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SLOW RELEASE OF PCB, TNT, AND RDX FROM SOILS AND SEDIMENTS

by

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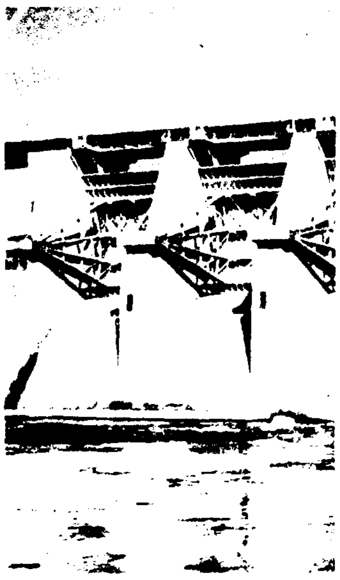

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One of the contaminant/soil interactions that can profoundly affect contaminant mobility and biodegradation is slow adsorption/desorption into soil and sediment micropores or the interior of stable aggregates. This process results in contaminants becoming less mobile over the short term, but allows the soil or sediment to serve as a long-term, slow-release source of the contaminant. This phenomenon greatly complicates the prediction of leaching and microbial degradation rates.

This study explored the adsorption/desorption of PCB, TNT, and RDX onto activated carbon and soils over time and the implications for contaminant mobility. Presented herein is an evaluation of the mechanisms, kinetics, and effects of slow adsorption/desorption on contaminant mobility in soils, sediments, and activated carbon. Algorithms for describing the magnitude and rate of slow adsorption/desorption have also been evaluated.

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Sorption of PCB, TNT, and RDX onto activated carbon resulted in the expected rapid adsorption. However, the kinetics of PCB, TNT, and RDX movement into soils proved to be complex.

Sorption results for PCB in soils were consistent with rapid initial adsorption onto all available adsorption sites. However, the Rathbun extracted soil, from which most organic matter had been removed, showed a steady concentration increase in pore water PCB over time. Therefore, instead of slow movement of PCB into pore spaces, movement into the aqueous phase was noted. The extraction process may have altered the adsorption sites, resulting in release of PCB into pore water, or competitive adsorption by an unidentified compound that migrated gradually from the interior of the soil pores may have occurred.

TNT results are consistent with slow kinetic adsorption from day 30 to day 270. On day 1, TNT was not in the pore water, perhaps because rapid adsorption had occurred. TNT may have sorbed to globules, micelles, lamella, or some other structure that loosely binds TNT. Then, between day 1 and day 30, disintegration of these structures released part of the TNT back into the pore water where readsorption occurred. Competitive adsorption, a process whereby some other species adsorbed between day 1 and day 30, forcing part of the adsorbed TNT into solution, may also have occurred. Abiotic transformation of the TNT to another, more soluble form, that was released at day 30, then slowly readsorbed by the soils, is another possibility.

Desorption of TNT and RDX over time was complex, but was also consistent with field observations on the relative mobility of TNT and RDX, i.e., RDX is more mobile than TNT. Desorption data for water and acetone showed that RDX remained mobile longer than TNT. By day 180, TNT did not desorb in either water or acetone, while RDX was still extractable at day 180. RDX would, therefore, be mobile longer and potentially migrate further in the soil.

Development of an algorithm to describe slow adsorption/desorption of PCB, TNT, and RDX was difficult because of the complexity of the processes and kinetics affecting soil/contaminant interactions. In the approach employed to describe slow release, the amount of PCB, TNT, or RDX that was unavailable for extraction should have increased as time of exposure to the sediment increased. However, the desorption isotherm data showed that the amount of TNT and RDX resistant to desorption did not increase in a predictable manner over the course of the study. The desorption isotherm data and pore water adsorption data for PCB and TNT were inconsistent with homogeneous surface diffusion models for most soils. For these reasons, film and surface diffusion coefficients were not identified from the internal diffusion algorithm. Additional research is needed to characterize the complicated process(es) that resulted in complex isotherms and nonideal incorporation of contaminants into soil phases that were resistant to extraction.

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Adsorption
Desorption
Fractionation
Internal diffusion
PCB
RDX
TNT

PREFACE

The work reported herein was funded by the Discretionary Research Program of the U.S. Army Engineer Waterways Experiment Station (WES).

This report was prepared by Drs. James M. Brannon and Judith C. Pennington, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL) WES; Mr. Tommy E. Myers, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL; Ms. Charolett Hayes, AScI Corporation; and Dr. Donald Dean Adrian, Louisiana State University, Baton Rouge, LA. Analytical support was provided by Mses. Karen F. Myers and Erika F. McCormick, Environmental Chemistry Branch, EED, EL. Ms. Mary K. Vincent, Chief, Office of Technical Programs and Plans, WES, is Manager of the Discretionary Research Program.

The work was conducted at WES under the direct supervision of Dr. Richard E. Price, Acting Chief, EPEB, and Mr. Norman R. Francingues, Jr., Chief, ERB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED, Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Director, EL.

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CONTENTS

SLOW RELEASE OF PCB, TNT, AND RDX FROM SOILS AND SEDIMENTS

PART I: INTRODUCTION

Background

Interactions with soils and sediments are complex and exert a strong influence on the mobility and fate of contaminants in the environment (soils and aquifers). One contaminant/soil interaction that can profoundly affect contaminant mobility and biodegradation is slow adsorption/desorption into soil and sediment micropores or the interior of stable aggregates. Slow desorption was discovered due to the presence of "bound," unrecoverable residues of contaminants in soils. Extensive extraction procedures (Khan 1982, Steinberg et al. 1987, Pennington 1990, Pignatello 1991, Smith et al. 1988, Graveel et al. 1985) are ineffective for removal of such residues. In addition to diffusing into micropores or the interior of stable soil aggregates, contaminants also move into the soil by means of intrasorbent diffusion (Brusseau and Rao, 1989a,b; Brusseau et al. 1991). Intrasorbent diffusion is movement into mineral particles or into organic matter (Brusseau and Rao 1989a,b), depending upon which type of sorption sites are dominating. Intra-organic matter diffusion is the diffusion controlled adsorption/desorption mechanism responsible for extended adsorption times and slow desorption of hydrophobic organic chemicals (Brusseau and Rao 1989a,b; Brusseau et al. 1991).

Mineral surfaces may be important long-term sinks for militarily important compounds such as trinitrotoluene (TNT) and hexahydro 1,3,5-trinitro 1,3,5-triazine (RDX) because of their slightly polar nature and the influence of the soil mineral phase (Pennington and Patrick 1990, Koskinen and Harper 1990). The movement of contaminant into intraparticle pore spaces fundamentally alters the fate of a contaminant, reducing accessibility to convective transport and possibly protecting it from microbial degradation (Smith et al. 1988).

Adsorption into intraparticle pore spaces often results in contaminants becoming less mobile over the short-term, but allows the soil or sediment to serve as a long-term, slow release, source of the contaminant. This phenomenon greatly complicates prediction of leaching and microbial degradation rates. Pore spaces may be too small to allow bacteria access to the contaminant, a necessary condition for microbial degradation to occur. Evaluation of contaminant concentrations in soils during leaching or degradation studies is also complicated because the contaminant may be resistant to extraction by organic solvents used to prepare samples for chemical analysis. Studies requiring incorporation of added contaminants into sediment are also compromised because of uncertainty regarding the time required for full incorporation.

Objectives

This study explored the adsorption and desorption of PCB, TNT, and RDX onto activated carbon, soils, and sediments over time and the implications for contaminant mobility. Specific objectives of this study were:

a. To evaluate the mechanisms, kinetics, and affects of slow adsorption/desorption on contaminant mobility in soils, sediments, and activated carbon.

b. To evaluate algorithms for describing the magnitude and rate of slow adsorption/desorption of PCB, TNT, and RDX by soils.

PART II: SORPTION THEORY

Basic Concepts

Adsorption/desorption

Adsorption has long been used to remove contaminants from a liquid or a gas by attaching the contaminant to a solid. For example, drinking water that contains small concentrations of undesirable industrial organic chemicals may be filtered through activated carbon to remove the chemicals. Adsorption processes are categorized as reversible and irreversible, according to the degree of binding between the adsorbed species and the adsorbing solid. For reversible adsorption, the adsorbing species will attach to the solid when the contaminant concentration in the liquid is high; however, when the contaminant concentration in the liquid is low, the adsorbed species will desorb, or leave the solid, to redissolve in the liquid. Irreversible adsorption describes attachment that is so firm that the contaminant is not easily removed from the solid phase. Many chemicals that are irreversibly adsorbed in an aqueous system may be desorbed by application of certain solvents or heat.

Adsorption of a chemical species on a solid may occur rapidly or slowly. This has led to the term "instantaneous equilibrium" to describe the extreme manifestation of rapid adsorption. Instantaneous equilibrium is an ideal that is never fully achieved in practice. However, the concept has received wide application in groundwater modeling and waste treatment. If the liquid phase is moving slowly past the solid phase, equilibrium may be achieved in the time scale of the flow, and the instantaneous equilibrium concept can be applied. Kinetic models of sorption are needed to describe adsorption that is slow compared to the flow regime. The process of desorption has received less attention than the process of adsorption, but the concepts of instantaneous equilibrium and dynamic or kinetic desorption are also applicable to desorption.

Experimental evidence points to the existence of an equilibrium state between each concentration of a contaminant in a liquid and the amount of the contaminant adsorbed on a unit mass of the solid. When a series of similar equilibrium measurements are made under constant temperature conditions for different concentrations in the liquid, the resulting relationship is called an isotherm. The ordinant of an isotherm shows the mass of the species adsorbed per unit mass of the solid, so the units might be gram/gram or milligram/gram or microgram/gram. The abscissa has units of concentration, such as milligrams per liter. In some cases the isotherm relationship can be described by an equation based on adsorption theory. In other cases the isotherm relationship is described by an empirical equation.

Solid surfaces onto which adsorption occurs can be visualized as possessing certain sites which are receptive to adsorption. When all of these sites are occupied, adsorption ceases. This concept also helps in visualizing the kinetic nature of adsorption. When adsorption begins, many sites are available, resulting in rapid adsorption. As the available sites become occupied, adsorption slows because the adsorbing species must be in the right location to find a vacant site. How the previously described concept accounts for time variable desorption from a solid is unclear. Presumably, an adsorbed species would not desorb until it has reached an energy level which allows it to break its ties with the solid and desorb to the liquid. As the population of adsorbed species have different energy levels, initial desorption would occur rapidly as the more energetic species overcome the energy barrier required for desorption. Desorption then slows as the species with high desorption energy requirements await conditions that allow them to desorb.

Thus far, the implicit assumption has been that only one species was adsorbing or desorbing. In many experiments this is the case. However, multispecies adsorption is also of interest. When several species adsorb simultaneously, some available sites on the solid may be occupied by weakly attached species, and some of the sites may be occupied by strongly attached species. As the population of vacant sites decreases, competition for both vacant sites and occupied sites sets in. A strongly adsorbing species unable to find a vacant site may displace a weakly adsorbing species. This gives rise to the concept of competitive adsorption. Under competitive adsorption, the strongly attached species displaces the weakly attached species. Competitive adsorption can result in the concentration of a species in the liquid phase decreasing as the species is adsorbed, then increasing as the species is displaced by a species having greater affinity for solids. The competitive adsorption process is easier to visualize than the competitive desorption process. If conditions are right for the strongly adsorbed species to desorb, the more weakly adsorbed species could readsorb. This process by which desorption of one specie makes sites available for adsorption of other species could give rise to fluctuations with time in the concentration of the weakly adsorbed species in the liquid phase.

Internal diffusion

Adsorption is generally thought of as a surface phenomenon, but particles have internal as well as external surfaces. For example, activated carbon has long been recognized to have many times greater internal surface area than external surface area. The internal surface area is believed to hold or adsorb more species than the external surface area. When internal pore spaces of a particle are potential sites for adsorption then the question arises as to how the adsorbing species can reach an internal site. The adsorbing species has two pathways available; it can travel in liquid in the pore until a suitable adsorption site is reached, or it can adsorb to the surface and travel along the surface to another receptive site. Both transfer mechanisms rely upon diffusion; the liquid pathway transfer occurs by diffusion of the adsorbing species through the liquid, and the surface transfer route occurs by surface diffusion. Regardless of the exact transfer mechanism and the relative role played by each of the separate mechanisms, the sum of the internal transfer mechanisms is referred to as internal diffusion. Internal diffusion may be important in certain soils comprised of particles that are not regarded as containing significant amounts of pore space, i.e., sand. If sand grains are joined together by cementing agents, or organic compounds, pore spaces that can become pathways for internal diffusion may exist. Aggregates of soil particles can have significant internal pore space. Internal diffusion can have a major impact on contaminant mobility, especially on removal of contaminants from soils. When first contacted with soil, a contaminant is most likely to adsorb to external surfaces. However, a large concentration gradient between the particle surface and the internal pore spaces tends to cause diffusion into the particle. The concentration gradient is the difference in concentration per unit length; therefore, the maximum concentration gradient exists at the start of the adsorption process when the distance between high surface contaminant concentration and zero interior concentration is short. The concentration gradient gradually decreases as the interior of the particle becomes more populated by the adsorbed species.

The internal diffusion rate for desorption, while proportional to the concentration gradient, is based on the difference in concentrations outside and inside the particle. The concentration gradient for desorption is likely to be smaller than the adsorption concentration gradient. The reason for this difference is that the internal concentration of adsorbed species is likely to be less than the maximum because internal diffusion is slow and the interior of the particle is unlikely to have reached equilibrium. In fact, if the maximum internal adsorbed concentration has not been achieved prior to the start of desorption, two concentration gradients exist in the particle. One concentration gradient will act to transport the adsorbing species toward the center of the particle while the other, nearer the surface of the particle, acts to transport the desorbing species outward. As time passes, the boundary between concentration gradients migrates toward the center of the particle, resulting in one gradient acting to transport the desorbing species out of the particle. Thus, for adsorption onto clean soils the concentration gradient is always directed toward transport of the adsorbing species toward the center of the particle until equilibrium is reached. For desorption from a particle initially at equilibrium, only one concentration gradient would exist, and this would transport the desorbing species out of the particle. For desorption during nonequilibrium conditions, two counteracting concentration gradients exist initially. Thus, desorption rates are at best as slow as adsorption, and can be significantly slower than adsorption, depending on the starting point of the desorption process.

Classical Adsorption Models

The relationship between adsorbed versus dissolved contaminant concentrations can be expressed in equation form. Some equations are convenient empirical expressions while others have a theoretical basis. Conceptually, many such model equations could be generated. The literature, however, is surprisingly restricted in the number of equations applied in groundwater modeling and environmental engineering. The commonly used isotherm equations will be presented here. The first is the linear adsorption isotherm of the following form:

$$q = K_d C \tag{1}$$

where q is the adsorption isotherm ordinate having units of mass adsorbed per unit mass of soil, K_d is the partition or distribution coefficient having units of volume per mass, and C is the equilibrium concentration of the contaminant solution, having units of mass per volume. In desorption studies, isotherms often doe not pass through the origin. Isotherms that intercept the ordinate are discussed later (Equation 8). The linear adsorption isotherm is an empirical isotherm which is widely used due to its simplicity.

Another empirical isotherm widely used is the Freundlich isotherm which has the form

$$q = K\,C^{n} \tag{2}$$

where q and C are the same as in equation 1, K is the Freundlich coefficient, and n is an empirical coefficient. Since C is raised to the power n , the units of K are more complicated than the units of K_d in equation 1. The Freundlich coefficient has the units of (mass adsorbed)$^{1-n}$ (Volume)^{n}/(mass of soil). When $n = 1$, the Freundlich isotherm becomes identical to the linear isotherm. When $n \neq 1$, the Freundlich isotherm is non-linear. The case $n = 0$ means sorption is not controlling interphase transfer of contaminant, since q does not change with change in C .

