakthrough curves are small, making calculation of accurate K_d values difficult. However, the agreement is fairly good between the two techniques except for the Ocala C4 soil. The observed discrepancy in this soil is a direct result of the addition of alumina to the soil in order to achieve reasonable flow characteristics. However, multiplication of the high velocity K_d value by 2 yields a reasonable estimate of what the whole soil would be, and these values agree well with the batch K_d.

Table 5-2. Comparison of the column study determined K_d values from the sorption limb and K_d values[a] calculated from the batch sorption isotherms (a complete compilation of the column study data is presented in Table B-1; Appendix B).

Soil	column studies			Batch studies
	experiment duration (h)	Total mass TNT injected (µg)	K_d (mL/g)	K_d (mL/g)
Norborne C	27	545	1.24	2.69
Westmoreland B1	9.6	236	0.51	2.02
	18	76.8	0.65	2.02
Cloudland C	6.8	167	0.82	1.64
	15	110	0.80	1.64
Ocala C4	21	494	3.10	16.6
	44	235	5.50	16.6
Burbank Ap	5.8	93.2	0.88	2.01
	18	93.8	1.20	2.01

[a] The K_d values for the batch studies were calculated assuming the Freundlich equation ($q = K_fC^{1/n}$) equilibrium concentration (C) was equal to the TNT injection concentration for the column studies (4.35 µg/mL); q was determined and k_d calculated ($K_d = q/C$).

At slower velocities, TNT mass loss was more evident and appeared to impact the K_d values determined from both limbs of the breakthrough curve. The K_d values calculated from the sorption limb at the lower velocities were generally larger than those calculated in the higher velocity experiments; this was probably caused by a slow sorption/transformation reaction as evidenced by the slower approach to $C/C_0 = 1$ (if $C/C_0 = 1$ was attained at all) exhibited at the lower pore water velocities. In addition, the K_d values calculated from the desorption limbs were substantially lower than those calculated from the sorption limb suggesting mass loss.

Taken together, these findings suggest that TNT mass loss is a relatively slow reaction, or is controlled by diffusion into restricted pores; the transformation reaction appears to have a half-life ($t_{1/2}$) of roughly 350 h ($t_{1/2}$ values were calculated based on <100 h column studies and therefore must be considered estimates). In the batch studies, steady-state conditions were reached in a maximum of 4 days (96 h). This apparent discrepancy is probably due to the difference in the soil structure between the two experiments. That is, in the column experiments the soil structure is maintained, but in the batch studies soil structure is probably broken down to some degree making diffusion in and out of small pores (or what used to be small pores) much more rapid.

It is not clear if the transformation products (e.g., 2-ADNT and other isomers) are eluted from the column with a similar retardation factor as TNT or if they are retarded to a slightly greater degree. If the latter is the case, one may expect greater tailing in the desorption limb (as observed in these studies) compared to the case were the products are transported with the TNT or not transported through the soil at all. Because continuous UV/VIS detection used for TNT in this study are absorbance peaks for the pi electrons in the aromatic rings, there would also be absorbance at this wavelength for the transformation products. In addition, if the extinction coefficient for the transformation products are considerably higher than for TNT, the absorbance related to the product could be much greater than TNT despite a lower product concentration. Both of these factors would tend to effect the observed tailing in the desorption limb and the calculation of mass loss. In the present study, however, column effluent was periodically collected and HPLC analysis performed and no evidence of transformation products was observed.

5.3 TNT PULSED COLUMN STUDIES AT DIFFERENT TEMPERATURES

All five soils utilized in the large mass injection TNT column studies yielded breakthrough curves that exhibited, or at least, suggested that TNT was being loss from the system. This phenomenon was also noted during the batch isotherm studies. Therefore, in an attempt to understand this phenomenon more fully, the Norborne C and Cloudland C soil horizons were used in a series of small mass (8.2 μg total TNT) pulsed injection experiments at 25, 45, 65, and 85 ^{0}C. The injections were performed in a serial manner; that is, a pulse of TNT was injected into a column, flushed out, and once $C/C_0 = 0$ was reached another pulse was injected. The actual column residence time of each of these TNT pulses was small (10.5 to 11.9 min). Relative K_d values were calculated from retardation factors determined by the difference between the center of mass of the breakthrough curve, and the center of mass of the injection pulse.

Six pulsed injections were conducted with the Norborne C soil at 25 ^{0}C. As is evidenced by the changes in elution curve shape [area under the elution peak (mass of TNT eluted), peak height, and tailing], TNT mass loss was not constant in these experiments (Figure 5-6a; only 3 injections shown). The mass loss and relative K_d decreased sharply through the first three pulses but then remained fairly constant (Table 5-5). These results suggest that the actual transformation reaction is quite rapid but is limited by transport to "transformation sites" which vary in accessibility. This hypothesis is in agreement with the large mass injection experiments that exhibited greater mass loss in the slower velocity experiments. These results also suggest that transformation is a nonlinear reaction and is influenced by sorption. Because of this a simple first-order mass loss would not be able to account for the mass loss behavior, as it would produce the same amount of mass loss with each injection; this is probably why the attempt to model the Ocala C4 column with a first-order mass loss model failed (Fig. 5-4).

The variations in elution peak characteristics noted above for 25 ^{0}C injections were considerably reduced as temperature is increased (Fig. 5-6b, c, and d; Table 5-5). Both mass loss and relative K_d were low and essentially constant at 45 and 65 ^{0}C, and nonexistent at 85 ^{0}C. These results suggest that sorption is an exothermic process; a similar conclusion was reached in the batch temperature studies for the Norborne C soil. However, both sorption and TNT mass loss decrease concomitantly with increasing temperature in the column experiments, but the batch studies exhibited decreased sorption and increased TNT transformation as temperature increased. The comparison between the batch and column temperature results would appear to be contradictory, but they are not.

The batch sorption studies were conducted over a time frame designed to allow the overall process to attain steady-state conditions regardless of temperature. Since steady-state conditions were obtained, transformation of TNT did not go to completion; that is, the TNT was not totally consumed. Therefore, the transformation sites are suggested to be finite in number and do not regenerate under the conditions of these studies. On the other hand, the column studies were performed under dynamic conditions were the transformation reaction was shown to be a slow process or diffusion controlled. Since residence time was short in the pulsed column experiments, less TNT was transformed with increasing temperature. The results of these two temperature studies and the above conclusions suggest that 1) sorption is required prior to transformation, 2) sorption is an exothermic reaction (for the Norborne soil) and decreases with increasing temperature, 3) transformation is an endothermic process and increases with temperature, 4) there are a limited number of "transformation sites", and 5) these sites are less accessible than the other "sorption sites". Schematically, this hypothesized pathway may be represented as:

$$\mathrm{TNT}_{(aq)} + \mathrm{SOIL} \begin{array}{l} \rightleftharpoons \mathrm{TNT\text{-}SOIL} \\ \\ \rightleftharpoons \mathrm{TNT\text{-}SOIL^{*}} \longrightarrow \text{Transformation products} \end{array} \tag{2}$$

where the SOIL* sorption sites are also the transformation sites but are not regenerated under the conditions of the present study.

Consecutive small mass injections of TNT with Cloudland C soil exhibited less variation in elution peak characteristics than observed with the Norborne C soil at 25 ^{0}C (Fig. 5-7), but exhibited decreased transformation with each consecutive injection which suggests a limited transformation capacity. The relative K_d's for the Cloudland C were significantly less than that observed in the Norborne C soil but, unlike the Norborne C soil, showed a general increase with temperature as did mass loss (Table 5-5). In the batch studies, interestingly, the Cloudland Ap sorption of TNT appeared to be endothermic at low initial concentrations resulting in greater sorption at elevated temperatures. Similarly, the column temperature studies also suggest an endothermic sorption process as well as an endothermic transformation process. These results, although in contrast to those from the Norborne C soil, are in agreement with the proposed sorption-transformation process (Eq. 2).

