EQUILIBRIUM AND KINETIC STUDIES OF ATRAZINE ADSORPTION AND DESORPTION ON SOILS AND SOIL CONSTITUENTS

by

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ABSTRACT

Adsorption-desorption of pesticides is critical in controlling the concentration of pesticides in the soil solution and thus the amount that will be leached. Equilibrium and kinetic aspects of atrazine adsorption-desorption were investigated on humic acid, montmorillonite, vermiculite, goethite, humic acid-coated montmorillonite and goethite, and two selected Delaware soils. The equilibrium and long-term kinetic studies were carried out using a batch technique. The short-term kinetic studies on vermiculite were conducted using a stirred-flow method. The equilibrium studies showed that adsorption of atrazine on humic acid (K_d= 95.60 L Kg^{-1}) was considerably higher than on montmorillonite (K_d=18.52 L Kg^{-1}) and vermiculite (K_d=26.80 LKg^{-1}). Adsorption of atrazine on goethite was negligible. Humic acid coatings significantly increased atrazine adsorption on montmorillonite and goethite. Atrazine adsorption-desorption on montmorillonite was completely reversible, while nonsingularities were observed for vermiculite and humic acid. The short-term adsorption kinetic studies on vermiculite indicated that a concentration-dependent kinetic model is suitable to describe the reaction rates. The long-term kinetic studies indicated that atrazine adsorption-desorption on humic acid continued up to 90 days, while equilibrium on montmorillonite was reached in 2 h. The humic acid coating on montmorillonite decreased the reaction rate compared to that observed on the uncoated montmorillonite. Adsorption-desorption on a Pocomoke surface soil, which has a high organic matter (OM) content was slower than on a Matapeake subsoil which was mainly a mineral soil with a low organic matter content. A two-site model and a radial pore diffusion model described the kinetics reasonably well, capturing the fast initial desorption and the relatively slow desorption that followed.

INTRODUCTION

Groundwater pollution from agricultural organic chemicals has become an important national and global concern. Atrazine is one of the most widely used pesticides for weed control of corn and other broadleaf crops in Delaware and throughout the country. Atrazine is also the most frequently detected pesticide in groundwater. A thorough understanding of the chemical, physical and biological processes that affect groundwater pollution is vital for the prevention of the pollution problem.

Once a pesticide is applied to the environment it may be adsorbed, transported or degraded. Adsorption-desorption of herbicides is critical in controlling the concentration of herbicides in the soil solution and thus the amount that can be leached. A knowledge of these processes is particularly needed for soils in the Delmarva region, since these soils are characterized by high sand and low organic matter contents. In these soils, contaminants such as pesticides are more prone to leach. Very few studies have been conducted on the kinetics of pesticide reactions in soils, and particularly, the desorption rates of pesticides from soils. Moreover, many current transport and degradation models account for sorption by assuming an equilibrium distribution of the contaminant, but there is a growing body of evidence that sorption and desorption may not reach equilibrium within time scales characteristic of solute transport or degradation. Such rate limitations can influence contaminant transport in the subsurface and may potentially hinder remediation efforts.

Accordingly, the objectives of this study were: to measure the kinetics of atrazine adsorption and desorption on major soil constituents, humic acid, montmorillonite, goethite, these constituents coated with humic acid, and on selected Delmarva soils; and to investigate the characteristics of the adsorption-desorption process, such as the affinity of the selected soil constituents for atrazine, adsorption-desorption hysteresis, and the factors affecting these process, i. e., pH values.

A unique aspect of the kinetic studies is their long-term nature: such investigations more closely mimic the slow time-dependent reactions that occur in the field. Humic acid-coated montmorillonite and goethite were selected as sorbents because they more realistically represent natural soil surfaces. In natural soils, constituents may not exist as separate entities. For example, organic matter and clay can form organo-clay complexes. Oxides and hydroxides may exist in soils as separate phases but most likely they exist as coatings or surface layers on aluminosilicates. Oxides can also form complexes with soil humic substances through ligand exchange reactions. The commonly used methods for selectively dissolving soil components (e. g., H_2O_2 for organic matter and Na-dithionite-citrate-bicarbonate for iron oxides) may cause dissolution of these complexes and create totally new surfaces. Thus, the relative importance of each component responsible for pesticide adsorption and the mutual interaction of soil constituents and their effects on pesticide adsorption can be explored by investigating three groups of samples, as was employed in this study: pure soil constituents, coated constituents, and natural soils.