The Langmuir isotherm is a widely used model that theoretically describes a monomolecular layer adsorbing onto a solid. When all the adsorption sites are occupied, no more adsorption can take place. More complex isotherms based on the Langmuir have been developed which relax the assumption of adsorption taking place in a one molecule layer. The Langmuir isotherm has the form

$$q = \frac{Q\,K_L\,C}{(1 + K_L\,C)} \tag{3}$$

where q and C have the same meaning as in equation 1, K_L , the Langmuir coefficient, has units of volume per mass, and Q is the maximum adsorption capacity in mass per mass. When K_L is very small, the Langmuir model approaches

$$q = Q\,K_L\,C \tag{4}$$

which is a linear isotherm. When C is very large, the Langmuir model approaches meaning that all of the adsorption sites are filled.

$$q = Q \tag{5}$$

Curl and Keolelan (1984) present a competitive Langmuir isotherm for two species A and B. The isotherm equations are

$$C_A^* = \frac{Q_A K_A C_A}{(1 + K_A C_A + K_B C_B)} \tag{6}$$

and

$$C_B^* = \frac{Q_B K_B C_B}{(1 + K_A C_A + K_B C_B)} \tag{7}$$

in which C_A and C_B are the equilibrium solution concentrations of adsorbates (mass per volume), C_A^* and C_B^* are the equilibrium adsorbed concentrations (mass adsorbate per mass sorbent), Q_A and Q_B are "site," or maximum adsorbed concentrations (mass adsorbate per mass sorbent), and K_A and K_B are adsorption equilibrium constants in volume per mass sorbent. Curl and Keolelan (1984) discuss the ability of the model to describe apparent anomalies in experimental data in which desorption isotherms behaved differently than adsorption isotherms by exhibiting an apparent hysteresis. The competitive adsorption model could help to explain other types of desorption anomalies in which the distribution coefficient varies with the adsorbent concentration. One feature of the competitive adsorption model is that it emphasizes the role played by a competing adsorbate. The species of interest, C_A , in adsorption and desorption studies is measured by experimentation. By contrast, C_B may not be measured when working with natural materials because the identity of species B is usually unknown. Consequently, competitive sorption theory can be used to explain in a qualitative way nonideal adsorption and desorption phenomena, but without measured concentration dynamics of competing species as C_A varies, complete quantitative descriptions cannot be obtained.

Internal Diffusion Model

When adsorption isotherm experiments are conducted over extended periods of time, apparent equilibrium between the sorbate (contaminant) and the sorbent (solid) has been observed, but true equilibrium is often not achieved. The sorbate concentration may slowly decrease. This behavior is sometimes explained as a result of internal diffusion taking place. Rapid adsorption occurs initially on the surface of the solid, followed by slow diffusion of the sorbate into internal pores of the sorbent. This behavior is common with activated carbon particles, but can take place in aggregates of soils. In recent years internal diffusion has been studied for both batch and column experiments. While most experiments have been restricted to pure compounds with activated carbon as the adsorbing medium, some experiments with mixed compounds whose concentration was measured by a surrogate, such as total organic carbon (TOC), have been reported. To date, the sorption models that have been coupled with internal diffusion include linear, Freundlich, and Langmuir isotherms. No models or experiments have utilized competitive adsorption and internal diffusion models. The class of models that have been developed and applied to adsorption onto activated carbon are referred to as homogeneous surface diffusion models (HSDMs).

The equations for HSDMs are given in Table 1. Researchers including Weber and Chakravorty (1974), Mathews and Weber (1975), Crittenden and Weber (1978), and Traegner and Suidan (1989) have used HSDMs to describe adsorption onto granular activated carbon. The mathematical formulation uses nonlinear equations which include physical and kinetic parameters. HSDMs can also be applied to parameter estimation when experimental concentration distribution data are available. Several investigators have applied HSDMs to estimate parameters such as film transfer coefficients, K_f , and surface diffusion coefficients, D_s, by matching experimental results and HSDM predictions. Closed batch tests are performed, and the HSDM is applied while varying K_f and D_s until a satisfactory agreement between the model and experimental observations is obtained. Traegner and Suidan (1989) used the Levenburg-Marquardt algorithm while varying K_f and D_s to minimize the sum of the squared residuals between experimental data and the model prediction. The equations presented in Table 1 form the theoretical basis for developing algorithms to describe the slow adsorption of contaminants into soils.

PART III: MATERIALS AND METHODS

Selection, Preparation, and Characterization of Test Materials

Selection of test materials

Test materials were selected to represent the broadest practical range in properties associated with sorption processes, i.e., clay content, total organic carbon (TOC), and cation exchange capacity (CEC). To represent very low levels of all three parameters, masonry sand was selected. To represent high levels of TOC, activated carbon was selected. A muck soil from Rathbun Lake, Iowa, was selected so that the test could be conducted with a high TOC soil; the TOC was extracted from a subset of the Rathbun soil to represent soils without the organic carbon. Tunica silt represented soils high in silt.

Particle size

Particle size distribution was determined by using the methods of Day (1956) as modified by Patrick (1958). Although this particle size method defines the clay, silt and sand fractions in soils, the method is inappropriate in mucks, such as the Rathbun Lake sample, which contain primarily undecomposed organic carbon. The sedimentation test is ineffective for mucks since most of the organic material is less dense than water and floats rather than sinks at rates characteristic of specific size fractions. Therefore, no particle size distribution was determined for the unextracted Rathbun sample. The sedimentation test is also ineffective for activated carbon; however, activated carbon for the test was procured with a known particle size of less than 45 microns as determined by dry sieving through a 325 mesh sieve (Calgon Carbon Corp., Pittsburgh, PA).

Total organic carbon

Total organic carbon was determined by American Public Health Association (1989) Method 5310 D in all soils except the activated carbon and the unextracted Rathbun. The activated carbon was 94 percent carbon as determined gravimetrically after 3 h in a 1750 °C muffle furnace. Total organic carbon in the unextracted Rathbun was determined by loss on ignition (550 °C for 24 hr), because the extremely high organic matter content and the coarse nature of the material interfered with complete oxidation by the Standard Method.

Cation exchange capacity

Cation exchange capacity of all five test materials was determined by the ammonium saturation method Plumb (1981). Extracts were analyzed according to EPA Standard Method 350.1 (EPA 1982).

Organic matter extraction from rathbun

Organic matter was extracted from the Rathbun soil with NaOH under nitrogen (Schnitzer 1982).

Sterilization of test materials

To reduce microbial degradation by soil microorganisms during incubation, test materials were subjected to gamma irradiation prior to spiking with contaminants. Soils were exposed to a gamma-ray source at Louisiana State University for 16 hr. This exposure time assures at least one megarad of radiation to all parts of the sample. The source consisted of an annular array of Co-60 rods and plates clad in stainless steel centered in a pit under 5.5 meters of water. The total activity of the source was 3071 Curies on July 30, 1986.

Preparation of samples for incubation

Different solid to solution ratios were used for different materials because of significant differences in densities. Sand and silt were tested at a 1:1.5 solid to solution ratio, activated carbon at 1:5, and Rathbun extracted and unextracted at 1:3. Samples were spiked with 10 μg contaminant per gram of material on an oven dried weight basis. Contaminants were [ring-U-^{14}C]2,4,6-trinitrotoluene (TNT) (Chemsyn Science Laboratories, Lenexa, Kansas) having a specific activity of 21.58 mCi/mmol, a chemical purity >98% as determined by high performance liquid chromatography (HPLC), and a radiochemical purity >98% as determined by radio-HPLC; [2,4,6-^{14}C]1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX) (Chemsyn Science Laboratories) having a specific activity of 7.75 mCi/mmol, a chemical purity >97.6% as determined by HPLC, and a radiochemical purity >99% as determined by radio-HPLC; and 2,2',4,4',5,5'-hexachlorobiphenyl-UL-14C (Sigma Chemical Company, St. Louis, MO) having a specific activity of 12.2 mCi/mmol, a chemical purity >99.4 as determined by HPLC, and a radiochemical purity >98.3 as determined by radio-HPLC.

Spiking of soils was achieved by coating the inside walls of glass centrifuge tubes with solvent solutions of the contaminant and allowing the tube to turn slowly on a roller drum under the hood until the solvent was evaporated away. Previous test results indicated that loss of these contaminants was insignificant during solvent evaporation. Test material and water were weighed into treated tubes in three replicates, and tubes were placed on a reciprocating box shaker for 24 h at highest speed (280 excursions/min) to allow partitioning of contaminant from the walls of the container into the aqueous and solids phases. Results of kinetics studies conducted previously indicated that 24 h was sufficient time for steady state to develop for each of these contaminants. When removed from the shaker, samples were incubated for the following times: 1, 30, 90, 180, and 270 days.

Samples were prepared with limited head space above the aqueous phase and were incubated in the dark at ambient temperature.

Sample fractionation

After incubation, overlying water was removed[1] and the test material centrifuged for 45 min at 12,000 rpm (0.0135 μ maximum particle size in aqueous phase, 7,400 RCF) to separate interstitial water. One ml of the overlying and interstitial water were counted in 15 ml of UltimaGold Liquid Scintillation Cocktail (Packard Instruments Company, Inc., Meriden, CT) in a Packard TriCarb 2500 Liquid Scintillation (LS) Analyzer. Each sample was counted for 5 min through two cycles and the disintegrations per minute averaged. Interstitial water from PCB treatments was counted before and after passage through a C-18 Sep-Pak (Water Associates, Inc., Milford, MA) to separate the truly dissolved from the colloidal-associated PCB. The Sep-Pak traps the truly dissolved contaminant, while the humic acids and associated contaminants quantitatively pass through (Landrum et al. 1984).

Four sequential aqueous desorption cycles were conducted by replacing the overlying and interstitial water removed (by weight) with fresh distilled deionized water and returning samples to the reciprocating shaker for 24 h. After shaking, samples were centrifuged and the aqueous phase counted as described above. After the four sequential aqueous desorption cycles were completed, samples were subjected to four sequential acetone desorption cycles. These cycles were conducted and assayed in the same manner as the aqueous cycles. One g of the residue from the acetone extractions was extracted with 10ml of 0.5N NaOH to separate humic plus fulvic materials (Rice and MacCarthy 1989). Three replicates of 0.2 g of the acetone extracted material was combusted in a Packard Sample Oxidizer, the radiolabeled $^{14}CO_2$ trapped in 20ml of CarboSorb and Permafluor (1:1 v/v) (Packard Instruments

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[1] The Rathbun extracted soil had no overlying water.

Company, Inc.), and counted by LS. Residues from removal of humic plus fulvic fractions were also combusted and counted.

Check for degradation

Two samples with each contaminant were incubated for nine months to serve as controls for degradation. These samples were centrifuged, the aqueous phase removed and counted, and the soil analyzed by both complete combustion for recovery of radiolabel and by High Performance Liquid Chromatography (HPLC). Soils for HPLC analysis were extracted according to EPA Standard Method SW846-8330 (US EPA 1989). The HPLC (Waters Associates, Inc., Milford, MA, with a 600E system controller and a 712 Wisp Sample Auto Injector and Supelco LC-18 column) used a Waters 486 Variable Ultraviolet Detector and a Packard Radiomatic Flow-One-Beta Series A-100 Detector. The solvent system was 520:480 water:methanol with isocratic delivery at a rate of 1.0 ml/min. Sample matrix for the soil was 1:1 acetonitrile/water. Solvent for the Radiomatic was Flow-Scint II (Packard Instruments, Inc., Meriden, CT) at 4.0 ml/min.

Data Analysis

Data were catalogued and processed and regression coefficients were determined using Quattro Pro 3.0 (Borland, Scott Valley, CA). Graphics were plotted with Sigma Plot Scientific Graph System DOS Version 4.1 (Jandel Scientific, San Rafael, CA).

PART IV: RESULTS

Sediment Physical and Chemical Characteristics

Test soils and sediments were selected to provide a broad range of physical and chemical properties (Table 2). Soil particle size ranged from predominantly sand (95%) to predominately silt (93.8%). Particle size data for the Rathbun soil are unavailable because undecomposed organic matter in the soil interfered with test procedures. Extraction of the Rathbun soil with NaOH prior to use resulted in a pronounced drop in total organic carbon (TOC) (89.9%) and a decrease in cation exchange capacity (CEC). The contribution of organic matter to CEC is a phenomenon that has been noted by others (Brusseau, Jessup, and Rao 1991).

Soil Pore Water

Contaminant concentrations in soil pore water were determined prior to initiation of water extraction (Table 3). These data indicated that pore water concentrations of RDX were generally higher than concentrations of PCB and TNT. Concentrations of PCB remained fairly constant over time. Trends over time were not as clear for TNT and RDX. TNT concentrations were generally highest at 30 days, while RDX was generally highest initially (Figure 1).

Extraction of humic and fulvic acids from Rathbun sediment prior to testing resulted in higher concentrations of PCB and TNT in pore waters (Figure 2). Pore water concentration of PCB remained greater in the extracted sediment over the entire testing period. Higher concentrations of bound PCB in pore water of Rathbun extracted sediment were probably due to destabilization and breakup of soil aggregates following removal of soil organic matter. This was reflected in higher concentrations of bound PCB in the Rathbun extracted compared to unextracted pore waters.

Aqueous Extracts

Concentrations of RDX and TNT were generally higher than PCB in a series of four aqueous extracts (Table 4 through 8). Concentrations of RDX were generally higher than TNT concentrations. Pore water concentrations of TNT and RDX were highly correlated with concentrations in the first aqueous extraction step ($r^2 = 0.975$ and $r^2 = 0.696$ for TNT and RDX, respectively) in the sand, silt, and Rathbun soils combined data set.

Desorption isotherms for RDX, TNT, and PCB are presented in Figures 3 through 6 for sand, silt, Rathbun, and Rathbun extracted soils, respectively. Desorption isotherms are not presented for activated carbon, because of indeterminate desorption isotherms at most sampling periods. Desorption isotherms for RDX and TNT were linear. Isotherms for PCB, with rare exceptions, were indeterminate. Aqueous concentrations of RDX exhibited the greatest range in all soils. Despite the widely varying aqueous concentrations, desorption coefficients for RDX and TNT in specific soils remained relatively constant over time (Table 9). This is reflected in a plot of $K_d$app/K_d270 days versus time as derived from desorption isotherms (Figure 7) for RDX and TNT. Very few differences, aside from some perturbations in the Rathbun extracted soil, were observed for TNT and RDX. These results indicate that despite variations in water and soil concentrations, surface partitioning behavior did not change greatly over time for TNT and RDX. Decreased aqueous concentrations indicated, however, that less of the contaminant was available for desorption into the water. The values plotted for PCB are the average of the single point distribution coefficients for each of the four desorption cycles. The ratio of $K_d$app/K_d270 days for PCB generally stabilized following 180 days of incubation. These results indicate that steady state desorption conditions had been achieved following 180 days of incubation.

Aqueous concentrations were not constant over time. These results paralleled concentration changes observed in soil pore waters. For example, in the silt (Figure 4), RDX concentrations were highest initially, decreased sharply following 30 days of incubation, then increased at the 90 day sampling. For the same soil, aqueous concentrations of TNT were much higher after 30 days than at all other sampling times. PCB concentrations generally showed no distinct trends over time.

Soil Fractionation

PCB

The highest concentrations of PCB 151 extracted from soils and activated carbon was in the acetone extractable phase (Tables 10 through 14). Differences in initial soil concentrations in these tables reflect the mass of contaminants in the overlying water after incubation. Acetone was an effective extractant, removing most of the PCB from all substrates, except activated carbon (Figure 8). PCB 151 in activated carbon was found in the residual phase. With the exception of activated carbon, which ignited and burned at the high temperatures generated in the sediment oxidizer, recovery of added compounds from the soils was poor. This was due to incomplete combustion, as confirmed by high counts of all contaminants obtained by scintillation counting of burned soil residues.

Water plus acetone extractions removed from 45% to 99.6% of added PCB from soils. Approximately 70% to 90% of added PCB was recovered in the activated carbon residue following water and acetone extraction. The fraction of PCB 151 removed by water did not change substantially during incubation in any of the substrates tested. Sand and silt showed the clearest trends of increasing PCB 151 concentrations in the acetone extractable phase as a function of incubation time. The fraction of acetone extractable PCB stabilized in sand after 30 days and in silt after 60 days. Trends were less clear in the Rathbun and Rathbun extracted soils.