Table 5-3. Comparison of serial pulsed injection data for the Norborne C and Cloudland C soil horizons at 4 temperatures; contact time and injection mass are 10.5 min and 8.2 µg, respectively.

	Norborne C		Cloudland C	
Temp. (^{0}C)	Mass loss (µg)	Relative K_d (mL/g)	Mass loss (µg)	Relative K_d (mL/g)
25	2.94	1.66	1.58	0.48
25	1.13	1.14	0.97	0.43
25	1.02	1.08	0.87	0.44
25	0.93	0.92	-	-
25	0.99	0.91	-	-
25	0.96	0.80	-	-
45	0.24	0.57	1.39	0.71
45	0.33	0.56	0.41	0.58
45	0.17	0.49	0.12	0.69
65	0.07	0.53	0.94	0.86
65	0.34	0.39	0.76	0.80
65	0.11	0.42	0.47	0.67
85	0.08	0.08	0.94	0.67
85	0.00	0.04	1.00	0.42
85	0.06	0.00	0.94	0.43

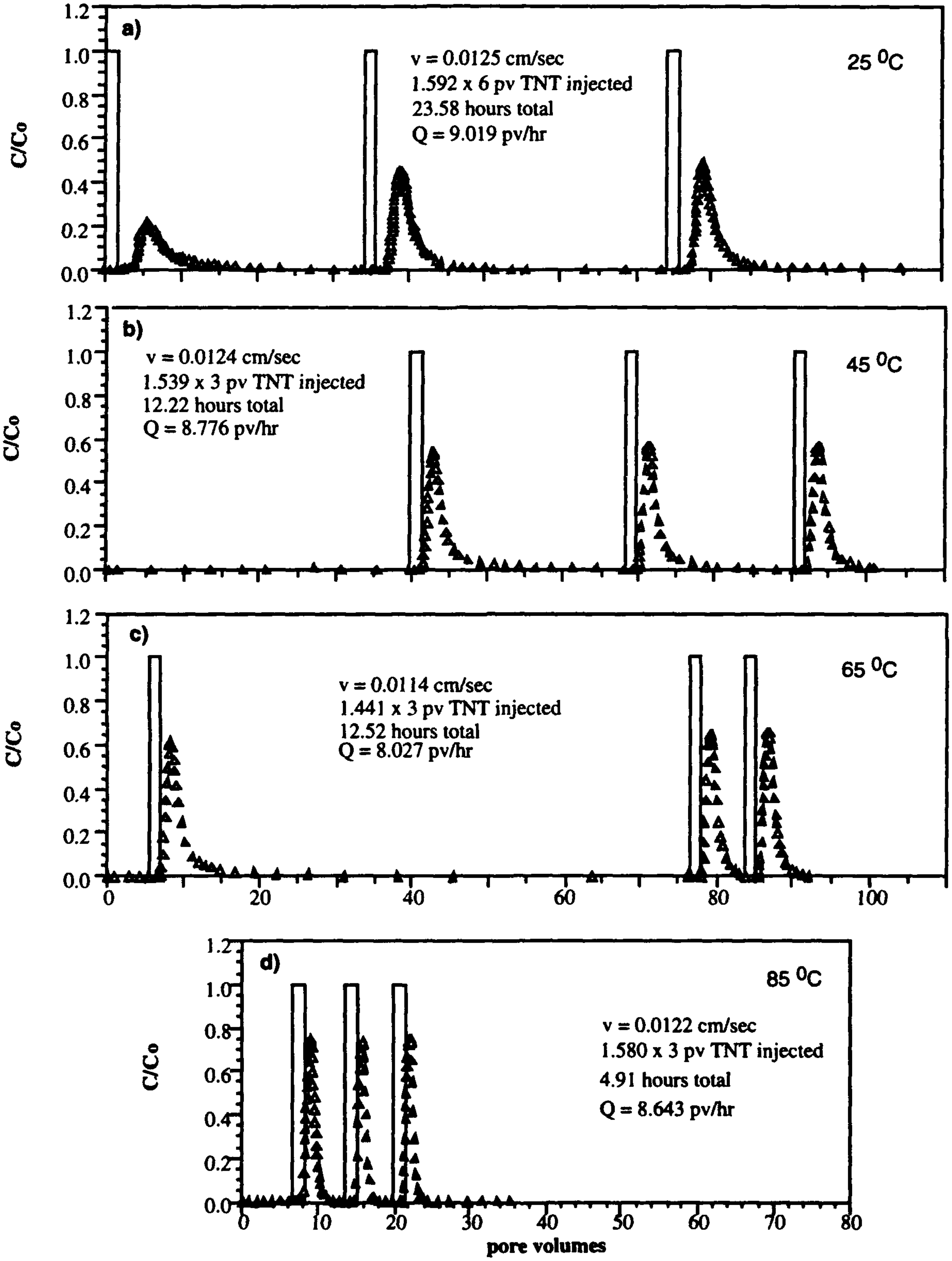


Figure 5-6. TNT/Norborne C soil pulsed column experiments at 4 temperatures.