Chapter 1

EQUILIBRIUM STUDIES OF ATRAZINE ADSORPTION-DESORPTION

1.1 Introduction

Adsorption-desorption phenomena are critical in controlling the distribution of pesticides in soils. They influence concentrations in the soil solution and thus, intimately affect transport and adsorption by living organisms. The distribution of a pesticide between the liquid and the adsorbed phases affects the phytotoxicity and selectivity of pesticides, their effects on non-target organisms, and potential for surface and groundwater pollution. Most pesticides have low vapor pressures, and even in unsaturated soils there are generally several layers of water molecules on the solid surfaces. Therefore, the dominant phenomenon involved in pesticide interactions with soils is adsorption at the solid-water interface.

Most agricultural soils are mixtures of different materials: organic matter, microbial biomass, and inorganic crystalline and noncrystalline components. The particle size of minerals varies from colloidal dimensions to pebbles. Soil-pesticide interactions may be better understood if the interactions of the soil components including organic matter, clay, and other inorganic minerals with pesticide are better understood. The amount of pesticide sorbed by a given soil is influenced by properties of the soils and of the pesticides. Important properties related to the soil's retention ability would include: the clay mineralogy, organic matter content, soil pH and the amount of iron and aluminum oxides. These properties would then in turn affect the cation and anion exchange capacities (Bailey and White, 1970). Important properties of the pesticide would include the charge, polarity, and size (Green, 1974). Since some pesticides are ionizable, the charge of a pesticide can be influenced by the soil pH.

1.1.1 Pesticide Sorption on Soil Organic Matter

It is widely accepted that the retention of pesticides by natural soils is most readily affected by the soil organic matter content (Sullivan and Felbeck, 1968; Weber et al., 1969; Wershaw et al., 1969; Bouchard and Lavy, 1985; Clay et al., 1988). Quite often, organic matter content is the only parameter that is correlated with the adsorption of pesticides on soils. There is some evidence suggesting that small amounts of organic matter can effectively block the soil mineral surface. Thus, the mineral surface is no longer an effective adsorbent for pesticides (Hance, 1969; Walker and Crawford, 1968). Most pesticides contain hydrophobic regions, therefore entropy generation could be important in their adsorption on hydrophobic soil organic matter. However, charge transfer and dipole interactions are also likely mechanisms for adsorption. Senesi and Testini (1983) used electron spin resonance (ESR) techniques to study the adsorption mechanisms of atrazine on soil organic materials.

They found that s-triazines are adsorbed by humic acids, forming stable complexes via ionic bonding, proton transfer, and hydrogen bonding.

The adsorption of nonionic organic compounds (NOC) on soils is generally characterized by adsorption isotherms that are approximately linear over a substantial concentration range, and they can be adequately described by a constant distribution coefficient, K_d. The K_d values are generally correlated with the organic carbon content of the soil. By attributing all the sorption to organic matter, an organic carbon partition coefficient, K_{oc}, can be defined as,

$$K_{oc} = \frac{K_d}{f_{oc}}$$

where f_{oc} is the mass fraction of organic carbon in the soil. The K_{oc} values typically correlate well with properties of the sorbate, such as the aqueous solubility (S) or the octanol-water partition coefficient (K_{ow}). The correlation of K_{oc} to K_{ow} has led to the definition of linear relationships of the form,

$$\log K_{oc} = a \log K_{ow} + b$$

where a and b are constants resulting from a regression analysis.

In addition to the dependence of sorption on the organic fraction of the sorbent and the K_{ow} of the sorbate, Chiou et al. (1989) cited the following observations as support for the hypothesis that the sorptive mechanism of NOC is hydrophobic partitioning onto the organic fractions of soils: (1) the linearity of the isotherms as the concentration approaches the solubility of the sorbate, (2) the small effect of temperature on sorption of the organics, and (3) the lack of competition between sorbates for the sorbent.