The fraction of PCB 151 associated with humic and fulvic acids (NaOH extractable) was low in all soils at all incubation times. Extraction procedures for humic and fulvic materials were not used for sand and activated carbon because of the low concentration of TOC in sand and the lack of a humic and fulvic phase in activated carbon.

RDX

The fraction of water extractable RDX generally decreased over the nine months of incubation (Figure 9). However, substantial increases were observed for the sand, Rathbun, and silt following three months of incubation. This decrease and increase in water soluble RDX activity was not paralleled by changes in the fraction of RDX activity associated with either acetone, sediment organic matter (NaOH extractable humic and fulvic materials), or the residue. RDX that was not water soluble appeared to be tightly bound to the soils. As was the case for PCB 151, an appreciable fraction of added RDX was recovered in the activated carbon residue, although not to the same extent as for PCB 151.

TNT

Concentrations of TNT generally peaked in the water, acetone, and NaOH extracts as well as in the residue following one month of incubation (Figure 10). Thereafter, all extracts and the residue decreased and were lower in

TNT. Recovery of added TNT was lower than PCB and RDX in the soil water, acetone, and NaOH extracts plus the residue, ranging from 0.5% in the 24 hr exposures to 71.5% in the 30 day silt treatment. Recovery of added TNT in the activated carbon was also highest at the 30 day sampling, averaging 93.4%, almost all of which was in the residue. TNT concentration was also low in NaOH extracted organic matter. The high level of unextractable residual TNT following prolonged contact with soils agrees with the findings of others (Cataldo et al. 1989, Kaplan and Kaplan 1982, Pennington 1988).

PART V: DISCUSSION

Equilibrium in batch tests is generally regarded as a two-stage phenomenon consisting of a short initial phase of rapid uptake, followed by an extended period of slower uptake. Numerous studies, summarized in Brusseau and Rao (1989), have demonstrated that the period of fast uptake generally accounts for approximately half of the total contaminant uptake, with the remainder occurring over days or months. The reasons for this uptake phenomenon have been attributed to film diffusion initially followed by intra-aggregrate diffusion during the slow sorption period (Brusseau and Rao 1989, Roberts et al. 1987, Ball and Roberts 1991). Movement of contaminants into soils by intra-aggregrate diffusion may occur by pore diffusion, surface diffusion, or both, with the faster of the two processes predominating and controlling the contaminant transfer rate (Brusseau and Rao 1989).

Soil Pore Water

The equilibrium of pore water and soil was examined by plotting the ratio of apparent K_d at each sampling time to the K_d measured at the end of 270 days of incubation (Figure 11). Similar plots are provided for TNT, RDX, and PCB with activated carbon (Figure 12). The contrast between curves for activated carbon and soils provides information on the sorption processes occurring between the soil and contaminant. Surface diffusion predominates for activated carbon uptake of strongly sorbed, low-molecular weight compounds (< 3400 g/mol) (Fettig and Sontheimer 1987). This occurs because of the high degree of tortuosity associated with the internal pore structure of activated carbon, which results in very slow pore diffusion.

$K_d$app/K_d for TNT and PCB were generally high at the initial one day sampling period, then declined to values near one for the remainder of the incubation period (Figure 11). Similar curves were observed for TNT, RDX, and PCB with activated carbon (Figure 12). The similarity of curves for soils and activated carbon for TNT and PCB indicates that surface diffusion was probably important for these compounds in the soils as well as in the activated carbon. RDX, however, behaved quite differently in the soils than in activated carbon. In soils, RDX showed behavior that would be expected (Ball and Roberts 1991, Brusseau and Rao 1989) if pore diffusion, i.e., initial sorption of a portion of the added RDX followed by a slow approach to the K_d measured at 270 days, were the controlling long-term sorption mechanism. This was especially true for the Rathbun and silt soils. RDX incorporation into the Rathbun extracted and sand soils deviated from this behavior somewhat, in that K_d's at intermediate times exceeded the K_d measured following 270 days of incubation. Overall, however, the behavior of RDX was that expected of a compound undergoing pore diffusion. RDX is much more soluble than TNT and PCB, which may explain the deviation of RDX from the behavior of TNT and PCB compounds.

Soils can be considered in terms of surfaces and compositions. Sand has few adsorbing sites per unit mass. Rathbun extracted is a soil with the adsorption sites reduced in number by extraction of the organic carbon and potential alteration of the remaining sites by the extraction process. The silt soil, a silty loam, is more likely to form aggregates and internal pores, and probably has more adsorption sites per unit mass than the sand or Rathbun extracted soil. Finally, the Rathbun soil is highest in organic carbon and, therefore, has the highest number of sorption sites per unit mass. A steady state of adsorption for PCB, TNT, and RDX onto activated carbon was achieved rapidly. After day one, no desorption from activated carbon occurred, except for PCB on day 180 (Figure 1). Therefore, adsorption behavior with activated carbon, except for one datum which may be a measurement anomaly, followed expected trends.

PCB

The pore water concentration of PCB was almost independent of time for sand, except that at 180 days the concentration increased and then returned to its former value at 270 days (Figure 1). This behavior is consistent with rapid initial adsorption that fills all of the adsorption sites.

The adsorption of PCB by Rathbun extracted soil produced a puzzling result in which the pore water concentration increased slowly and steadily with time. This type of behavior indicates that PCB was initially adsorbed, then gradually desorbed with time. At least two explanations are possible for the observed phenomenon; reactions occurring at the adsorption site, and competitive adsorption. The sodium hydroxide used to extract organic carbon from the Rathbun soil may have altered the adsorption sites so that after PCB adsorbed onto the receptive sites, the sites underwent a slow reaction. The result of this presently unknown reaction was gradual desorption of PCB back into the pore water. Alternatively, some unidentified compound may have migrated gradually from the interior of the Rathbun extracted soil to the surface area where it competitively displaced adsorbed PCB back into the pore water.

PCB adsorption onto silt and Rathbun soils behaved conventionally with all adsorption taking place by day one. On day 180 a small anomaly occurred in which the pore water concentration increased, but subsequently dropped to the normal level by day 270.

TNT

The pore water results for all soils for TNT are orderly and consistent, except for day one (Figure 1). On day one TNT was not in the pore water, and is presumed to be adsorbed to the soil. However, on day 30 not all TNT was adsorbed by any of the soils, with the possible exception of Rathbun. The results for days 30, 90, 180 and 270 are consistent with slow kinetic adsorption and intraparticle diffusion, with adsorption complete by day 180. Day one results are inconsistent with that pattern.

Several hypotheses can be advanced to explain this result. One is that the TNT was adsorbed on day one, perhaps in the form of globules, micelles, lamella, or some other loosely bound structure. Then between days one and 30 these structures disintegrated releasing part of the TNT back into the pore water, where it underwent a dynamic readsorption as shown by the data from day 30 to day 270. Competitive adsorption offers another hypothesis. Adsorption of TNT on preferred sites on all soils was essentially complete on day one. Then some other species adsorbed during the period between days one and day 30, forcing part of the TNT back into the pore water where it was able to slowly adsorb onto less preferred sites. Perhaps the slow rate of readsorption is showing the effects of internal diffusion of TNT to receptive sites. A third hypothesis is that TNT underwent abiotic chemical transformation following day one to a compound having greater aqueous solubility and different partitioning characteristics than the parent compound. The greater peak at one month would represent the release of the transformed product, while all subsequent data represents gradual sorption of the product. The fact that the greatest pore water concentrations at one month occurred with the medium expected to exhibit the fewest sorption sites, i.e., sand and Rathbun extracted soil, suggests that the transformation was greatest when TNT was only loosely sorbed. Since the study relies on radiolabeled compounds with no data for the identification of the compounds, and since TNT transformation to products such a 4-amino-2,6-dinitrotoluene are common reactions, this hypothesis carries some credibility. Previous studies have indicated that adsorption kinetics for TNT in soils, including the silt used in the present study, reach steady state within the first two hours of soil contact (Pennington and Patrick 1990).

RDX

Adsorption of RDX on Rathbun extracted soil was consistent with slow dynamic adsorption or with internal diffusion. The pore water concentration decreased steadily but slowly from day one to day 270 (Figure 1). RDX interaction with sand and silt was similar, but more RDX was adsorbed by silt than by sand. Both sand and silt showed a low pore water concentration of RDX at 30 days with higher concentrations on days 1 and 90. This behavior is consistent with competitive adsorption theory in which an unidentified compound became available after day 30 and caused part of the adsorbed RDX to desorb back into the pore water from which it slowly readsorbed by day 180. RDX interaction with Rathbun soil showed a slight effect of competitive adsorption on day 30. From day one to day 30 a small amount of dynamic adsorption or internal diffusion occurred. By day 90 the available adsorption sites were largely filled and only very slow adsorption took place, perhaps showing the effects of internal diffusion. Transformation of RDX in sand and silt as suggested for TNT at one month, is also a possible explanation for the 90 day peaks.

Pore water summary

Various explanations for the pore water adsorption data are summarized in Table 15. An entry for a row or a column indicates that the phenomenon may have been observed for the particular sorbate-sorbent combination. An entry in parentheses indicates a possible but weaker relationship. The process-sorbate-sorbent associations indicate that none of the processes previously discussed can alone explain the entire data set. The table indicates uncertainty about the interactions taking place between contaminants and the soils. This uncertainty is illustrated in the several alternatives developed to explain parts of the data.

Rapid initial adsorption was the most generally observed phenomenon. Rapid initial adsorption was evident for activated carbon with all three sorbates and for the PCB- and TNT-soil combinations. RDX with Rathbun, silt and sand failed to adsorb rapidly. Rapid initial adsorption is a good explanation for day one through 270 activated carbon data, but is adequate for the day one PCB and TNT soils data only.

The RDX soil data suggest that internal diffusion was affecting the disappearance of RDX from pore water for Rathbun, silt and sand. While Table 15 does not suggest that PCB, TNT and RDX underwent internal diffusion into activated carbon, the activated carbon adsorption literature strongly suggests that internal diffusion should be expected. To test whether internal diffusion was taking place with activated carbon, measurement of sorbate pore water concentrations would have had to start earlier than day one.

As indicated in Table 15, competitive adsorption may have been present during adsorption of TNT and RDX on all the soils except Rathbun. Competitive adsorption as a controlling process, however, involves significant uncertainty related to the competing, but unidentified, species. In the complex system of natural soils, competitive sorption occurs, but the relative significance of this process cannot be evaluated with the data available in this study.

The reactive site hypothesis previously discussed was constructed to explain the PCB data for the extracted Rathbun soil. Little in the way of theoretical or experimental evidence exists for this hypothesis. It is included in Table 15 to indicate the inadequacy of the available hypotheses for explaining the entire data set.

Initial formation of micelles, lamella, or globules, was included as a possible explanation for the TNT pore water data for the soils. Like the reactive site hypothesis, little theoretical or experimental evidence for this hypothesis exists. The possibility of transformation of TNT or RDX during the incubation periods was not investigated; therefore, no direct proof of this hypothesis is available.

Aqueous Extracts and Soil Fractionation

Very little PCB, TNT, and RDX was recovered in the NaOH extractable phase. Recovery of spiked compounds in the residual phase, determined by soil combustion, was poor due to incomplete combustion. Therefore, the water and acetone extractable data provide the most useful information on slow release of PCB, TNT, and RDX.

The engineering significance of the water and acetone extraction data is as important as understanding why the pore water data showed nonideal behavior. Figures 8, 9 and 10 have much practical significance for site remediation. These data indicated what can be expected with respect to contaminated site remediation.

PCB

Figure 8 shows the fraction of adsorbed PCB that was extractable from activated carbon and the several soils. Once PCB was adsorbed onto activated carbon, desorption either by water or by acetone was extremely limited. Therefore, activated carbon was very effective in holding PCB. In a pump and treat remediation system in which activated carbon is used as adsorbent, very little leakage of PCB from the adsorbent is expected. Additional study would be necessary to determine the adsorption capacity of a particular activated carbon bed.

Figure 8 also shows the difficulty in extracting adsorbed PCB from sand with water. A measurable, but very small, amount of adsorbed PCB was extracted. On the other hand, extraction of PCB by acetone yielded recovery rates that vary in the range of 40 to 70 percent. A pump and treat system using water to clean up a PCB contaminated sand would be a slow procedure, so remediation would take a very long time. On the other hand, acetone would strip large amounts of PCB from sand; therefore, acetone extraction could be considered as an alternative in designing a remediation system.

Results were similar for the other soils contaminated with PCB. Water removed a little, perhaps 10 percent, of the PCB from the Rathbun extracted soil, about 5 percent from the Rathbun soil, and virtually none from the silt. On the other hand, acetone recovered from 70 to 100 percent of the PCB from Rathbun soil, from 60 to 90 percent from the Rathbun extracted soil, and from 75 to 100 percent from the silt soil. Due to the sequence of the extractions in this study, first with water and then with acetone, the extractions with acetone probably underestimate the recovery that could be achieved with acetone as the sole extractant. The recoveries were approximately independent of how long PCB had been exposed to the soils. Thus, the PCB not recovered from the soils may have migrated into interior pores where the PCB was protected from extraction. Therefore, removing the final fraction of PCB from contaminated soils in a field remediation project would be a slow tedious process.

RDX

Figure 9 shows the fraction of total adsorbed RDX that was extractable from activated carbon and the several soils. Unlike the PCB data, RDX is extracted to a small, but measurable, extent by water from activated carbon. In a pump-and-treat remediation scheme, activated carbon would be an effective adsorber of RDX, but the adsorber design and operation should account for the slight tendency of RDX to desorb. Acetone recovered from 20 to 40 percent of the adsorbed RDX from activated carbon. The recovery trend was downward, that is, the fraction of RDX recovered decreased the longer RDX was exposed to activated carbon. The implication is that much of the RDX had moved by internal diffusion into interior pore space of the activated carbon, where the RDX was sheltered from extraction. Internal diffusion is known to take place in activated carbon, so unrecovered RDX in interior pores of the activated carbon is likely.

The RDX extraction data for sand with water and acetone is very interesting. Eighty (80) percent of the RDX was extracted with water on day one. Afterwards, a downward trend in extraction with water was observed until almost none of the RDX was extracted with water on day 180. Acetone did not extract RDX from sand at any time. The implication is that the water removed all of the removable RDX leaving none for the acetone to extract. Extraction of RDX showed an overall decreasing trend with time. For example, while 80 percent of the RDX was recoverable from sand after one day of exposure, almost none was recoverable after 180 days. Apparently the RDX found some interior pores in the sand in which to move to escape extraction, or the RDX became bound more tightly to the adsorption sites on the sand.

The general trend of the data for RDX adsorbed to the other soils was similar to the data for sand. The highest recovery was for RDX exposed to the soil for the shortest time; recovery declined with increasing exposure time. Rathbun soil showed that water extraction did not recover all extractable RDX; acetone extraction recovered an additional 10 to 20 percent. Rathbun soil and Rathbun extracted soil still had about 30 and 10 percent extractable, respectively, after 180 days. However, the extractable amount was a marked decrease from about 80 and 50 percent extractable, respectively, for the soils on day one. The decreasing recoveries of RDX has important implications for an RDX remediation operation. All the soil data indicated that remediation of RDX at old sites by soil flushing may be very difficult.

TNT

Figure 10 shows the fraction of total adsorbed TNT that was extractable from the activated carbon and the several soils. Virtually none of the TNT in activated carbon was extracted by either water or acetone. These data indicate that activated carbon effectively binds adsorbed TNT, with little tendency for TNT to leak past an activated carbon filter until its adsorption capacity is reached. The acetone and water extraction data suggest that TNT was able to move into internal pores where TNT was protected from extraction.

None of the TNT was extracted from any soil by either water or acetone on day one. TNT was quickly and tightly bound or found internal pores into which it could rapidly move. On day 30, however, the extraction percentage for sand, silt, Rathbun, and Rathbun extracted rose to about 50, 30, 20, and 5 percent, respectively. The surge in recovery percentages on day 30 suggests that TNT was being forced from its sheltered position by an unknown competitor or released by some process such as the disintegration of micelles, lamella, or globules previously discussed. By day 90, TNT was recoverable only from the Rathbun soil, about 15 percent, and Rathbun extracted soil, about 5 percent. By day 180 TNT was not extractable from any of the soils. The implication of these data is that TNT adsorbs quickly and tightly to soils and is able to move into protected internal pores in the soil. If these observations are correct, extraction of TNT from soil in a remediation project is unlikely to be very effective.