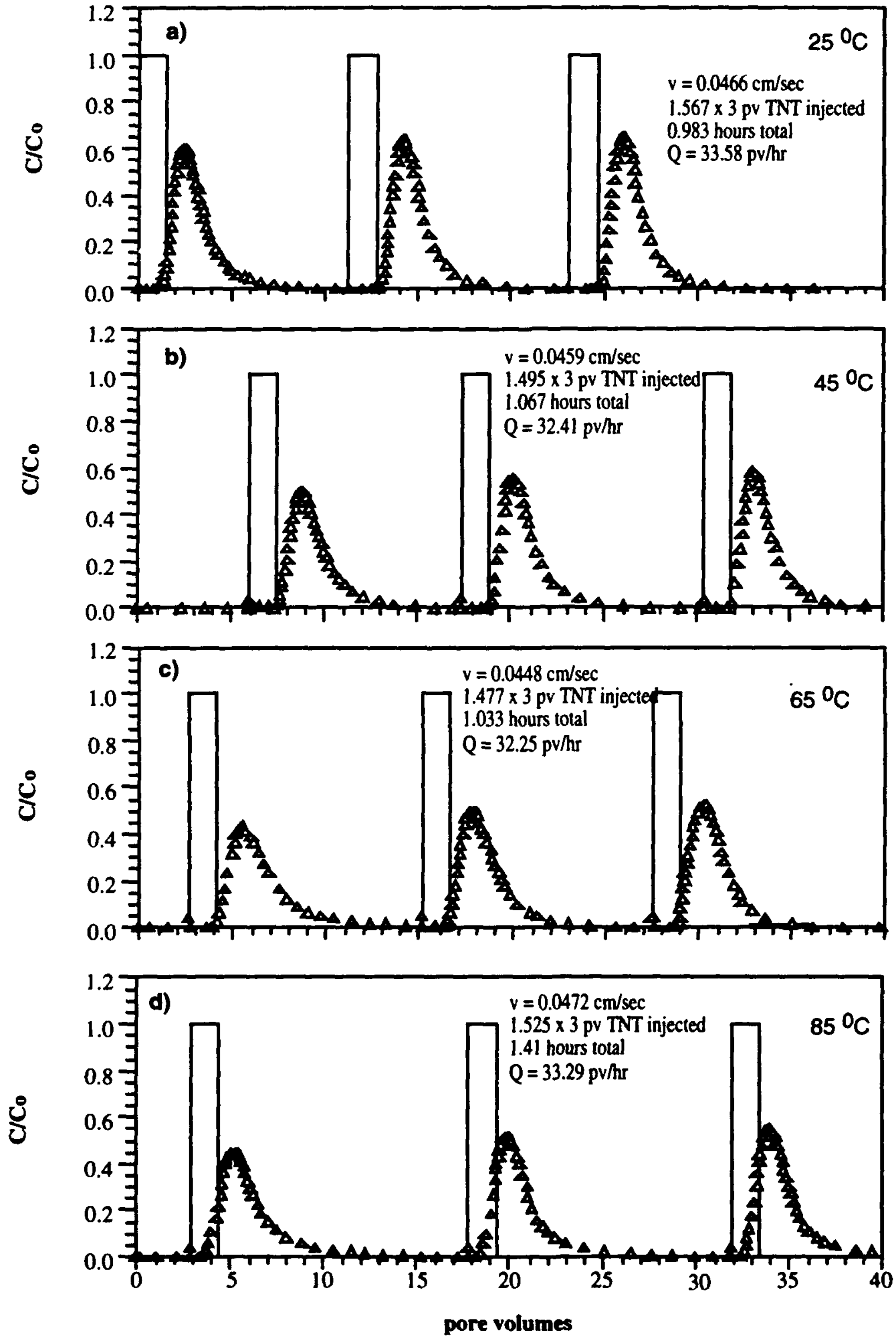


Figure 5-7. TNT/Cloudland C soil pulsed column studies at 4 temperatures.

6.0 SUMMARY AND CONCLUSIONS

6.1 RDX

RDX sorption to the soils used in this study was relatively rapid and low. Sorption steady-state conditions in sterilized soils were obtained in batch studies by about 6 h and remained constant for 24 days. Sorption was described well by either the linear model or the Freundlich model, but model development based on soil chemical-physical properties suggests that the linear model could approximate sorption for all soils used in this study. The K_d values from the linear model were low (typically less than 1); suggesting minimal sorption to soil materials. In addition, sorption was totally reversible with no mass loss noted under the conditions utilized in this study.

Column experiments with RDX and five soils exhibited rapid breakthrough with symmetric sorption and desorption limbs. In all cases, solute breakthrough could be accounted for using a transport model incorporating dispersion and fast, reversible sorption described by a linear isotherm. These findings were in accord with those from the batch sorption studies; that is, fast, reversible sorption described by a linear isotherm. In general, the sorption/desorption limb determined K_d values were similar and very low; in fact, the K_d values calculated from the area under the sorption/desorption limbs of the breakthrough curves were at or near our ability to discern differences between the solute and tracer. However, the K_d values were about the same magnitude as those measured in the batch studies.

The RDX sorption isotherms were fitted to three possible isotherm models; linear, Fruendlich and Langmuir. Both the linear and Fruendlich models produced the smallest MSEs for roughly half the soils each, but three of the soils best described by the Fruendlich model had confidence intervals for 1/n that overlapped 1. Therefore the linear model was fit to all soils to produce a single sorption model based on soil physical-chemical properties. This model was a linear combination of three principle components whose values were dependent on a soils' CEC, pH, clay content, OC, and DCB extractable Fe. Three principle components were used, rather than the soil properties directly, in order to reduce the number of variables from five to two or three, and thereby increase the number of degrees of freedom associated with the error term and decrease the confidence intervals about the parameter estimates. The model developed for RDX estimated the K_d for the soils used in this study to within a factor of 2.25 and most often within a factor of 2 or less.

There is no way to discern the RDX sorption mechanism or the active site or sites of RDX sorption from these studies. However, it is evident from the results of these investigations that RDX sorption is not solely the result of hydrophobic partitioning to the OC phase of these soils. From temperature studies with three soils, RDX sorption appears to be an exothermic process with a substantial isosteric heat of sorption (ΔH_r is about -20 kJ/mol) which is similar to that ascribed to hydrogen bonding or van der Walls forces. In addition, K_d values calculated via carbon-referenced partitioning were variable and poor predictors of actual sorption in both the batch and column studies. Whatever the sites of RDX sorption are, at least a subset of these sites are common to both RDX and TNT as evidenced by the decrease in sorption in the presence of TNT as a cosolute; RDX is suggested to be sorbed less strongly to these sites due to the larger cosolute effect observed for RDX compared to TNT.

6.2 TNT

In batch systems, attainment of steady-state conditions was slower than RDX, but a greater mass of TNT was partitioned to the solid phase. Determination of the solid phase concentration was confounded by the abiotic transformation of TNT to the aminodinitrotoluene isomers and diaminonitrotoluene. However, steady-state aqueous phase TNT concentrations were obtained in the soils in less than 96 h. It is believed that the long equilibration time was related, in part, to the transport of TNT to the transformation active sites, transformation and site reequilibration with aqueous TNT. After the 96 h equilibration, TNT sorption isotherm data were collected by determining the aqueous and solid phase TNT concentrations directly. Sorption data determined in this manner exhibited a curvilinear relationship between the aqueous and solid phase concentrations that was best fit with the Freundlich model. While TNT did sorb more strongly to the solid phase than RDX, its sorption was not great; K_d values calculated for a TNT equilibrium concentration of 4.4 µg/mL were about 3 to 6 times greater than those determined for RDX. Similar to RDX, TNT sorption was totally reversible if transformation was taken into account. The presence of RDX as a cosolute did affect the magnitude of TNT sorption; however, the affect was less than that observed for RDX with TNT as a cosolute. As observed previously, TNT and RDX utilize at least a fraction of the same sorption sites.

TNT column experiments on five different soils exhibited reversible sorption with at least some mass loss occurring in all soils. At higher pore water velocities, the majority (95%) of the transport behavior in the soils could be accounted for by using a reversible nonlinear sorption model and knowledge of the hydrodynamic dispersion. Even at the higher pore water velocities, however, variable degrees of asymmetry between the sorption and desorption limbs of the solute breakthrough curves was observed; that is, the K_d values calculated from the sorption limb were invariably larger than those calculated from the desorption limb. The degree of asymmetry appeared to be dependant on the soil being studied, and suggests either irreversible sorption or mass loss. At the lower pore water velocities, asymmetry increased and mass loss became evident in all soils and was as much as 19% of the total mass injected. Mass loss as great as that observed in the Ocala C4 soil over a 44 h period suggests that abiotic transformation under field conditions (slower pore water velocities) may be a substantial retardation mechanism. In the flow systems used in this study, a half-life estimate of the transformation process was between 80 and 400 h.

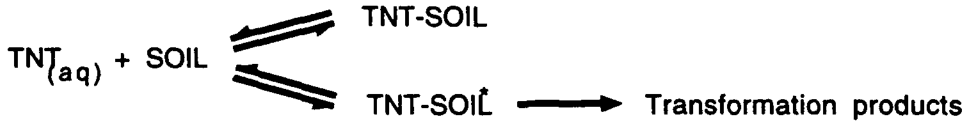
The findings of the column studies were in reasonable agreement with those of the batch studies. K_d values determined from the high pore water velocity experiments were generally in good agreement with those calculated for the batch experiments; however, the column derived values were always smaller than the batch derived K_d's (by up to a factor of 4). The column temperature studies corroborated the batch temperature study findings with regard to the exothermic nature of the sorption process for the Norborne C soil, but also suggested that the sorption process for the Cloudland C soil was endothermic at low concentrations (as was observed in the batch studies). At higher concentrations, sorption to all soils were exothermic, the batch determined isosteric heats of sorption (ΔH_r is about -25 KJ/mol) were slightly higher than those determined for RDX and are within the range ascribed to hydrogen bonding or van der Walls forces.