The results of this study are consistent with field observations about the relative mobility of TNT and RDX. The water and acetone extraction data in this study (Figures 9 and 10) showed that RDX remained in an extractable (mobile) form longer than TNT. By day 180, TNT did not desorb in water or acetone, while RDX remained extractable. Thus, RDX would be expected to be mobile over a longer period of time and should migrate further. RDX did not show the phenomenon that TNT showed of being completely adsorbed on day one. Based on these results, an RDX plume is expected to migrate because the RDX at the front of the plume is mobile.

Limitations to Application of Homogeneous Surface Diffusion Models (HSDMs)

The last equation in Table 1 represents, in a general form, equilibrium partitioning of sorbate on the sorbent external surface. In order to apply HSDMs, this partitioning must be explicitly stated in mathematical terms. The equations used for this purpose (linear, Freundlich, and Langmuir isotherms) were previously discussed. In this section, the limitations of the isotherm data for application in a HSDM are discussed.

The results of the desorption equilibrium isotherm experiments are shown in Figures 3, 4, 5, and 6 for RDX, TNT and PCB on the following soils: sand, silt soil, Rathbun, and Rathbun extracted soil, respectively. Table 16 shows a classification of the isotherm data for each of the contaminants and each of the soils for the periods of adsorption used in this study. In some cases the data suggest linear isotherms, but in other cases the data were not compatible with development of any isotherm. One characteristic of the linear isotherm presented earlier (equation 1) was that the isotherm goes through the origin (0,0). The desorption data which resulted in straight line plots, however, did not go through the origin. For this reason, parentheses are used in Table 16 to denote straight-line isotherms that do not go through the origin.

Desorption isotherms for RDX were usually in the form of straight lines, but in no case did the line go through the origin. Many TNT desorption isotherms showed straight-line characteristics, but again the isotherms did not go through the origin. In other cases, TNT desorption isotherms showed no consistent trends and were identified as "indeterminant". The PCB isotherm data were generally in the "indeterminant" category. In a few cases where PCB desorption isotherms plotted as a straight line, the isotherm did not go through the origin. The nonlinear Freundlich or Langmuir isotherms did not apply to the data.

The tendency of the straight-line isotherms to enter the desorption isotherm ordinate well above zero is significant and suggests the following model:

$$q = K_d C + q_r \tag{8}$$

where

q_r = sorbed contaminant concentration resistant to water extraction, mass/mass

Equation 8 is a modification of equation 1 that accounts for sorbate that is unavailable for extraction. Conversion of sorbate from extractable to difficult to extract could be due to diffusion of sorbate into internal pores where it was protected from extraction and/or irreversible sorption to sites that tightly bind the sorbate.

The inclusion of a term for non-extractable sorbate, q_r , in the surface sorption equation does not present difficulties for HSDMs, as q_r would be expected to increase with exposure time. However, the isotherms in Figures 3, 4, 5, and 6 show that q_r was greater at 30 days than at 90 days in most cases. This observation is inconsistent with the basic assumptions behind development of HSDMs.

In addition to the lack of compatibility of the isotherm data with the formulation of HSDMs, the pore water adsorption data for PCB and TNT are inconsistent with HSDM formulation for most of the soils. For these reasons, no attempt was made to identify the film and surface diffusion coefficients from the internal diffusion algorithm. Additional research is needed to discover the process(es) that result in the complex and nonideal isotherms obtained in this study.

PART VI: SUMMARY AND CONCLUSIONS

This study explored the adsorption of PCB, TNT, and RDX onto activated carbon and soils over time and the implications for contaminant mobility. Sorption onto activated carbon resulted in expected behavior. However, the kinetics of PCB, TNT, and RDX movement into soils proved to be complex.

Sorption results for PCB in soils was consistent with rapid initial adsorption onto all available adsorption sites. However, the Rathbun extracted soil from which most organic matter had been removed showed a steady concentration increase in pore water PCB over time. Therefore, instead of slow movement of PCB into pore spaces, movement into the aqueous phase was noted. The extraction process may have altered the adsorption sites, resulting in release of PCB into pore water, or competitive adsorption by an unidentified compound which migrated gradually from the interior of the soil pores may have occurred.

TNT results are consistent with slow kinetic adsorption from day 30 to day 270. On day one, TNT was not in the pore water, perhaps because rapid adsorption had occurred. TNT may have sorbed to globules, micelles, lamella, or some other structure that loosely bound TNT. Then, between day one and day 30, disintegration of these structures released part of the TNT back into the pore water where readsorption occurred. Competitive adsorption, a process whereby some other species adsorbed between day one and day 30, forcing part of the adsorbed TNT into solution, may also have occurred. Abiotic transformation of the TNT to another, more soluble form, which was released at day 30, then slowly readsorbed by the soils is another possibility.

Desorption of TNT and RDX over time was complex, but was also consistent with field observations on the relative mobility of TNT and RDX, i.e., RDX is more mobile than TNT. Desorption data for water and acetone showed that RDX remained mobile longer than TNT. By day 180, TNT did not desorb in either water or acetone, while RDX was still extractable at day 180. RDX would, therefore, be mobile longer and potentially migrate further in the soil.

Development of an algorithm to describe slow adsorption/desorption of PCB, TNT, and RDX was difficult because of the complexity of the processes and kinetics affecting soil/contaminant interactions. In the approach employed to describe slow release (equation 8), the amount of PCB, TNT, or RDX that was unavailable for extraction should have increased as time of exposure to the sediment increased. However, the desorption isotherm data showed that the amount of TNT and RDX resistant to desorption did not increase in a predictable manner over the course of the study. The desorption isotherm data and pore water adsorption data for PCB and TNT were inconsistent with homogeneous surface diffusion models for most soils. For these reasons, film and surface diffusion coefficients were not identified from the internal diffusion algorithm. Additional research is needed to characterize the complicated process(es) that resulted in complex isotherms and nonideal incorporation of contaminants into soil phases that were resistant to extraction.

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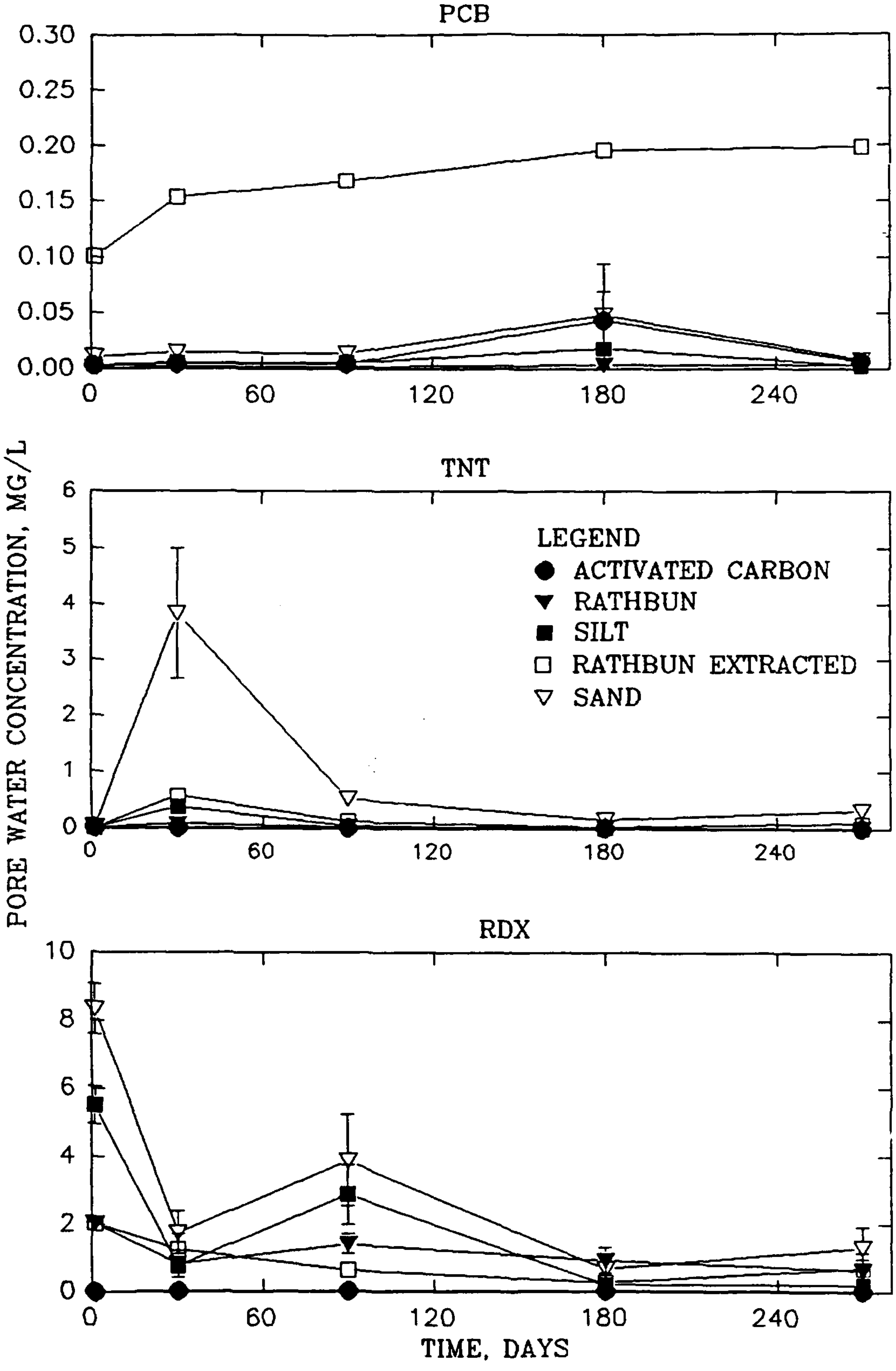

Figure 1. Pore water concentrations of PCB, TNT, and RDX versus time

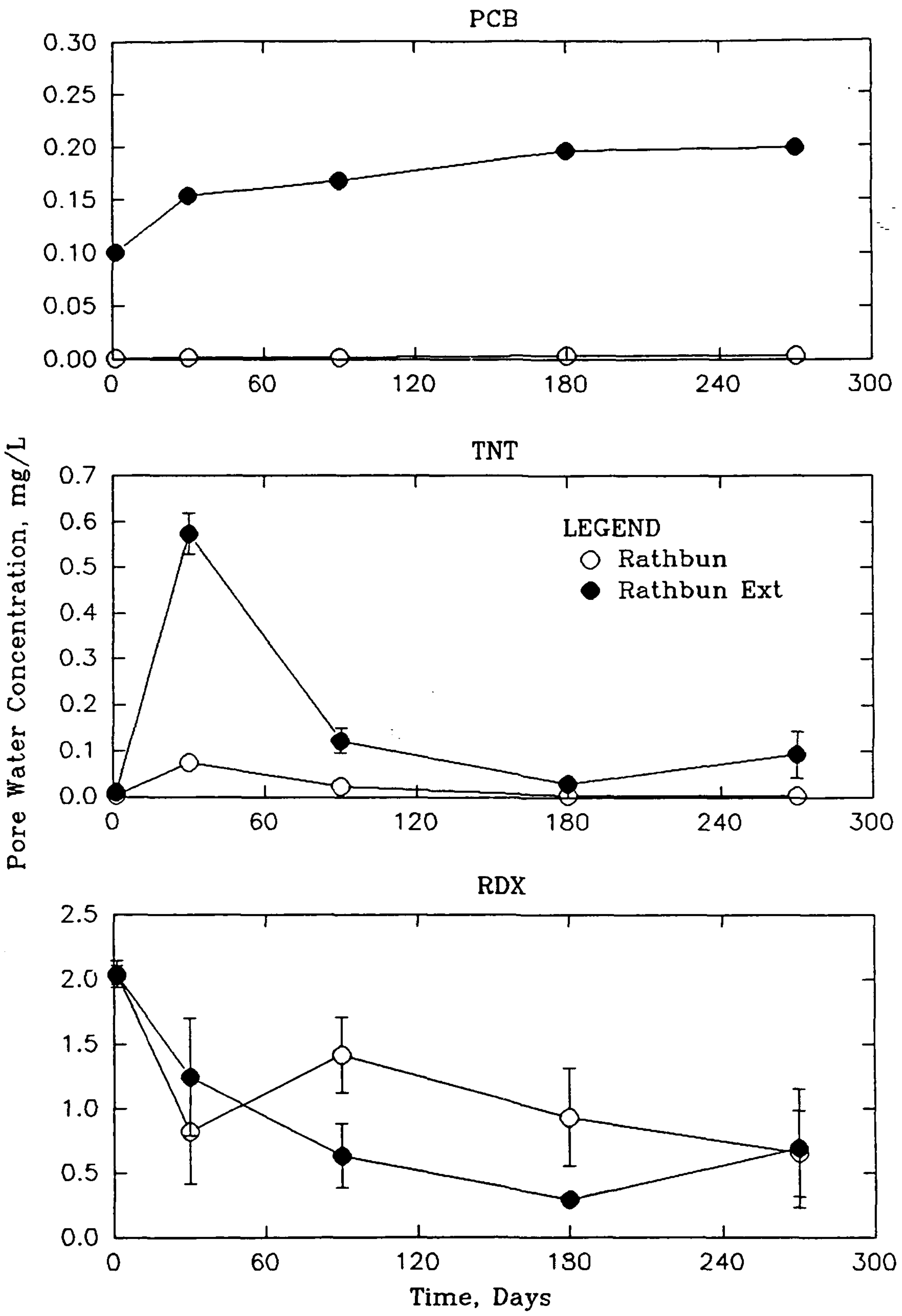

Figure 2. Pore water concentrations of PCB, TNT, and RDX versus time for Rathbun and Rathbun extracted sediments

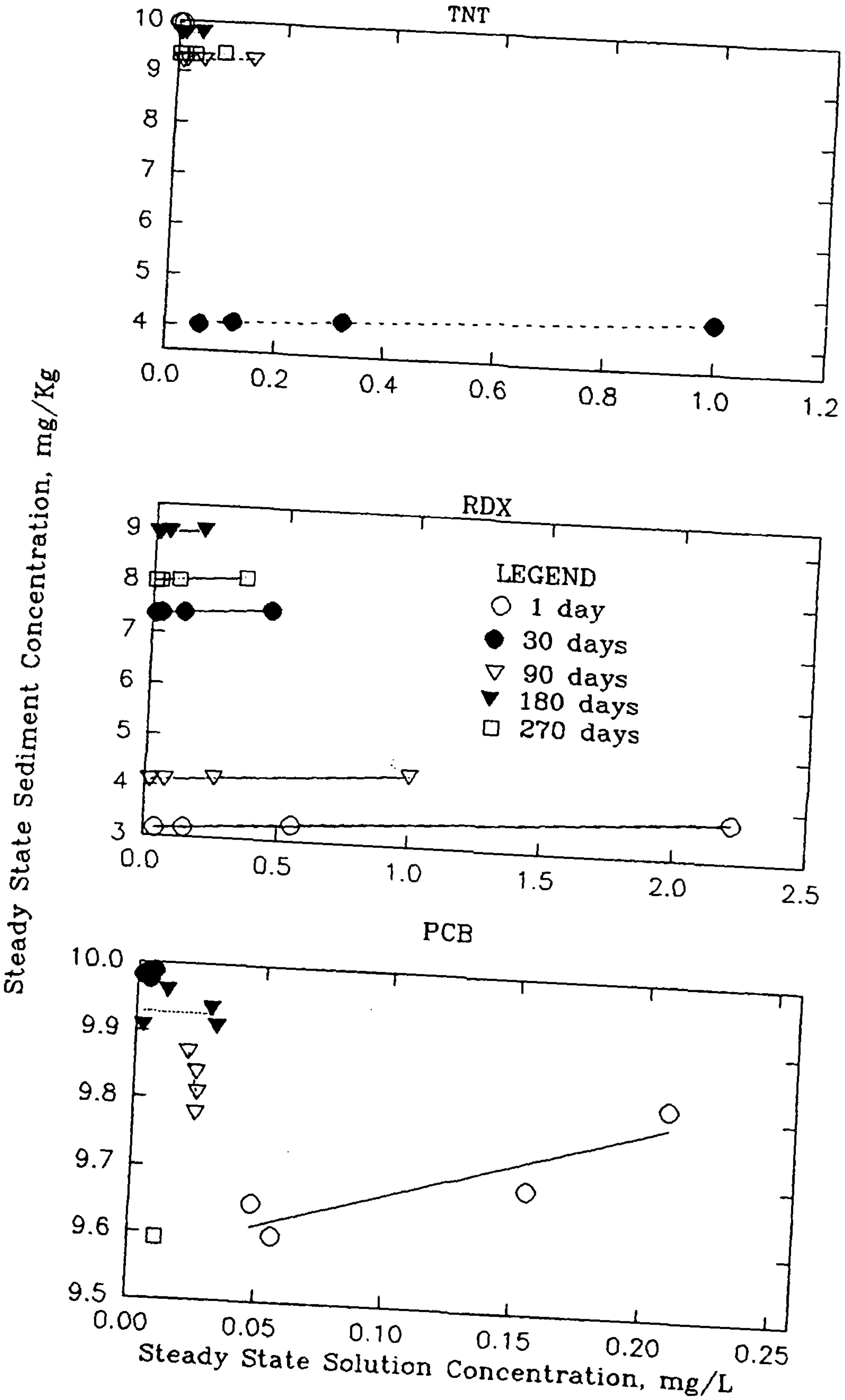

Figure 3. Desorption isotherms for PCB, TNT, and RDX in sand

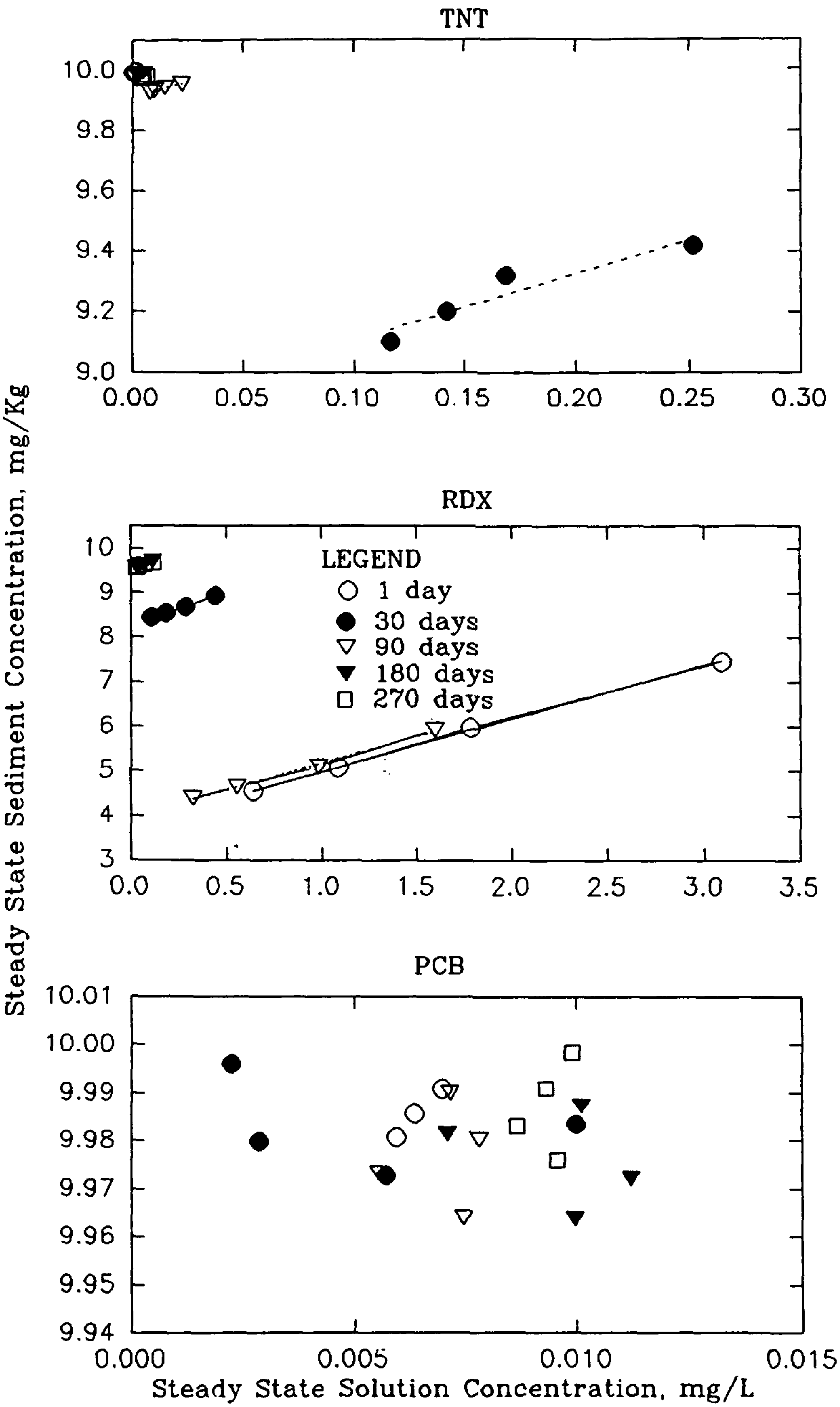

Figure 4. Desorption isotherms for PCB, TNT, and RDX in silt

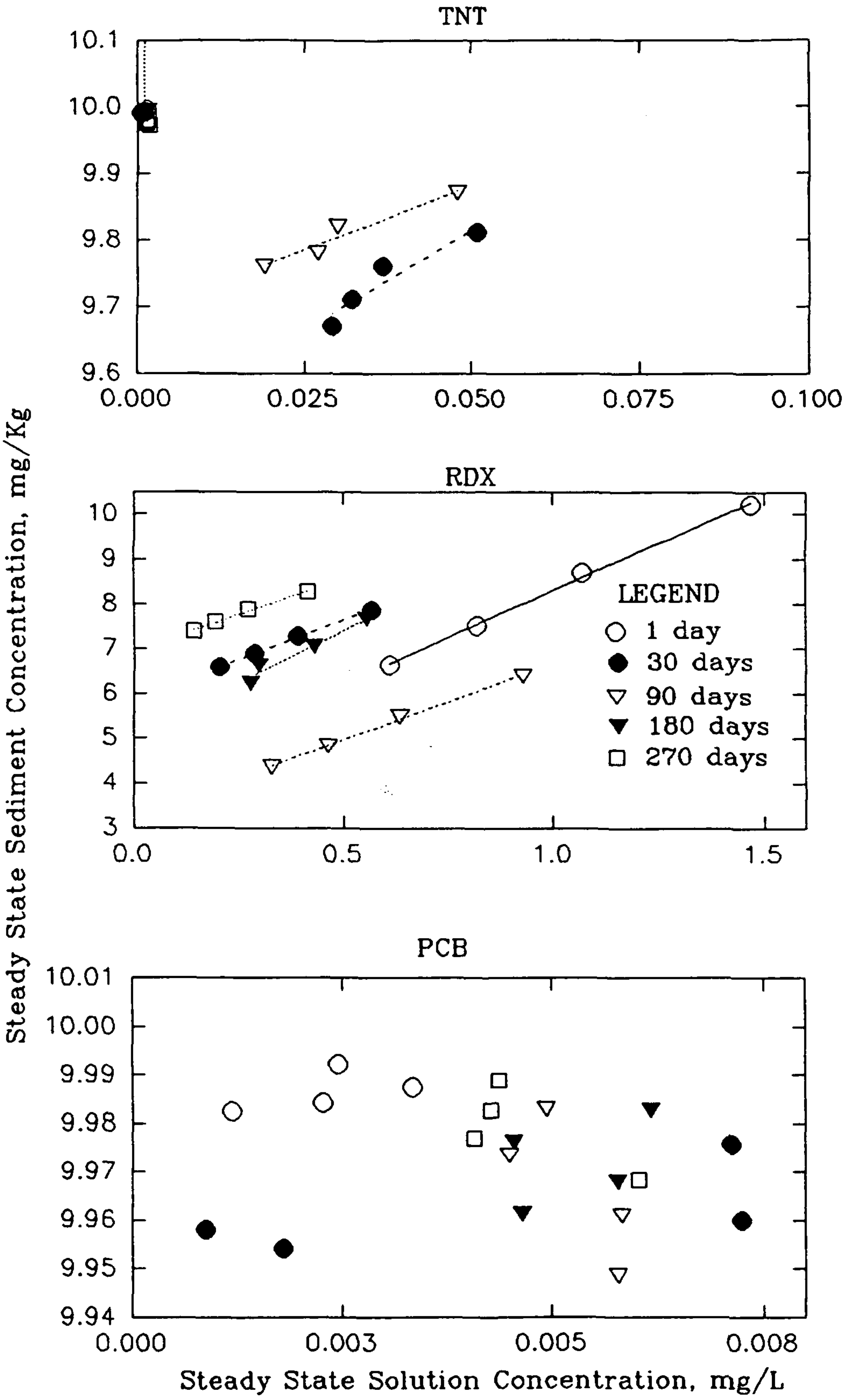

Figure 5. Desorption isotherms for TNT, RDX, and PCB in Rathbun

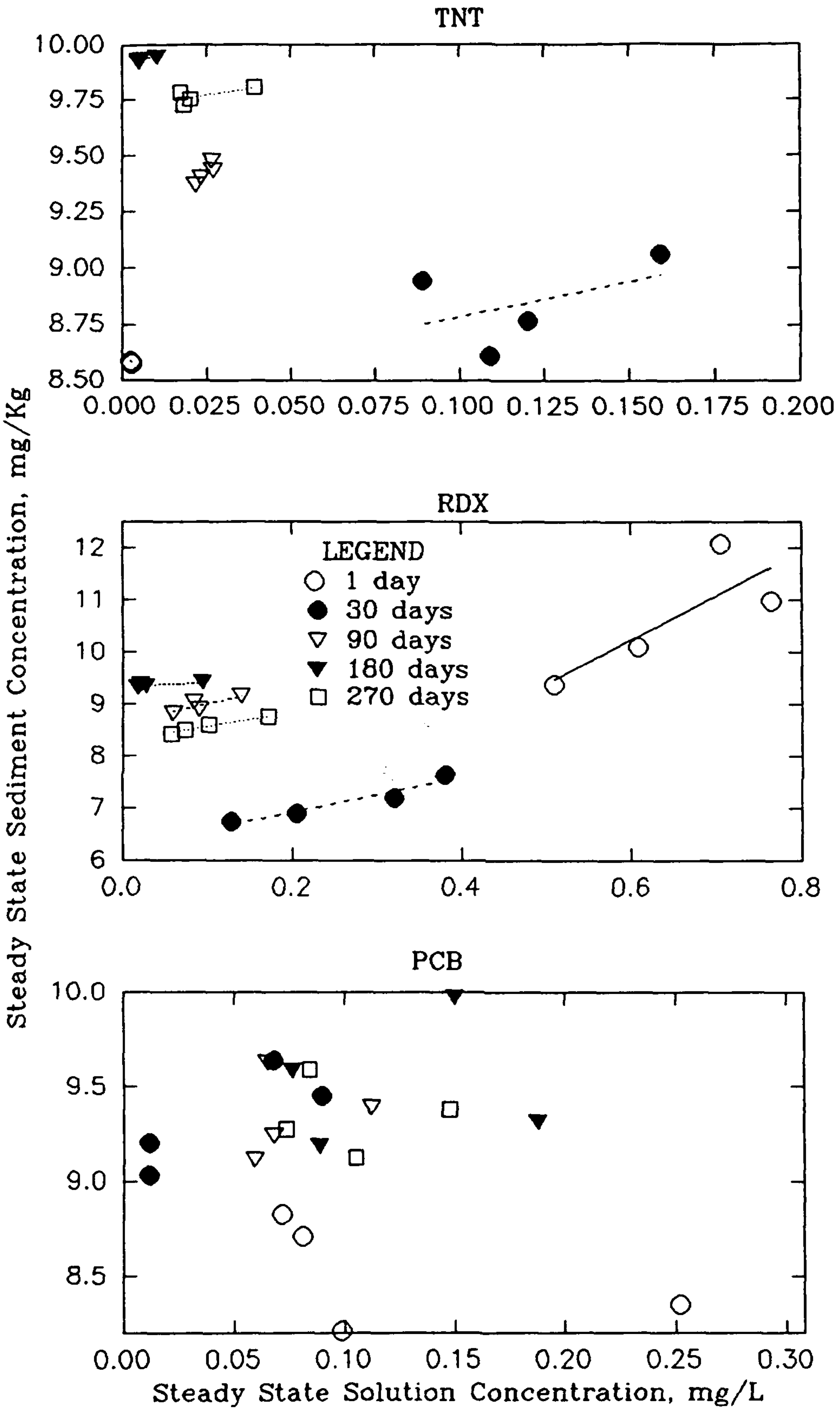

Figure 6. Desorption isotherms for TNT, RDX, and PCB in Rathbun extracted

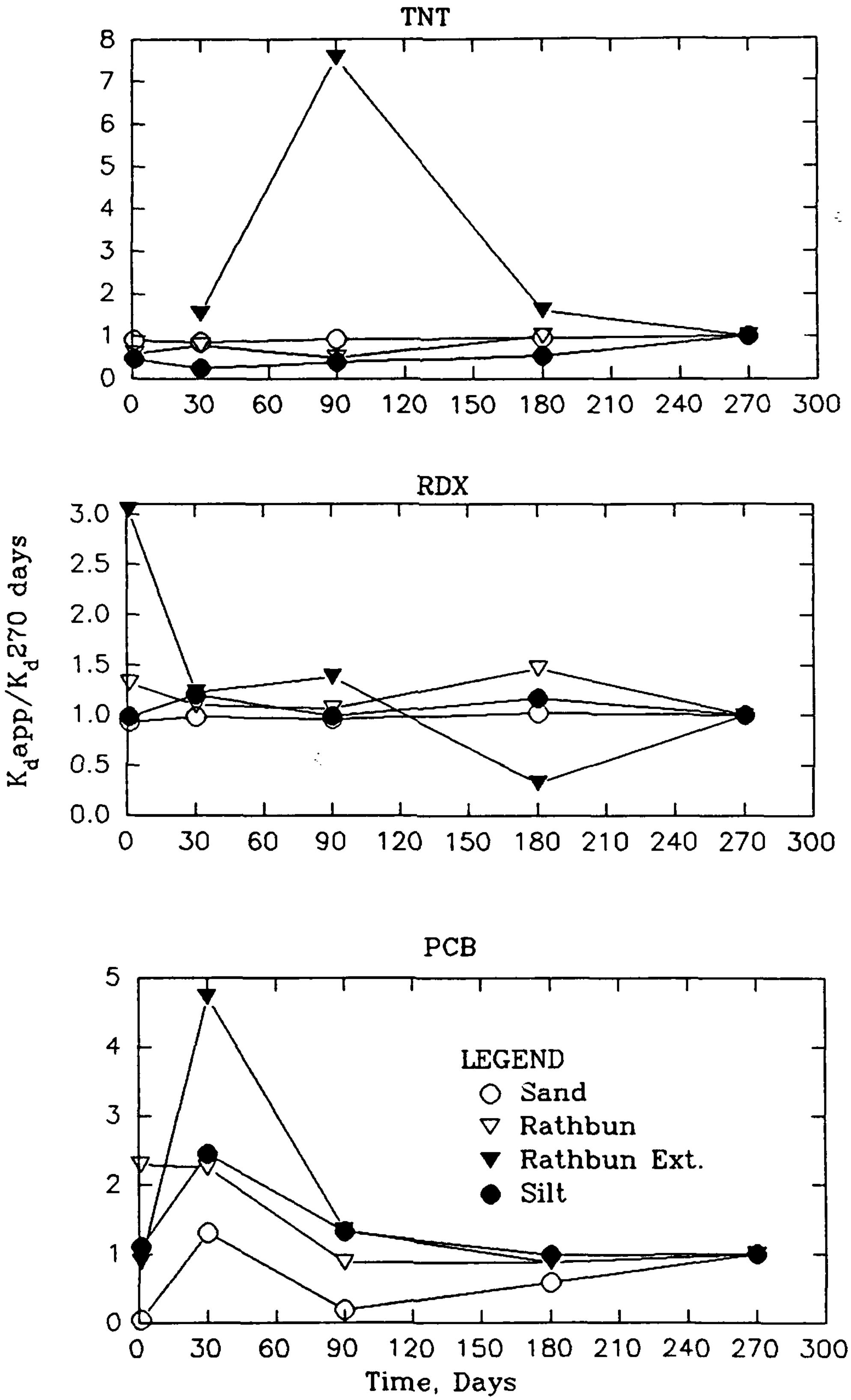

Figure 7. Normalized aqueous extract apparent distribution coefficients versus time