A TNT sorption model based on soil properties was best represented as a Fruendlich sorption isotherm with the predicted K_{fp} and $1/n_p$ values being a linear combination of pH and CEC, and OC, respectively. The ability to predict the K_f parameter was reasonable in that all of the measured K_f values were predicted to within a factor of 3.5 and most often better than a factor of 2. In addition, predicted values calculated for the soils used in a recent TNT study yielded very reasonable comparisons to the published K_f values (Pennington and Patrick 1990). With the exception of one soil, all predicted K_f values were within about a factor of 2.5 of those listed by Pennington and Patrick (1990), and for all but three of the soils the predicted value was within a factor of two. The 1/n values varied over a greater range than one would hope, but still reasonable considering the calculated value is only dependent on OC; for soils with OC greater than the range of soils used in the model development, 1/n values >1 should be expected. In these cases it would be preferable to use the average 1/n value of the soils reported here for model development.

6.3 TNT TRANSFORMATION

TNT undergoes a reduction of one or more of the NO_2- moieties (to NH_2) when in contact with soil. All the soils used in this study exhibited the capability of reducing TNT to 2ADNT, 4ADNT or 2,4-DANT, although the capacity to mediate this reaction is soil dependent. It would appear that the slow step in this process is diffusional in nature since greater TNT mass loss occurred at lower pore water velocities in the column studies. In the batch studies conducted at 25 ^{0}C, steady-state aqueous TNT conditions were reached in 72 to 96 h with TNT mass loss confined to this time frame; at higher temperatures, however, greater mass loss was observed. This suggests that the transformation process is an endothermic process.

The findings of the present study suggests that sorption is required prior to the transformation of TNT. It is unknown at this time what soil constituent(s) is acting as the electron donor for this reaction. It appears that only a subset of the "TNT sorption sites" are active in the transformation of TNT. A paradigm of this process may be viewed as:



$$\mathrm{TNT}_{(aq)} + \mathrm{SOIL} \begin{array}{l} \rightleftharpoons \mathrm{TNT\text{-}SOIL} \\ \rightleftharpoons \mathrm{TNT\text{-}SOIL}^{*} \longrightarrow \text{Transformation products} \end{array} \qquad (1)$$

where the SOIL^* sorption sites are also the transformation sites but are not regenerated under the conditions of the present study.

It is a common generalization that organic matter is a strong reducing agent and that organic matter will complex and reduce metals, which in turn can reduce organic pollutants (Macalady et al. 1986; Stevenson 1982). It has been well documented that under anaerobic conditions and reducing environments that Fe porphyrins and quinones can reduce nitroaromatic compounds to the amine product (Scharzenbach et al. 1990; Macalady et al. 1986; Tratnyek and Macalady 1989). These types of compounds are known to be structurally part of a soils OC (Stevenson 1982); porphyrins found in the soil are believed to be derived from plant chlorophyll as a result of microbial degradation. It is interesting that the distribution of these chlorophyll derivatives are soil type dependent (Stevenson 1982). These compounds have reduced Fe (or other transition metal) centers which can act as electron donors. It is these compounds that we speculate to be active in TNT abiotic transformation. While all of the present studies were conducted under aerobic conditions, reduced metal porphyrins could still be present and active; but under these conditions, once oxidized they would not be regenerated as they might under more anoxic conditions.

6.4 RESEARCH NEEDS

The present research was directed at developing predictive sorption models for TNT and RDX based on soil physical-chemical properties in the absence of biotic and abiotic reactions. While we believe that the predictive models developed from these investigation are reasonable and useful over a wide range of soils and subsurface materials, the results do point to the several areas that are believed to be important in understanding the fate and transport of RDX and TNT. Among these areas are: 1) the aerobic biological breakdown of RDX to presumably CO_2 by the Cloudland Ap soil (section 3.1.1), and 2) greater understanding of the cosolute effect observed for both TNT and RDX (section 3.2.2). Primary among these areas, however, is the abiotic transformation of TNT. As illustrated by the column study results, the abiotic transformation of TNT may be an important pathway in its fate in the natural environment due to the fact that pore water velocities in many soils and subsurface systems will be slower than those used in the current studies, which would most likely result in a greater percentage of TNT mass loss via this pathway.

It is our belief that an understanding of the transformation process would yield a better capability in determining the fate, transport, and ultimately health implications of TNT released to the environment. Information is needed to better define 1) the constituents in soils that actively take part in TNT transformation, 2) the mechanism of the transformation process, and 3) kinetic information concerning rates of transformation, limiting conditions, and rate limiting steps. This information could conceivably be incorporated into current models, and hence better describe abiotic fate of TNT. In addition, a detailed study on the interaction of biotic and abiotic reactions impacting TNT fate and transport would allow a more compete description of TNT fate. Data necessary to address these needs may be obtained via a series of detailed investigations using both whole soils and isolated constituents in both batch and column studies in combination with spectroscopic measurements designed to interrogate surface-solute interactions. These studies, in combination with microbiological experimentation, could delineate a more complete understanding of the fate and transport of TNT.

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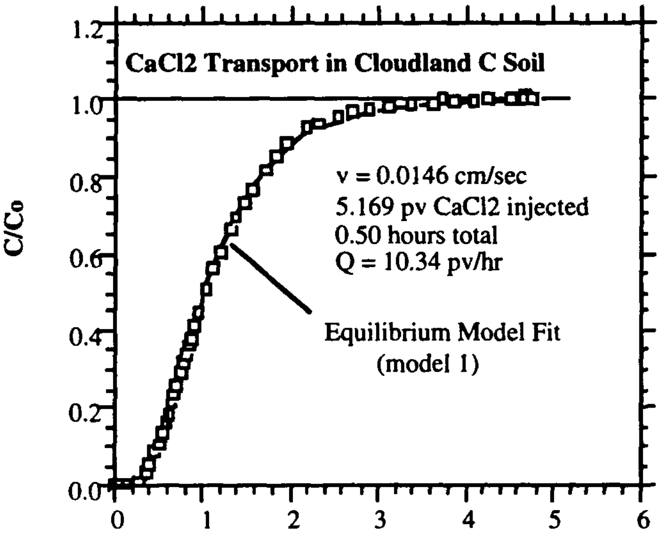
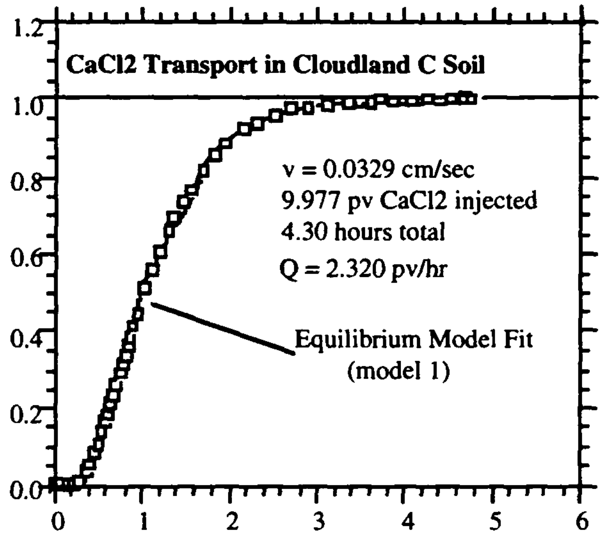
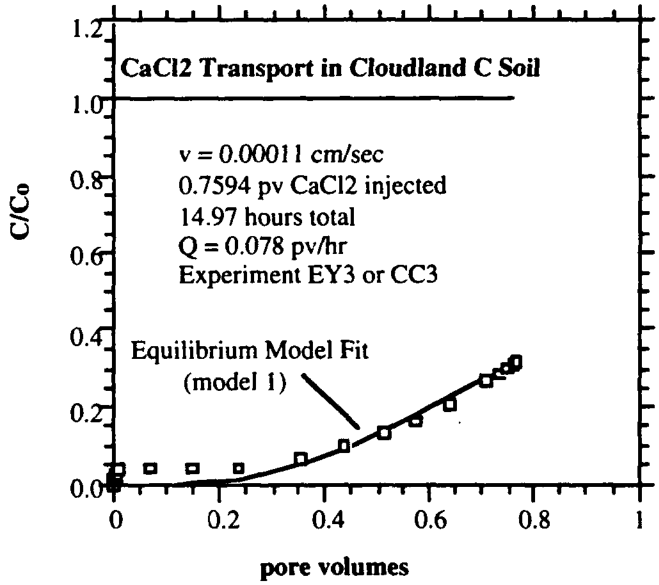
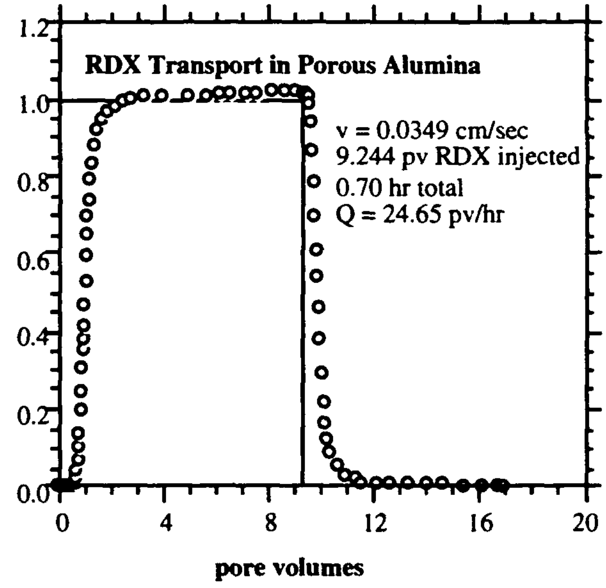
APPENDIX A