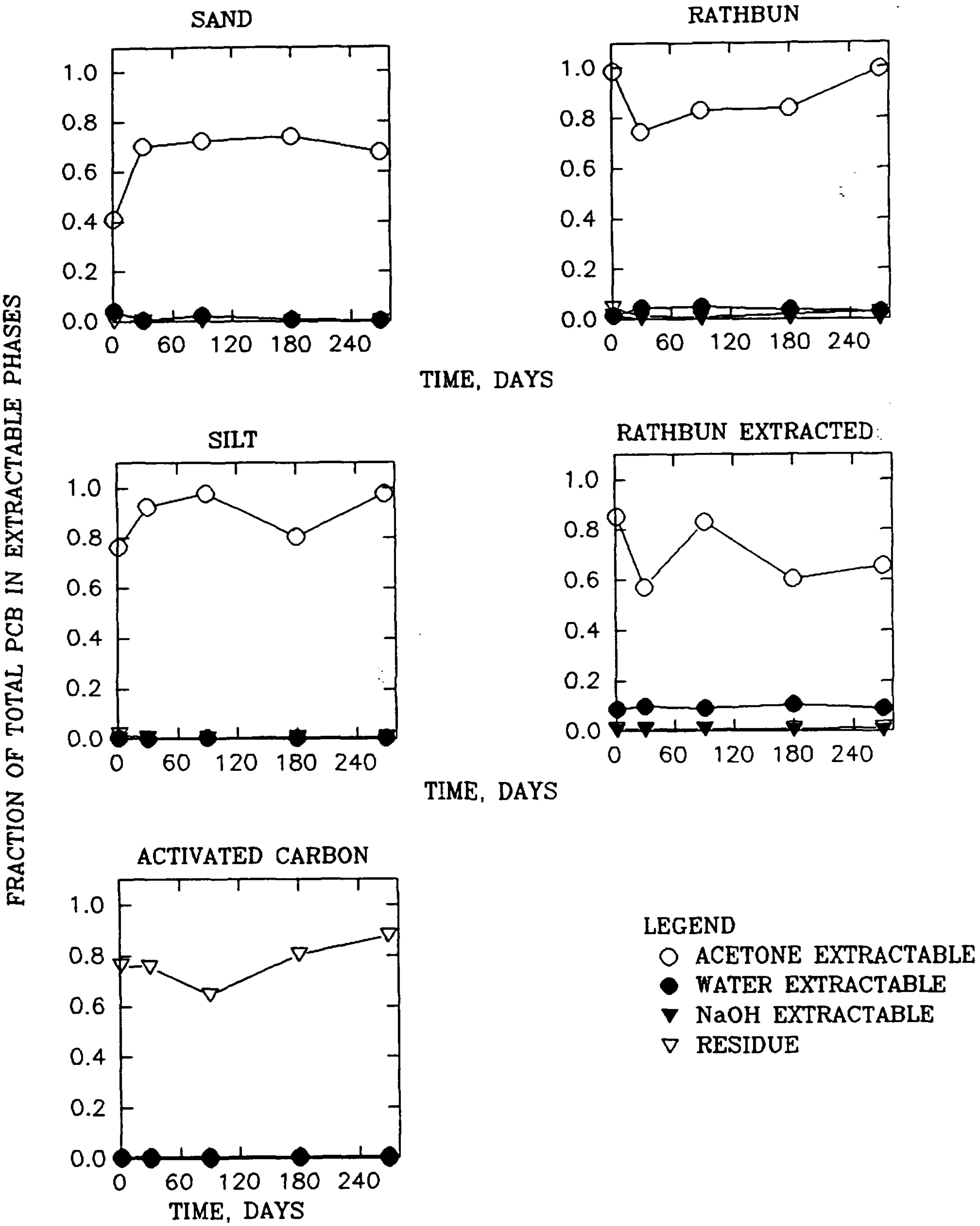

Figure 8. Total PCB extracted by acetone, water, NaOH, and in residue after each incubation period in each soil

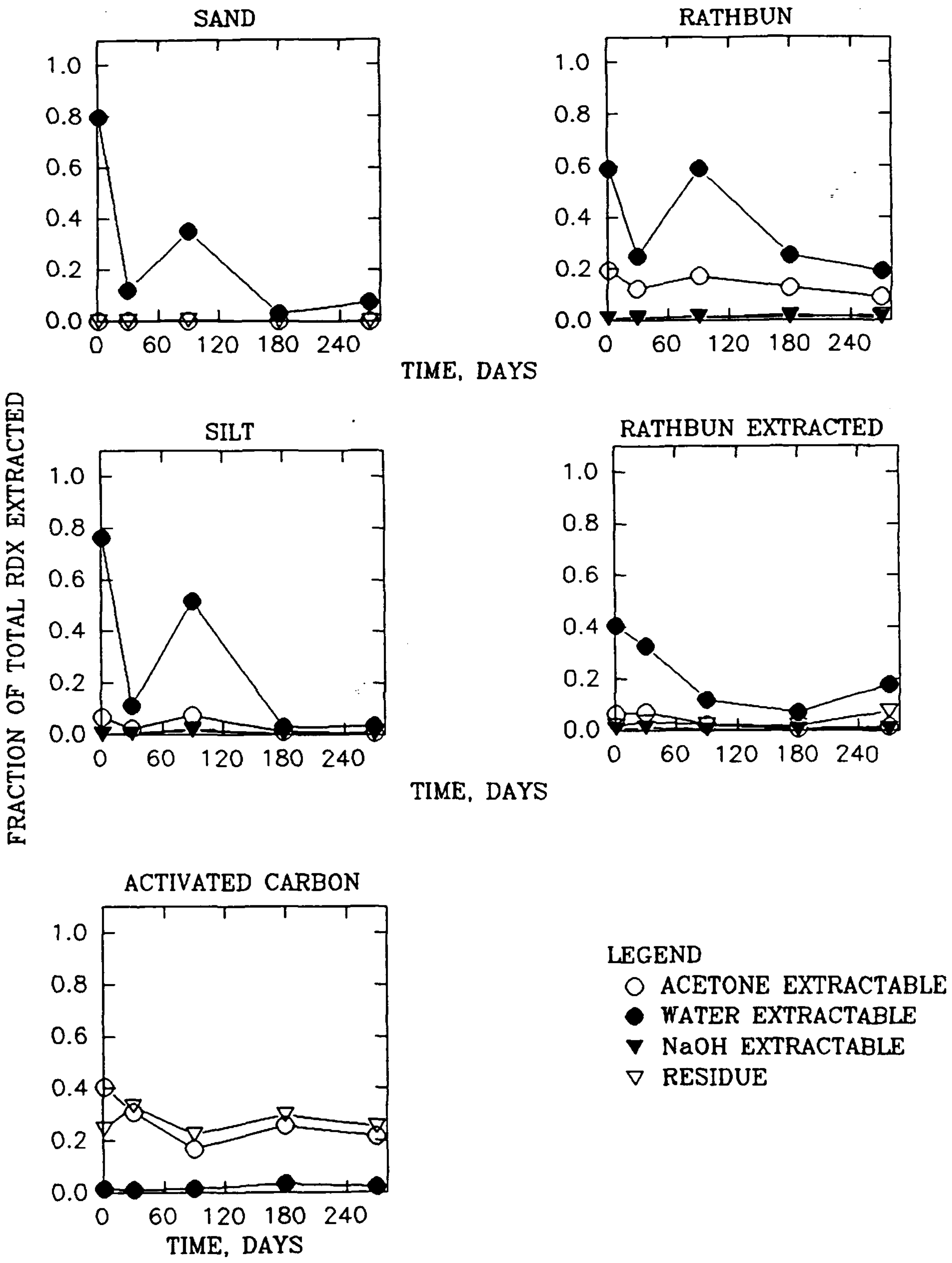

Figure 9. Total RDX extracted by acetone, water, NaOH, and in residue after each incubation period in each soil

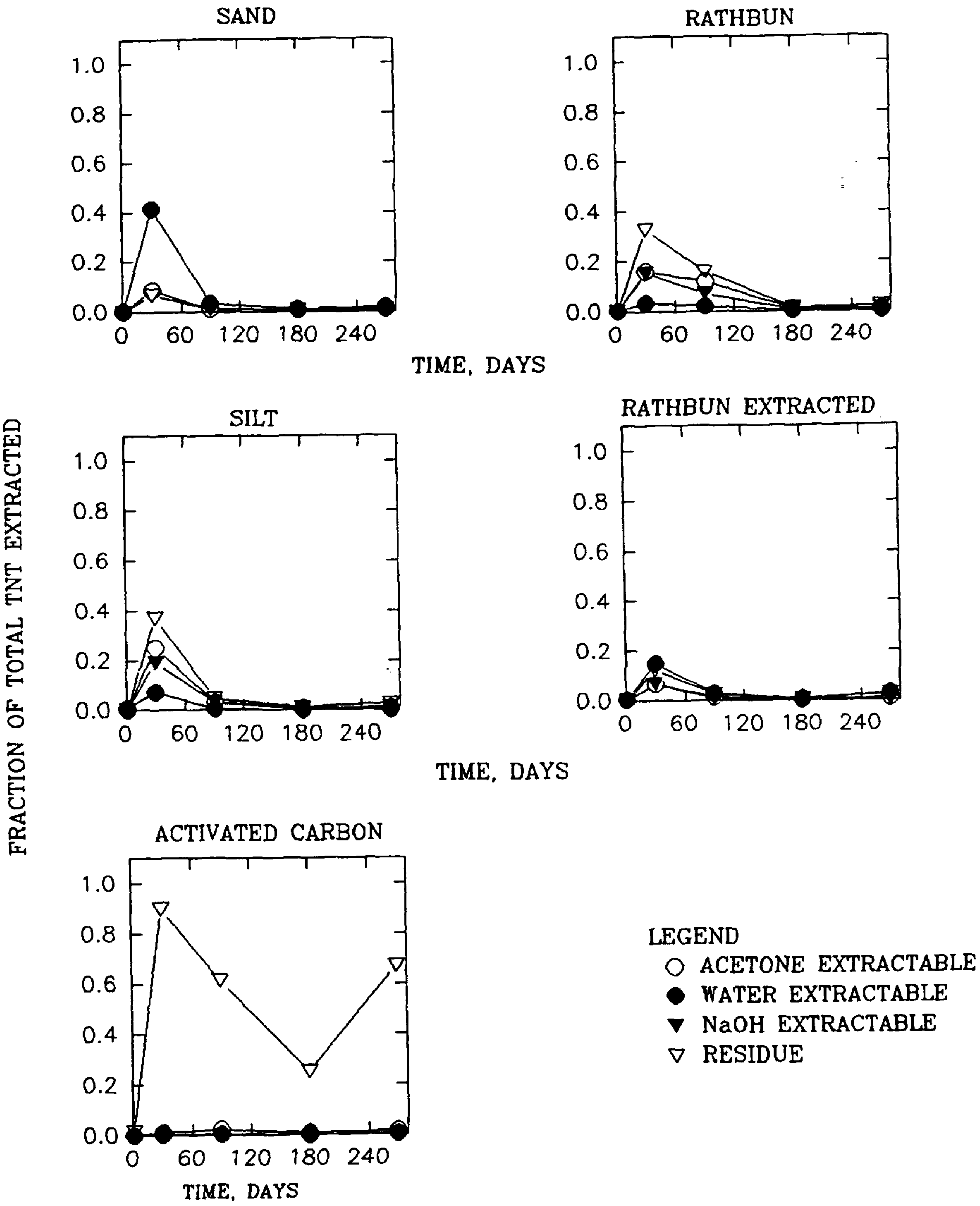

Figure 10. Total TNT extracted by acetone, water, NaOH, and in residue after each incubation period in each soil

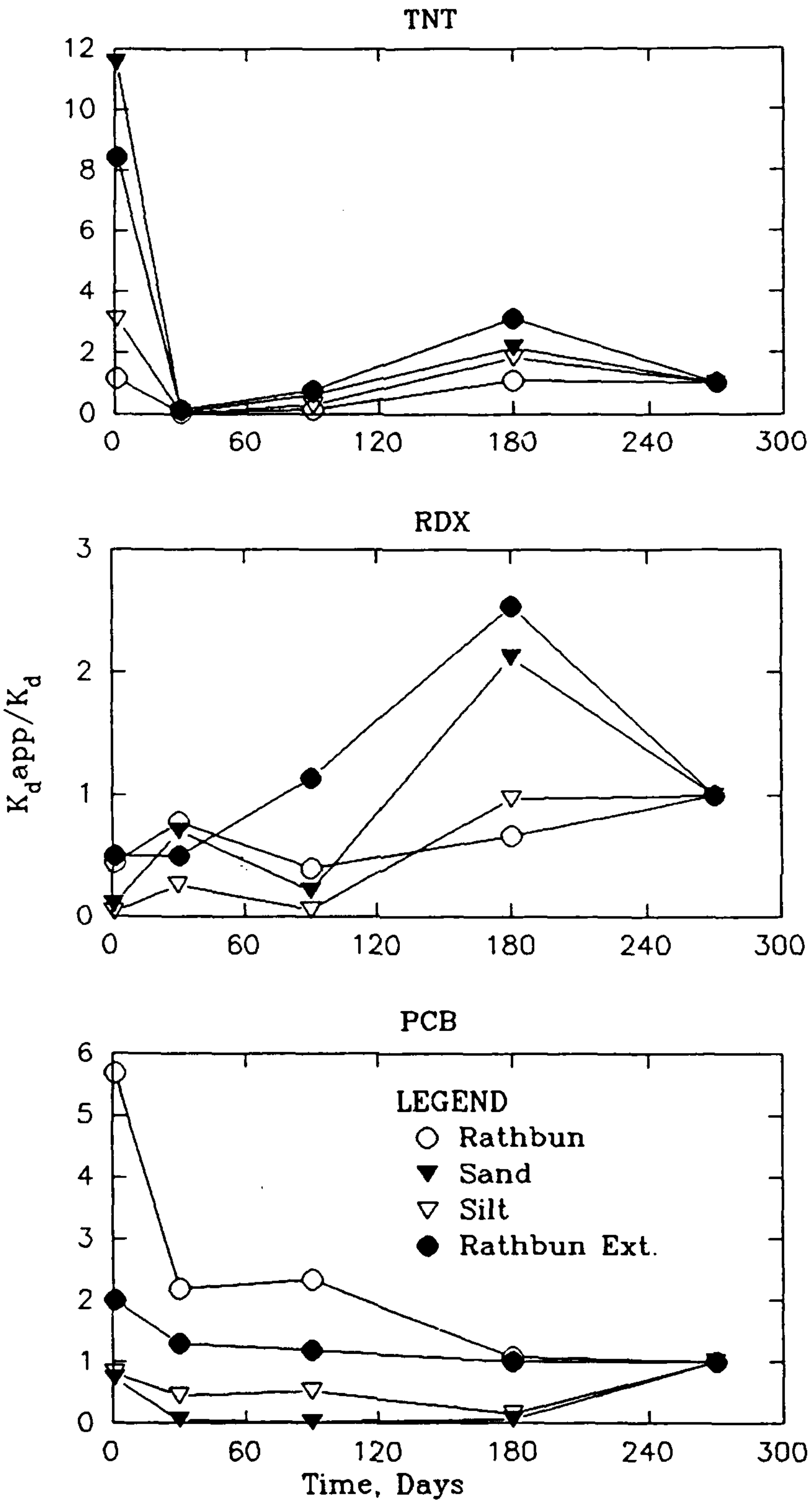

Figure 11. Normalized pore water apparent distribution coefficients versus time

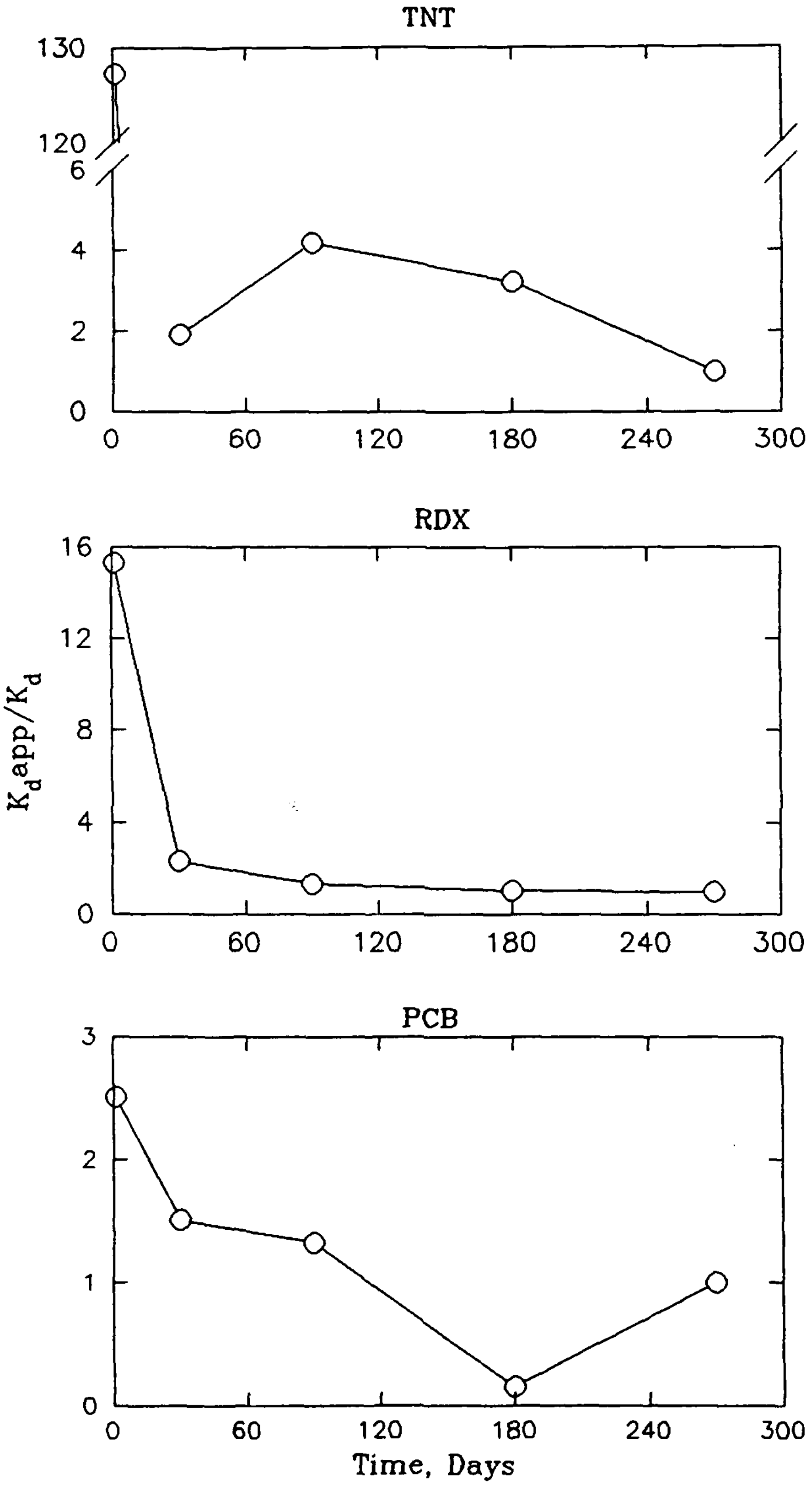

Figure 12. Normalized pore water apparent distribution coefficients versus time for activated carbon

Table 1
Equations for the Homogeneous Surface Diffusion Model

Equation	Role
$\frac{dC_b}{dt} V = -M \frac{dq_{avg}}{dt}$	Mass balance for closed batch test
$q_{avg} = \frac{3}{(d_p/2)^3} \int_0^{d_p/2} q(r,t)\, r^2\, dr$	Average sorbent load
$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial q}{\partial r})$	Diffusion equation for a spherical particle
$q(r,0) = 0 \quad for \quad r = 0$	Initial condition
$\frac{\partial q}{\partial r} = 0 \quad for \quad r = 0$	Boundary condition for center of spherical particle
$\rho_p D_s \frac{\partial q}{\partial r} = K_f (C_b - C_s)$	Boundary condition for continuity of flux at r = $d_p/2$
$q_s = f(C_b)$	Linear, Freundlich, or Langmuir isotherm equation for equilibrium at solid-liquid interface

where

C_b = bulk liquid adsorbate concentration, M/L^3
V = liquid volume, L^3
M = mass of sorbent, M
t = time
q_{avg} = average surface load on the carbon, M/M
d_p = particle diameter, L
q(r,t) = concentration along the inner surface of the particle, M/M
r = radial distance, L
D_s = surface diffusion coefficient, L^2/T
ρ_p = particle density, M/L^3
K_f = liquid film transfer coefficient, L/T
C_s = solid-liquid interface adsorbate concentration, M/L^3
q_s = solid phase concentration at the solid-liquid interface, M/M

Table 2
Physical and Chemical Characteristics of Soils and Activated Carbon

Sample	Particle Size %			Total Organic Carbon %	Cation Exchange Capacity meq/100 g
	Clay	Silt	Sand		
Sand	2.5	2.5	95	0.036	1.73
Activated Carbon	*	*	*	94.0**	41.0
Rathbun	***	***	***	9.13****	168.0
Rathbun Extracted	16.5	20.9	62.6	0.92	114.0
Silt	6.3	93.8	0.0	0.96	73.0

* = 90% of sample had a particle size less than 45 microns as determined by dry seiving
** = Total carbon concentration determined gravametrically (see text)
*** = Preponderance of undecomposed organic matter interfered with particle size determination
**** = Deterimined by loss on ignition

Table 3
Concentration of Contaminants [mg/l(Standard Error)] in Pore Water

	Activated Carbon	Sand	Silt	Rathbun Extracted	Rathbun
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.0026(0.0010)	0.0108(0.0036)	0.0033(0.0006)	0.0006(0.0004)	0.101(0.0042)
30 PCB	0.0044(0.0006)	0.0148(0.0046)	0.0060(0.0024)	0.0017(0.0010)	0.154(0.0065)
90 PCB	0.005(0.0024)	0.0137(0.0003)	0.0052(0.0031)	0.0016(0.0009)	0.168(0.0037)
180 PCB	0.0431(0.0257)	0.048(0.046)	0.0180(0.0010)	0.0035(0.0020)	0.196(0.0043)
270 PCB	0.0066(0.001)	0.0080(0.0017)	0.0027(0.0003)	0.0038(0.0005)	0.199(0.0047)
1 TNT	0.0001(0.000005)	0.0302(0.0015)	0.0034(0.0020)	0.0023(0.0004)	0.0096(0.0021)
30 TNT	0.0086(0.0018)	3.83(1.17)	0.374(0.0748)	0.0738(0.0161)	0.573(0.0460)
90 TNT	0.0039(0.00053)	0.524(0.128)	0.0358(0.0024)	0.0219(0.0088)	0.123(0.026)
180 TNT	0.0051(0.0028)	0.159(0.0358)	0.0572(0.0029)	0.0025(0.0004)	0.0300(0.0040)
270 TNT	0.0164(0.0024)	0.330(0.154)	0.0104(0.0054)	0.0027(0.103)	0.0929(0.0503)
1 RDX	0.0045(0.0003)	8.33(0.733)	5.51(0.560)	2.04(0.103)	2.03(0.0741)
30 RDX	0.0185(0.0052)	1.76(0.632)	0.768(0.203)	0.823(0.405)	1.25(0.791)
90 RDX	0.0323(0.0080)	3.88(1.33)	2.88(0.0877)	1.42(0.294)	0.631(0.251)
180 RDX	0.0408(0.0101)	0.672(0.407)	0.219(0.0227)	0.933(0.381)	0.289(0.0122)
270 RDX	0.0430(0.0090)	1.31(0.620)	0.211(0.0215)	0.650(0.335)	0.690(0.460)

Table 4
Concentration of Contaminants [mg/l(Standard Error)] in Each of the Four Sequential Aqueous Extracts of Sand

	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.2093(0.1921)	0.1549(0.1136)	0.0475(0.0402)	0.0556(0.0193)
30 PCB	0.0061(0.0027)	0.0031(0.0005)	0.0021(0.0002)	0.0046(0.0011)
90 PCB	0.0206(0.0111)	0.0239(0.0141)	0.0246(0.0137)	0.0243(0.0138)
180 PCB	0.0116(0.0042)	0.0290(0.0133)	0.0313(0.0262)	0.0026(0.0002)
270 PCB	0.0107(0.0038)	0.0023(0.0001)	0.0032(0.0004)	0.0163(0.0129)
1 TNT	0.0089(0.0001)	0.0032(0.0001)	0.0011(0.00004)	0.0005(0.00004)
30 TNT	1.0012(0.2612)	0.3238(0.0634)	0.1254(0.0105)	0.0645(0.0053)
90 TNT	0.1390(0.0286)	0.0481(0.0104)	0.0182(0.0032)	0.0098(0.0008)
180 TNT	0.0441(0.0099)	0.0144(0.0036)	0.0066(0.0016)	0.0045(0.0009)
270 TNT	0.0851(0.0393)	0.0323(0.0150)	0.0135(0.0057)	0.0084(0.0034)
1 RDX	2.2161(0.2280)	0.5566(0.0554)	0.1497(0.0146)	0.0419(0.0054)
30 RDX	0.4470(0.1589)	0.1175(0.0413)	0.0321(0.0112)	0.0092(0.0030)
90 RDX	1.0002(0.3463)	0.2575(0.0915)	0.0720(0.0227)	0.0173(0.0061)
180 RDX	0.1801(0.099)	0.0481(0.0273)	0.0142(0.0078)	0.0043(0.0023)
270 RDX	0.3469(0.1688)	0.0934(0.0454)	0.0251(0.0127)	0.0068(0.0035)

Table 5
Concentration of Contaminants [mg/l(Standard Error)] in Each of the Four Sequential Aqueous Extracts of Silt

	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.0070(0.0005)	0.0064(0.0021)	0.0060(0.0003)	0.0492(0.0354)
30 PCB	0.0022(0.0003)	0.0100(0.0042)	0.0029(0.0003)	0.0057(0.0005)
90 PCB	0.0072(0.0016)	0.0078(0.0047)	0.0056(0.0009)	0.0075(0.0011)
180 PCB	0.0101(0.0035)	0.0071(0.0017)	0.0122(0.0020)	0.0100(0.0024)
270 PCB	0.0089(0.0019)	0.0093(0.0024)	0.0087(0.0011)	0.0096(0.0011)
1 TNT	0.0021(0.0001)	0.0016(0.0001)	0.0012(0.00004)	0.0008(0.0001)
30 TNT	0.2524(0.0435)	0.1693(0.0236)	0.1421(0.0206)	0.1173(0.0234)
90 TNT	0.0221(0.0015)	0.0146(0.0008)	0.0100(0.0009)	0.0078(0.0007)
180 TNT	0.0047(0.0010)	0.0034(0.0006)	0.0026(0.0004)	0.0021(0.0003)
270 TNT	0.0065(0.0033)	0.0054(0.0028)	0.0047(0.0025)	0.0040(0.0025)
1 RDX	3.0888(0.3150)	1.7869(0.1622)	1.0887(0.1169)	0.6369(0.0473)
30 RDX	0.4442(0.1152)	0.2880(0.0736)	0.1816(0.0442)	0.1113(0.0229)
90 RDX	1.6003(0.4659)	0.9825(0.2869)	0.5573(0.1562)	0.3228(0.0882)
180 RDX	0.1158(0.0132)	0.0728(0.0093)	0.0452(0.0056)	0.0306(0.0037)
270 RDX	0.1210(0.0104)	0.0731(0.0064)	0.0397(0.0030)	0.0277(0.0024)

Table 6
Concentration of Contaminants [mg/l(Standard Error)] in Each of the Four Sequential Aqueous Extracts of Rathbun

	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.0024(0.0001)	0.0033(0.0006)	0.0023(0.0001)	0.0012(0.0002)
30 PCB	0.0071(0.0038)	0.0072(0.0025)	0.0009(0.00004)	0.0018(0.0001)
90 PCB	0.0049(0.0011)	0.0045(0.0005)	0.0058(0.0013)	0.0058(0.0013)
180 PCB	0.0062(0.0009)	0.0046(0.0015)	0.0059(0.0027)	0.0047(0.0016)
270 PCB	0.0044(0.0010)	0.0043(0.0022)	0.0041(0.0015)	0.0060(0.0028)
1 TNT	0.0014(0.0002)	0.0012(0.0002)	0.0008(0.0001)	0.0006(0.0001)
30 TNT	0.0509(0.0114)	0.0367(0.0089)	0.0321(0.0083)	0.0292(0.0054)
90 TNT	0.0478(0.0190)	0.0300(0.0127)	0.0267(0.0126)	0.0193(0.0089)
180 TNT	0.0015(0.0002)	0.0013(0.0002)	0.0010(0.0001)	0.0010(0.0002)
270 TNT	0.0017(0.0003)	0.0013(0.0002)	0.0014(0.0003)	0.0018(0.0004)
1 RDX	1.4705(0.0837)	1.0682(0.0650)	0.8199(0.0382)	0.6102(0.0536)
30 RDX	0.5693(0.2760)	0.3911(0.1829)	0.2881(0.1313)	0.2043(0.0892)
90 RDX	0.9285(0.2004)	0.6348(0.1285)	0.4631(0.0964)	0.3279(0.0647)
180 RDX	0.5557(0.2274)	0.4305(0.1760)	0.2979(0.1196)	0.2788(0.0948)
270 RDX	0.4150(.2110)	0.2740(0.1430)	0.1940(0.1010)	0.1430(0.0752)

Table 7
Concentration of Contaminants [mg/l(Standard Error)] in Each of the Four Sequential Aqueous Extracts of Rathbun Extracted

	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.0715(0.0022)	0.0812(0.0035)	0.2520(0.0825)	0.0988(0.0457)
30 PCB	0.0677(0.0049)	0.00897(0.0144)	0.0144(0.0116)	0.0799(0.0021)
90 PCB	0.0649(0.0036)	0.1123(0.0033)	0.0679(0.0060)	0.0590(0.0120)
180 PCB	0.0762(0.0083)	0.1879(0.0144)	0.0885(0.0135)	0.1496(0.0269)
270 PCB	0.0842(0.0016)	0.1483(0.0286)	0.0735(0.0048)	0.1045(0.0075)
1 TNT	0.0025(0.0007)	0.0030(0.0006)	0.0030(0.0006)	0.0029(0.0004)
30 TNT	0.1592(0.0282)	0.0890(0.0110)	0.1198(0.0080)	0.1088(0.0066)
90 TNT	0.0263(0.0045)	0.0269(0.0060)	0.0233(0.0059)	0.0216(0.0051)
180 TNT	0.0103(0.0014)	0.0058(0.0008)	0.0051(0.0005)	0.0049(0.0007)
270 TNT	0.0392(0.0220)	0.0172(0.0097)	0.0201(0.0113)	0.0183(0.0104)
1 RDX	0.7051(0.1203)	0.7645(0.0212)	0.6086(0.0237)	0.5100(0.0617)
30 RDX	0.3801(0.1470)	0.3195(0.0586)	0.2038(0.0841)	0.1271(0.0420)
90 RDX	0.1385(0.0260)	0.0834(0.0642)	0.0891(0.0359)	0.0585(0.0214)
180 RDX	0.0937(0.0020)	0.0209(0.0021)	0.0270(0.0018)	0.0177(0.0024)
270 RDX	0.1710(0.1000)	0.1010(0.0613)	0.0730(0.0441)	0.0572(0.0369)