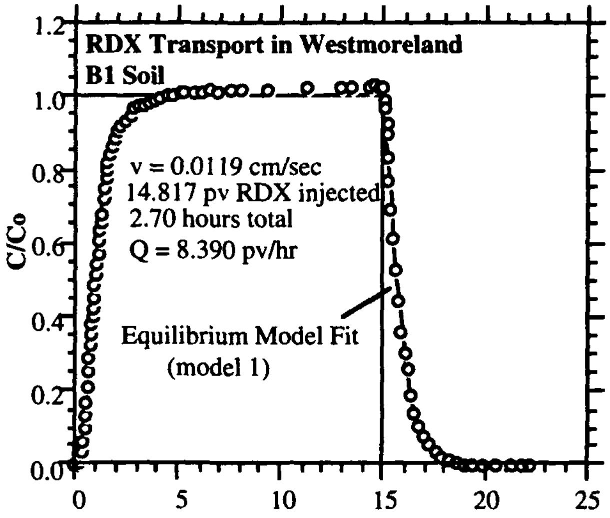
The tracer studies with $CaCl_2$ on the Cloudland C soil and the RDX breakthrough curves for the individual soil columns [Norborne C (3), Westmoreland B1 (2), Ocala C4 (2; with alumina), Cloudland C (2) and the Burbank Ap (2) soil horizons] are presented. The breakthrough curves for these soils, at a pore water velocity of 0.012 cm/sec, are depicted as a group in figure 5-1. All RDX breakthrough curves were conducted using a 4.18 µg/mL aqueous RDX solution. In addition, the RDX breakthrough curve for the alumina that was used with the Ocala C4 soil to obtain reasonable flow rates is also presented. The physical and flow parameters for each of the RDX column experiments are presented in Table A-1.

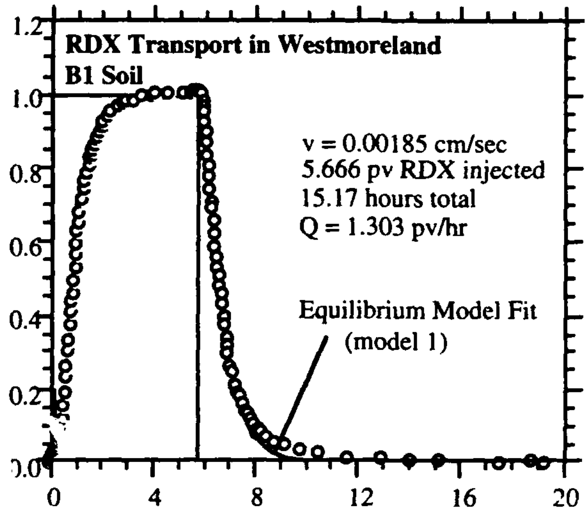

CaCl2 Transport in Cloudland C Soil
v = 0.0146 cm/sec
5.169 pv CaCl2 injected
0.50 hours total
Q = 10.34 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6

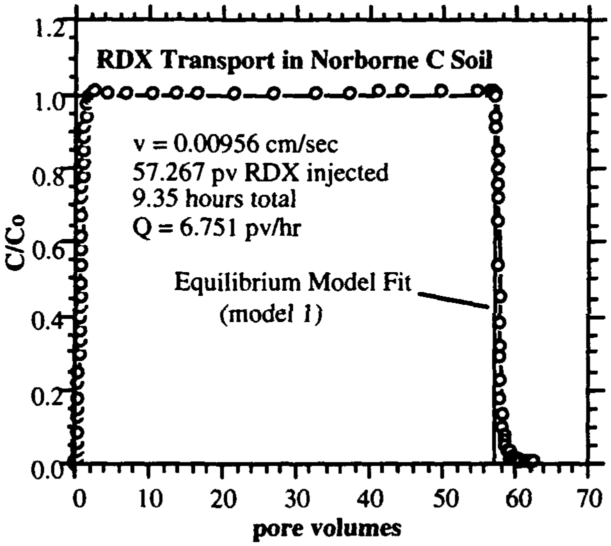

CaCl2 Transport in Cloudland C Soil
v = 0.0329 cm/sec
9.977 pv CaCl2 injected
4.30 hours total
Q = 2.320 pv/hr
Equilibrium Model Fit
(model 1)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6

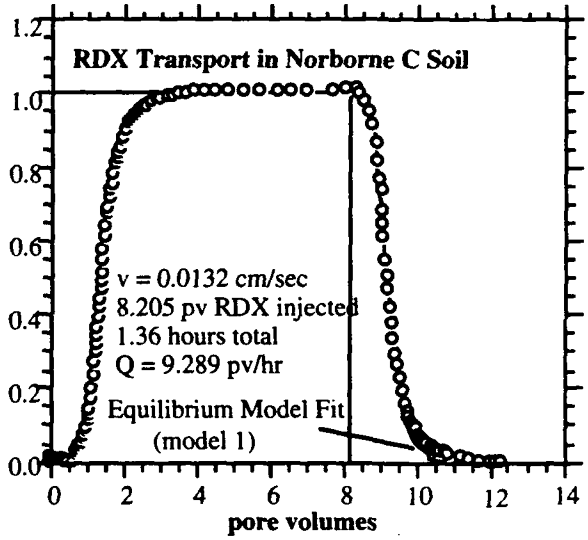

CaCl2 Transport in Cloudland C Soil
v = 0.00011 cm/sec
0.7594 pv CaCl2 injected
14.97 hours total
Q = 0.078 pv/hr
Experiment EY3 or CC3
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1
pore volumes