Table 8
Concentration of Contaminants [mg/l(Standard Error)] in Each of the Four Sequential Aqueous Extracts of Activated Carbon

	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
Time(Days)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)	Mean(Std Err)
1 PCB	0.0009(0.0005)	0.0002(0.0001)	0.0004(0.0001)	0.0001(0.0001)
30 PCB	0.000007(0.000006)	0.00001(0.000003)	0.00002(0.00001)	0.0001(0.00005)
90 PCB	0.0003(0.0001)	0.0002(0.0001)	0.0001(0.00002)	0.0003(0.0001)
180 PCB	0.0041(0.0030)	0.0005(0.0003)	0.0003(0.00004)	0.0007(0.0001)
270 PCB	0.00002(0.00004)	0.0002(0.00003)	0.0002(0.0001)	0.0002(0.000004)
1 TNT	0.0001(0.000004)	0.0001(0.000002)	0.0001(0.000001)	0.00001(0.000003)
30 TNT	0.0023(0.0004)	0.0004(0.00006)	0.0012(0.0001)	0.0008(0.0001)
90 TNT	0.0017(0.0005)	0.0013(0.0002)	0.0007(0.0002)	0.0005(0.00003)
180 TNT	0.0004(0.0001)	0.0006(0.0006)	0.0008(0.0005)	0.0002(0.0001)
270 TNT	0.0017(0.0004)	0.0012(0.0002)	0.0010(0.0002)	0.0004(0.0001)
1 RDX	0.0104(0.0013)	0.0161(0.0015)	0.0257(0.0026)	0.0240(0.0017)
30 RDX	0.0087(0.0019)	0.0071(0.0015)	0.0062(0.0020)	0.0098(0.0055)
90 RDX	0.0194(0.0051)	0.0143(0.0038)	0.0102(0.0026)	0.0004(0.0001)
180 RDX	0.0230(0.0057)	0.0153(0.0038)	0.0108(0.0026)	0.0080(0.0023)
270 RDX	0.0318(0.0038)	0.0215(0.0019)	0.0138(0.0012)	0.0067(0.0002)

Table 9
Distribution Coefficients (L/Kg) Between Water and Soil

Time (Days)	Sand		Silt		Rathbun		Rathbun Extracted		Activated Carbon	
	Kd	r^2	Kd	r^2	Kd	r^2	Kd	r^2	Kd	r^2
1 RDX	0.285(0.004)	0.999	1.20(0.022)	0.999	4.18(0.127)	0.998	8.44(4.27)	0.661	NLR	NLR
30 RDX	0.301(0.003)	0.999	1.46(0.034)	0.999	3.48(0.125)	0.997	3.43(0.67)	0.928	NLR	NLR
90 RDX	0.294(0.004)	0.999	1.21(0.041)	0.998	3.40(0.117)	0.998	3.85(1.34)	0.805	NLR	NLR
180 RDX	0.313(0.006)	0.999	1.43(0.036)	0.999	4.67(0.70)	0.957	0.899(0.50)	0.614	0.27(0.04)	0.958
270 RDX	0.305(0.0004)	0.999	1.22(0.07)	0.994	3.17(0.18)	0.994	2.78(0.04)	0.961	4.26(0.45)	0.978
1 TNT	0.473(0.012)	0.998	2.23(0.16)	0.989	4.45(0.69)	0.955	NLR	NLR	27.1(9.1)	0.817
30 TNT	0.442(0.03)	0.991	1.22(0.67)	0.025	5.95(1.36)	0.905	3.18(4.19)	0.223	NLR	NLR
90 TNT	0.475(0.028)	0.993	1.84(0.14)	0.988	3.76(0.73)	0.929	15.7(5.55)	0.801	3.22(0.87)	0.872
180 TNT	0.497(0.07)	0.962	2.63(0.24)	0.983	7.66(2.4)	0.835	3.31(1.33)	0.756	NLR	NLR
270 TNT	0.517(0.015)	0.998	4.85(0.13)	0.998	NLR	NLR	2.08(1.89)	0.375	NLR	NLR
1 PCB	121(39)**	NLR	1218(342)	NLR	4989(1196)	NLR	87(20)	NLR	43150(17812)	NLR
30 PCB	2924(671)	NLR	2670(792)	NLR	4892(2356)	NLR	458(193)	NLR	800000(305000)	NLR
90 PCB	423(19)	NLR	1449(117)	NLR	1919(124)	NLR	130(16)	NLR	66877(23500)	NLR
180 PCB	1317(821)	NLR	1071(114)	NLR	1919(145)	NLR	85(18)	NLR	16551(5644)	NLR
270 PCB	2245(886)	NLR	1096(24)	NLR	2182(180)	NLR	97(14)	NLR	104(15)	NLR

NLR = No Linear Relationship
*** Computed Using Single Point Distribution Coefficients

Table 10
Concentrations of Contaminants in Sand (ug/g [Standard Error]) Following Sequential Extraction

Time (Days)	Concentration Sorbed to Soil	Water	Acetone	Humic/Fulvic	Residue
1 PCB	9.989	0.398(0.303)	4.11(1.48)	NA*	0.01(0.003)
30 PCB	9.996	0.024(0.001)	6.98(0.50)	NA	0.01(0.001)
90 PCB	9.894	0.221(0.167)	7.21(0.82)	NA	0.006(0.002)
180 PCB	9.968	0.093(0.052)	7.34(0.39)	NA	0.013(0.001)
270 PCB	9.998	0.029(0.013)	6.79(0.52)	NA	0.009(0.002)
1 TNT	9.969	0.042(0.006)	0.003(0.0003)	NA	0.008(0.002)
30 TNT	5.289	2.19(0.565)	0.45(0.11)	NA	0.36(0.03)
90 TNT	9.384	0.307(0.065)	0.115(0.04)	NA	0.09(0.02)
180 TNT	9.807	0.095(0.022)	0.069(0.023)	NA	0.06(0.03)
270 TNT	9.443	0.165(0.07)	0.101(0.033)	NA	0.07(0.03)
1 RDX	5.62	12.56(1.10)	0.017(0.002)	NA	0.005(0.001)
30 RDX	8.36	0.989(0.365)	0.009(0.005)	NA	0.009(0.003)
90 RDX	6.29	2.19(0.77)	0.006(0.002)	NA	0.03(0.02)
180 RDX	9.14	0.28(0.16)	0.004(0.0007)	NA	0.012(0.003)
270 RDX	8.66	0.65(0.31)	0.004(0.0014)	NA	0.008(0.0005)

* Not Conducted for Sand Because of Low Organic Carbon Content.

Table 11
Concentration of Contaminants in Silt (ug/g [Standard Error]) Following Sequential Extraction

Time (Days)	Concentration Sorbed to Soil	Water	Acetone	Humic/Fulvic	Residue
1 PCB	9.9967	0.0616(0.028)	7.63(1.83)	0.006(0.001)	0.20(0.04)
30 PCB	9.9988	0.027(0.0046)	9.23(0.19)	0.004(0.001)	0.05(0.005)
90 PCB	9.9996	0.037(0.0048)	9.75(0.67)	0.003(0.007)	0.04(0.003)
180 PCB	9.996	0.035(0.0069)	8.03(0.39)	0.003(0.002)	0.09(0.01)
270 PCB	9.999	0.031(0.0054)	9.77(0.084)	0.008(0.001)	0.10(0.009)
1 TNT	9.997	0.0085(0.00027)	0.022(0.0012)	0.010(0.005)	0.023(0.003)
30 TNT	9.626	0.700(0.090)	2.41(0.44)	1.83(0.26)	3.56(0.32)
90 TNT	9.973	0.054(0.0021)	0.30(0.017)	0.278(0.06)	0.47(0.04)
180 TNT	9.994	0.013(0.002)	0.08(0.028)	0.06(0.02)	0.11(0.008)
270 TNT	9.991	0.018(0.009)	0.094(0.051)	0.133(0.051)	0.26(0.11)
1 RDX	10.039	12.01(0.53)	1.03(0.015)	0.003(0.002)	0.03(0.001)
30 RDX	9.522	1.05(0.213)	0.217(0.05)	0.016(0.003)	0.018(0.002)
90 RDX	8.22	4.25(0.83)	0.619(0.162)	0.121(0.057)	0.19(0.10)
180 RDX	9.848	0.276(0.009)	0.084(0.0086)	0.012(0.0003)	0.01(0.0008)
270 RDX	9.76	0.30(0.16)	0.06(0.004)	0.021(0.004)	0.014(0.003)

Table 12
Concentration of Contaminants in Rathbun soil (ug/g [Standard Error]) Following Sequential Extraction

Time (Days)	Concentration Sorbed to Soil	Water	Acetone	Humic/Fulvic	Residue
1 PCB	9.996	0.016(0.0006)	9.87(0.23)	0.146(0.10)	0.46(0.06)
30 PCB	9.991	0.046(0.013)	7.42(0.94)	0.004(0.002)	0.11(0.02)
90 PCB	9.994	0.049(0.002)	8.31(1.25)	0.010(0.002)	0.08(0.03)
180 PCB	9.992	0.038(0.007)	8.37(0.48)	0.007(0.002)	0.19(0.04)
270 PCB	9.995	0.030(0.011)	9.93(0.34)	0.007(0.001)	0.28(0.03)
1 TNT	9.996	0.011(0.0008)	0.039(0.004)	0.014(0.002)	0.04(0.01)
30 TNT	9.882	0.33(0.047)	1.57(0.47)	1.51(0.10)	3.24(0.33)
90 TNT	9.933	0.196(0.076)	1.18(0.31)	0.703(0.118)	1.56(0.33)
180 TNT	9.996	0.011(0.0009)	0.097(0.017)	0.074(0.01)	0.13(0.02)
270 TNT	9.984	0.011(0.002)	0.091(0.017)	0.144(0.023)	0.21(0.07)
1 RDX	12.32	9.28(0.34)	3.04(0.29)	*0.128(0.01)*	*0.14(0.03)*
30 RDX	9.62	2.39(0.97)	1.17(0.52)	0.057(0.03)	0.10(0.05)
90 RDX	9.22	5.42(0.70)	1.59(0.28)	0.124(0.04)	0.11(0.02)
180 RDX	9.45	2.40(0.86)	1.18(0.48)	0.078(0.003)	0.11(0.05)
270 RDX	8.864	1.69(0.76)	0.79(0.40)	0.107(0.059)	0.18(0.10)

Table 13

Concentration of Contaminants in Rathbun Extracted Soil (ug/g [Standard Error]) Following Sequential Extraction

Time (Days)	Concentration Sorbed to Soil	Water	Acetone	Humic/Fulvic	Residue
1 PCB	9.847	0.87(0.094)	8.42(2.24)	0.009(0.0003)	0.10(0.0007)
30 PCB	9.787	0.97(0.008)	5.59(0.23)	0.002(0.001)	0.08(0.009)
90 PCB	9.767	0.88(0.03)	8.11(0.53)	0.042(0.02)	0.07(0.009)
180 PCB	9.691	1.03(0.011)	5.86(0.11)	0.002(0.001)	0.09(0.008)
270 PCB	9.712	0.87(0.035)	6.36(0.22)	0.003(0.001)	0.12(0.01)
1 TNT	8.59	0.03(0.005)	0.024(0.003)	0.011(0.002)	0.03(0.01)
30 TNT	9.29	1.39(0.189)	0.60(0.093)	0.601(0.25)	1.13(0.46)
90 TNT	9.85	0.289(0.04)	0.134(0.018)	0.05(0.01)	0.27(0.09)
180 TNT	9.96	0.078(0.008)	0.03(0.003)	0.011(0.002)	0.07(0.02)
270 TNT	9.86	0.274(0.13)	0.10(0.04)	0.025(0.012)	0.27(0.19)
1 RDX	13.08	6.39(0.63)	0.997(0.16)	0.057(0.02)	0.26(0.07)
30 RDX	8.197	3.27(0.91)	0.679(0.20)	0.065(0.03)	0.26(0.08)
90 RDX	9.354	1.17(0.24)	0.193(0.05)	0.03(0.006)	0.20(0.02)
180 RDX	9.550	0.68(0.009)	0.07(0.003)	0.031(0.005)	0.17(0.06)
270 RDX	8.999	1.58(0.82)	0.127(0.07)	0.056(0.027)	0.67(0.45)

Table 14
Concentration of Contaminants in Activated Carbon (ug/g [Standard Error]) Following Sequential Extraction

Time (Days)	Concentration Sorbed To Soil	Water	Acetone	Humic/Fulvic	Residue
1 PCB	9.991	0.013(0.002)	0.06(0.005)	NA*	7.61(0.34)
30 PCB	9.997	0.004(0.0003)	0.083(0.001)	NA	7.53(0.65)
90 PCB	9.997	0.006(0.002)	0.059(0.007)	NA	6.44(0.80)
180 PCB	9.978	0.036(0.02)	0.054(0.003)	NA	8.02(0.54)
270 PCB	9.996	0.006(0.0009)	0.064(0.005)	NA	8.78(0.68)
1 TNT	9.998	0.0011(0.0001)	0.0003(0.0001	NA	0.14(0.02)
30 TNT	9.992	0.018(0.003)	0.012(0.002)	NA	8.98(2.21)
90 TNT	9.997	0.013(0.0018)	0.021(0.007)	NA	6.12(0.37)
180 TNT	9.996	0.0072(0.003)	0.008(0.003)	NA	2.51(1.31)
270 TNT	9.9916	0.015(0.002)	0.133(0.021)	NA	6.69(0.44)
1 RDX	15.768	0.206(0.014)	6.38(0.18)	NA	3.87(0.33)
30 RDX	9.992	0.094(0.024)	3.09(0.56)	NA	3.32(0.71)
90 RDX	9.997	0.139(0.036)	1.86(0.41)	NA	2.24(0.52)
180 RDX	9.996	0.327(0.157)	2.55(0.61)	NA	2.98(0.73)
270 RDX	9.9665	0.207(0.017)	2.14(0.26)	NA	2.51(0.14)

* Not Conducted for Charcoal Because of Lack of Humic and Fulvic Acid Content

Table 15
Summary of Pore Water Adsorption Studies

HYPOTHESIS	SORBENT				
	Charcoal	Rathbun	WES Ref.	Rath. Ext.	Sand
Rapid Initial Adsorption	PCB TNT RDX	PCB TNT	PCB TNT	PCB TNT RDX	PCB TNT
Internal Diffusion		RDX	RDX		RDX
Competitive Adsorption		(RDX)	TNT (RDX)	TNT (RDX)	TNT (RDX)
Reactive Site Evolution				PCB	
Initial Formation of Micelles, Lamella, or Globules		TNT	TNT	TNT	TNT
Abiotic Chemical Transformation		TNT (RDX)	TNT (RDX)	TNT (RDX)	TNT (RDX)

Table 16
Classification of Desorption Isotherm Data

		SOIL			
Chemical	Day	Sand	Silt	Rathbun	Rath. Ext.
RDX	1	(Linear)	(Linear)	(Linear)	(Linear)
	30	(Linear)	(Linear)	(Linear)	(Linear)
	90	(Linear)	(Linear)	(Linear)	(Linear)
	180	(Linear)	(Linear)	(Linear)	(Linear)
	270	(Linear)	(Linear)	(Linear)	(Linear)
TNT	1	(Linear)	(Linear)	(Linear)	Indeterm.
	30	(Linear)	Indeterm.	(Linear)	(Linear)
	90	(Linear)	(Linear)	(Linear)	Indeterm.
	180	(Linear)	(Linear)	(Linear)	Indeterm.
	270	(Linear)	(Linear)	Indeterm.	Indeterm.
PCB	1	(Linear)	Indeterm.	(Linear)	Indeterm.
	30	Indeterm.	Indeterm.	(Linear)	(Linear)
	90	Indeterm.	Indeterm.	Indeterm.	Indeterm.
	180	Indeterm.	Indeterm.	Indeterm.	Indeterm.
	270	Indeterm.	Indeterm.	Indeterm.	Indeterm.