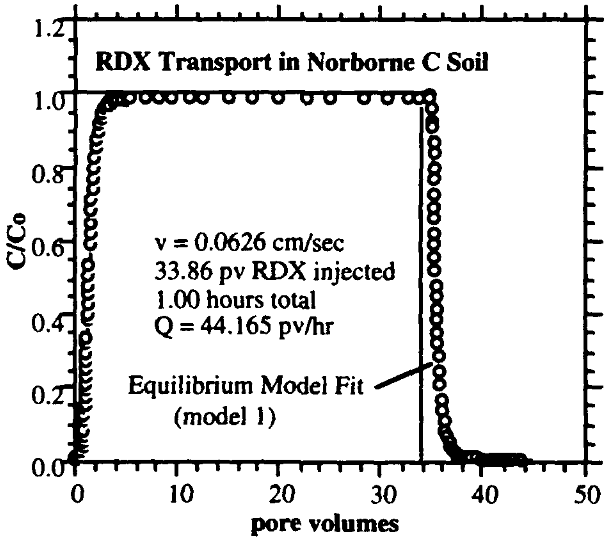

RDX Transport in Porous Alumina
v = 0.0349 cm/sec
9.244 pv RDX injected
0.70 hr total
Q = 24.65 pv/hr
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
4
8
12
16
20
pore volumes

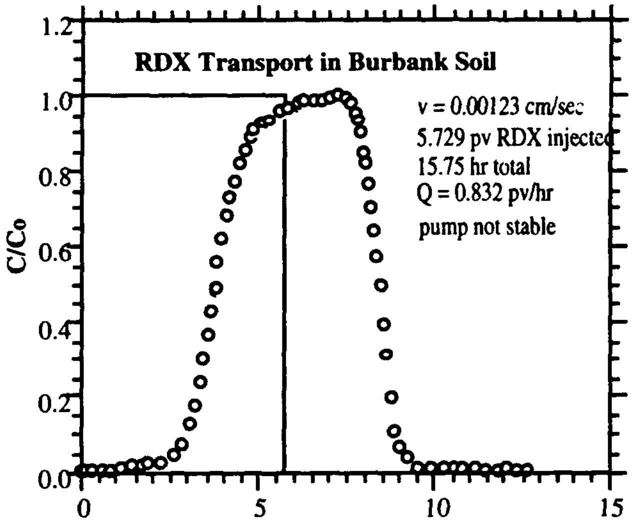

RDX Transport in Westmoreland B1 Soil
v = 0.0119 cm/sec
14.817 pv RDX injected
2.70 hours total
Q = 8.390 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
5
10
15
20
25

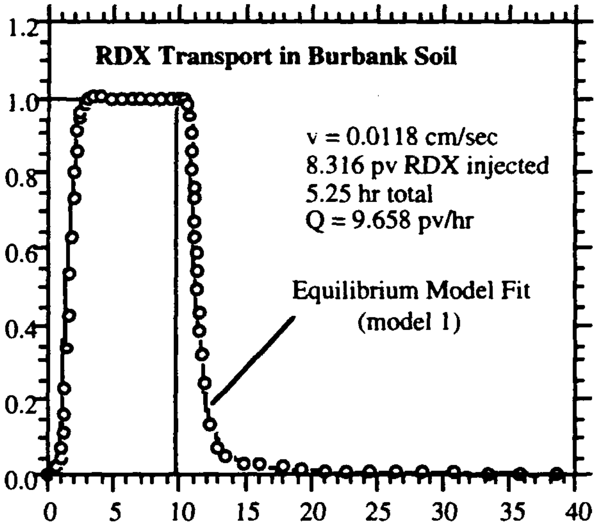

RDX Transport in Westmoreland B1 Soil
v = 0.00185 cm/sec
5.666 pv RDX injected
15.17 hours total
Q = 1.303 pv/hr
Equilibrium Model Fit
(model 1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
4
8
12
16
20

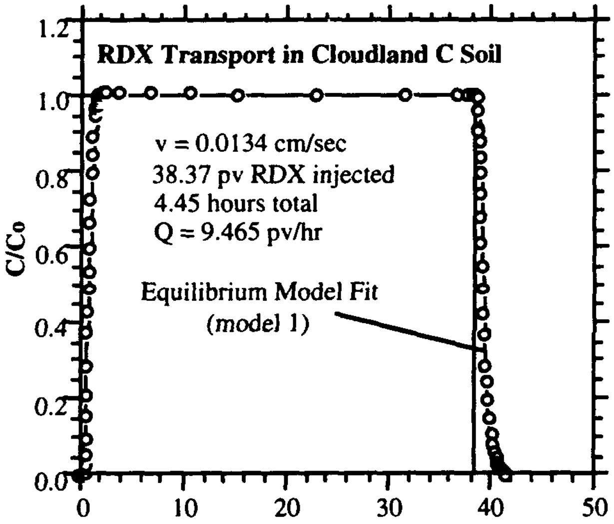

RDX Transport in Norborne C Soil
v = 0.00956 cm/sec
57.267 pv RDX injected
9.35 hours total
Q = 6.751 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
10
20
30
40
50
60
70
pore volumes

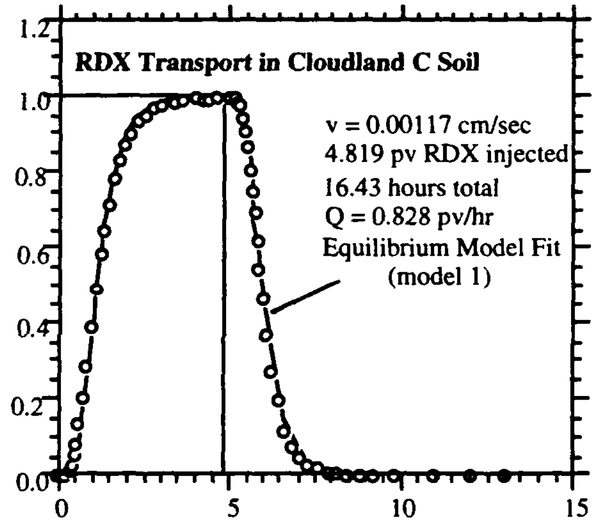

RDX Transport in Norborne C Soil
v = 0.0132 cm/sec
8.205 pv RDX injected
1.36 hours total
Q = 9.289 pv/hr
Equilibrium Model Fit
(model 1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
2
4
6
8
10
12
14
pore volumes

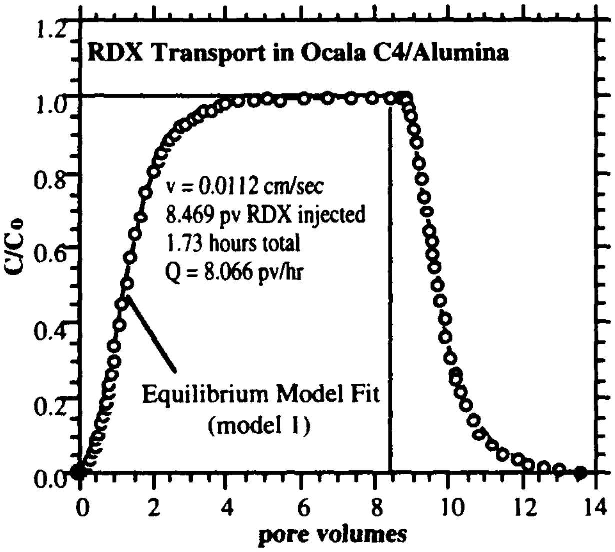

RDX Transport in Norborne C Soil
v = 0.0626 cm/sec
33.86 pv RDX injected
1.00 hours total
Q = 44.165 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
10
20
30
40
50
pore volumes


RDX Transport in Burbank Soil
v = 0.00123 cm/sec
5.729 pv RDX injecte
15.75 hr total
Q = 0.832 pv/hr
pump not stable
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15


RDX Transport in Burbank Soil
v = 0.0118 cm/sec
8.316 pv RDX injected
5.25 hr total
Q = 9.658 pv/hr
Equilibrium Model Fit
(model 1)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40


RDX Transport in Cloudland C Soil
v = 0.0134 cm/sec
38.37 pv RDX injected
4.45 hours total
Q = 9.465 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50


RDX Transport in Cloudland C Soil
v = 0.00117 cm/sec
4.819 pv RDX injected
16.43 hours total
Q = 0.828 pv/hr
Equilibrium Model Fit
(model 1)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15


RDX Transport in Ocala C4/Alumina
v = 0.0112 cm/sec
8.469 pv RDX injected
1.73 hours total
Q = 8.066 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
pore volumes

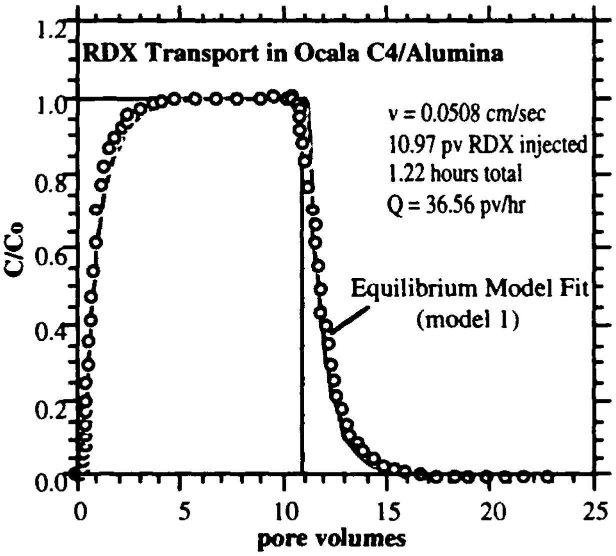

RDX Transport in Ocala C4/Alumina
v = 0.0508 cm/sec
10.97 pv RDX injected
1.22 hours total
Q = 36.56 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
pore volumes

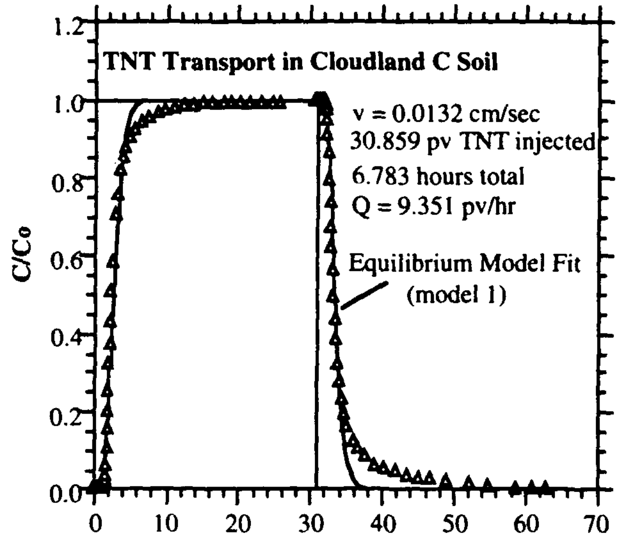
Table A-1. Flow and physical properties of soil columns used in RDX large mass injection studies.

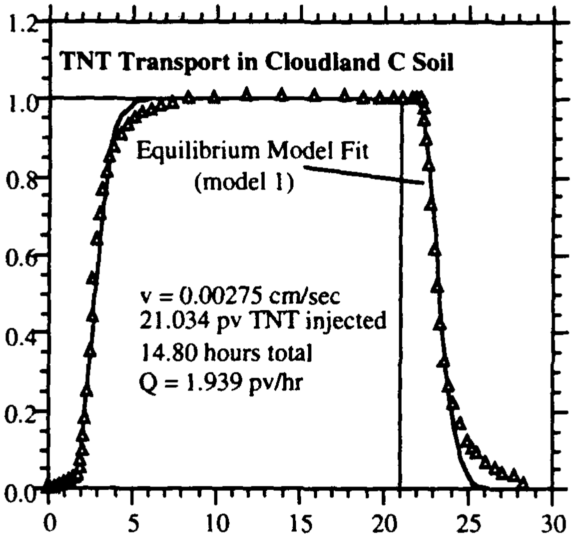
soil	initial conc (mg/L)	final conc (mg/L)	column area (cm2)	column length (cm)	column volume (cm3)	total porosity	bulk density (g/cm3)	Q (cm3/s)	Q (pv/hr)	average velocity (cm/s)
Norborne C	0.0	4.185	0.5027	5.1	2.56377	0.477	1.271	2.29E-03	6.751	9.56E-03
Norborne C	0.0	4.185	0.5027	5.1	2.56377	0.477	1.271	3.15E-03	9.289	1.32E-02
Norborne C	0.0	4.185	0.5027	5.1	2.56377	0.477	1.271	1.50E-02	44.165	6.26E-02
Westmoreland B1	0.0	4.185	0.5027	5.1	2.56377	0.481	1.172	2.87E-03	8.390	1.19E-02
Westmoreland B1	0.0	4.185	0.5027	5.1	2.56377	0.481	1.172	4.46E-04	1.303	1.85E-03
Ocala C4 + alumina	0.0	4.185	0.5027	5.0	2.5135	0.524	1.093	2.95E-03	8.066	1.12E-02
Ocala C4 + alumina	0.0	4.185	0.5027	5.0	2.5135	0.524	1.093	1.34E-02	36.558	5.08E-02
alumina	0.0	4.185	0.5027	5.1	2.56377	0.623	0.920	1.09E-02	24.651	3.49E-02
Cloudland C	0.0	4.185	0.5027	5.1	2.56377	0.467	1.165	3.15E-03	9.465	1.34E-02
Cloudland C	0.0	4.185	0.5027	5.1	2.56377	0.467	1.165	2.75E-04	0.828	1.17E-03
Burbank	0.0	4.185	0.5027	5.3	2.66431	0.363	1.355	2.16E-03	8.048	1.18E-02
Burbank	0.0	4.185	0.5027	5.3	2.66431	0.363	1.355	2.24E-04	0.832	1.23E-03

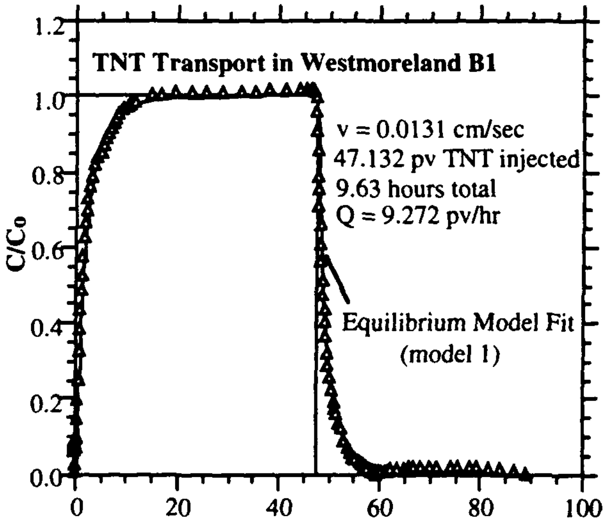
soil	pore volume (cm3)	solute inject (hr)	solute inject (pv)	solute inject (ug)	total inject (hr)	total inject (pv)	Rf sorption (pv)	Kd sorption (cm3/g)	Rf desorption (pv)	Kd desorption (cm3/g)
Norborne C	1.222	8.483	57.27	292.9	9.35	63.117	0.897	-0.039	0.597	-0.151
Norborne C	1.222	0.883	8.205	41.97	1.36	12.617	1.460	0.172	1.099	0.037
Norborne C	1.222	0.767	33.86	173.2	1.00	44.160	1.610	0.229	1.741	0.278
Westmoreland B1	1.232	1.766	14.82	76.41	2.70	22.654	1.132	0.054	1.014	0.006
Westmoreland B1	1.232	4.350	5.666	29.22	15.17	19.754	0.984	-0.007	1.178	0.073
Ocala C4 + alumina	1.316	1.050	8.469	46.65	1.73	13.981	1.519	0.249	1.476	0.228
Ocala C4 + alumina	1.316	0.300	10.97	60.41	1.22	44.479	0.945	-0.026	1.044	0.021
alumina	1.596	0.375	9.244	61.75	0.70	17.256	1.008	0.005	0.992	-0.005
Cloudland C	1.196	4.054	38.37	192.1	4.45	42.118	1.044	0.017	1.008	0.003
Cloudland C	1.196	5.817	4.819	24.13	16.43	13.615	1.302	0.121	1.214	0.086
Burbank	0.967	1.200	9.658	39.07	5.25	42.254	1.604	0.162	1.014	0.004
Burbank	0.967	6.883	5.729	23.18	15.75	13.110	2.837	0.492	2.651	0.442

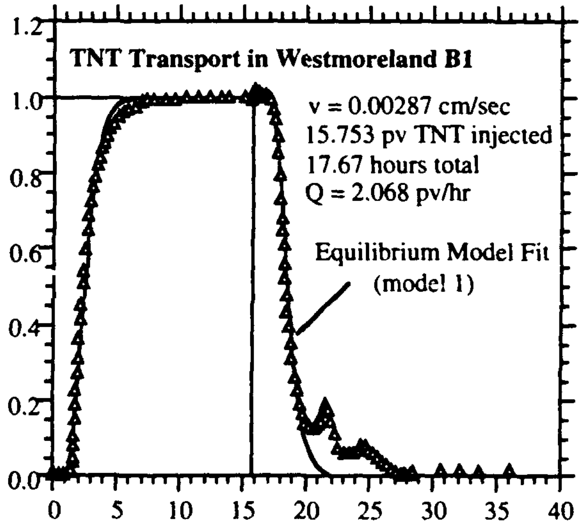
APPENDIX B

The figures presented here are the breakthrough curves of individual TNT column studies for the Westmoreland B1, Cloudland C and Burbank Ap soil horizons not shown in section 5.2. In addition, the physical and flow parameters for the TNT large mass injection column experiments performed in this study are presented in Table B-1.


TNT Transport in Cloudland C Soil
v = 0.0132 cm/sec
30.859 pv TNT injected
6.783 hours total
Q = 9.351 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70


TNT Transport in Cloudland C Soil
Equilibrium Model Fit
(model 1)
v = 0.00275 cm/sec
21.034 pv TNT injected
14.80 hours total
Q = 1.939 pv/hr
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30


TNT Transport in Westmoreland B1
v = 0.0131 cm/sec
47.132 pv TNT injected
9.63 hours total
Q = 9.272 pv/hr
Equilibrium Model Fit
(model 1)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100


TNT Transport in Westmoreland B1
v = 0.00287 cm/sec
15.753 pv TNT injected
17.67 hours total
Q = 2.068 pv/hr
Equilibrium Model Fit
(model 1)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40

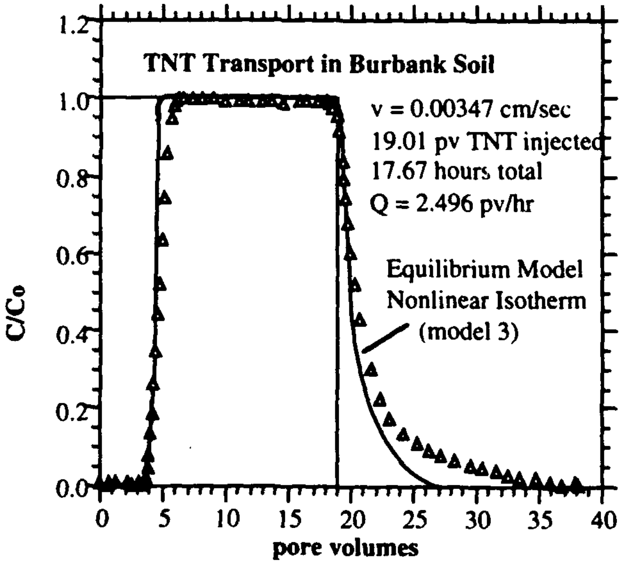

TNT Transport in Burbank Soil
v = 0.00347 cm/sec
19.01 pv TNT injected
17.67 hours total
Q = 2.496 pv/hr
Equilibrium Model
Nonlinear Isotherm
(model 3)
C/Co
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40
pore volumes

Table B-1. Flow and physical properties of soil columns used in TNT large mass injection studies.

soil	initial *conc* (mg/L)	final *conc* (mg/L)	column *area* (cm2)	column *length* (cm)	column volume (cm3)	total porosity	bulk density (g/cm3)	Q (cm3/s)	Q (pv/hr)	average velocity (cm/s)
Norborne C	0.0	4.350	0.5027	5.0	2.5135	0.510	1.319	1.44E-03	4.038	5.61E-03
Norborne C	0.0	4.350	0.5027	5.0	2.5135	0.471	1.283	2.97E-03	9.019	1.25E-02
Westmoreland B1	0.0	4.350	0.5027	5.1	2.56377	0.449	1.260	2.97E-03	9.272	1.31E-02
Westmoreland B1	0.0	4.350	0.5027	5.0	2.5135	0.446	1.302	6.44E-04	2.068	2.87E-03
Ocala C4 + alumina	0.0	4.350	0.5027	5.0	2.5135	0.524	1.093	3.01E-03	8.239	1.14E-02
Ocala C4 + alumina	0.0	4.350	0.5027	5.0	2.5135	0.531	1.067	6.31E-04	1.703	2.37E-03
Cloudland C	0.0	4.350	0.5027	5.1	2.56377	0.486	1.296	3.23E-03	9.351	1.32E-02
Cloudland C	0.0	4.350	0.5027	5.1	2.56377	0.470	1.170	6.49E-04	1.939	2.75E-03
Burbank	0.0	4.350	0.5027	5.0	2.5135	0.425	1.394	2.98E-03	10.041	1.39E-02
Burbank	0.0	4.350	0.5027	5.0	2.5135	0.451	1.373	7.86E-04	2.496	3.47E-03

soil	pore volume (cm3)	solute inject (hr)	solute inject (pv)	solute inject (ug)	total inject (hr)	total inject (pv)	Rf sorption (pv)	Kd sorption (cm3/g)	Rf desorption (pv)	Kd desorption (cm3/g)
Norborne C	1.282	24.42	98.59	549.6	27.47	110.907	4.211	1.241	1.265	0.102
Norborne C	1.184	1.06	9.552	49.18	23.58	212.690	--	--	--	--
Westmoreland B1	1.152	5.08	47.13	236.2	9.63	89.316	2.526	0.514	2.337	0.477
Westmoreland B1	1.121	7.62	15.75	76.80	17.67	36.538	2.895	0.649	3.309	0.791**
Ocala C4 + alumina	1.316	10.46	86.21	493.5	20.88	172.026	7.367	3.104*	5.416	2.115*
Ocala C4 + alumina	1.334	23.78	40.50	235.1	44.22	75.296	12.152	5.549*	4.362	1.673*
Cloudland C	1.245	3.30	30.86	167.2	6.78	63.431	3.193	0.822*	3.393	0.897*
Cloudland C	1.206	10.85	21.03	110.3	14.80	28.692	2.982	0.797	2.564	0.629
Burbank	1.067	2.00	20.08	93.21	5.82	58.405	3.902	0.884	3.933	0.893
Burbank	1.134	7.62	19.01	93.75	17.67	44.097	4.787	1.244	2.495	0.491

* Values are estimated because breakthrough did not reach 100%.

** Fe precipitate interfered with UV/VIS effluent detection.

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