Although the importance of organic matter in pesticide adsorption is well established, the properties of the organic colloids relevant to the adsorption are not well understood. We know that humic substances are composed of humic acid, fuvic acid, and humin, they have functional groups such as carboxyl, hydroxyl, carbonyl, methoxy, and amino, and they have high cation exchange capacity and surface area (Weed and Weber, 1974; Burchill et al., 1981).

1.1.2 Pesticide Sorption on Clay Minerals

Evidence exists that pesticides and other hydrophobic organic compounds interact more strongly with clay minerals than with the remaining larger soil particles such as sand and silt. Karickhoff and Brown (1978) reported that in natural sediments, where the coarse clay fraction accounted for less than 1% of the sediment mass, it contained 50-60% of the sorbed pesticide. The sand fraction, which accounted for as much as 99% of the sediment mass, always contained less than 10% of the sorbed pesticide. Karickhoff (1984) has noted that natural clay mineral surfaces will most likely have organic slime, microbial biomass, humic substances, or polymeric oxide and hydroxide coatings. Karickhoff et al. (1979) have showed that different amounts of organic carbon (OC) correlated with the different sediment size fractions and may be responsible for the different sorption behaviors of the size fractions.

Pesticide sorption on specific clay minerals has been studied by several workers (Karickhoff and Brown, 1978; Terrace and Calvet, 1978; Terrace, 1983; Borggaard and Streibig, 1988; Morillo et al., 1991; Laird et al., 1992). Of the various inorganic soil constituents, montmorillonite and vermiculite have the greatest potential for adsorption of pesticides due to their large surface area and abundance in agricultural soils. Terrace and Calvet (1978) have examined pesticide sorption on montmorillonite, illite, and kaolinite and correlated the amount of pesticide sorbed to the surface area and the cation exchange capacity (CEC) per unit mass of the clay. Montmorillonite had the highest surface area and CEC and thus sorbed the greatest quantity of pesticides. Glass (1987) reported that glyphosate is preferentially adsorbed by the clay minerals in the order montmorillonite > illite > kaolinite. Glyphosate sorption on montmorillonite decreased in the order $Fe^{3+} > Cu^{2+} > Mg^{2+} > Ca^{2+} > Na^{+}$ montmorillonite. Chopra et al. (1984) found that the adsorption of simazine depends on clay type and increased in the order bentonite > pyrophyllite > illite > kaolinite. Triazine is adsorbed on interlamellar surfaces of expanding clays. As a result of this process, Weber et al. (1965) found that the basal spacing in montmorillonite was expanded by the adsorption of prometone.

Investigations on reactions between weak basic pesticides and clay minerals have demonstrated that both protonated and neutral species are adsorbed as interlayer complexes (Weber, 1970; Ainsworth et al., 1987; Micera et al., 1988; Rodriguez et al., 1988). Ainsworth et al. (1987) suggested that protonated species were adsorbed preferentially over neutral species even when the pH of the smectite suspension is substantially greater than the equilibrium constant of the pesticide. Such preferential adsorption of protonated species is attributed to "surface acidity" due to Bronsted acidity that arises from the enhanced ionization of water molecules in solution spheres of adsorbed inorganic cations. This promotes protonation of weak bases as they are adsorbed. Laird et al. (1992) have shown that adsorption of atrazine on smectite decreased with increasing surface charge density of the smectite, suggesting that atrazine was primarily adsorbed as a neutral species. X-ray diffraction studies showed that the s-triazines were adsorbed in the interlayer spacings of Na- and H-montmorillonite and that the (001) spacing increased with the amount of pesticide adsorbed.

1.1.3 Pesticide Sorption on Iron and Aluminum Oxides

Iron and Aluminum Oxides hydroxides are very important soil constituents due to their high surface reactivity. However, little information concerning interactions between them and pesticides is found in the scientific literature. After removing Al- and Fe- oxides from soil, Huang at al. (1984) found that adsorption of atrazine was significantly decreased. However, the amount of extractable Al and Fe in the different particle size fractions of the soil was not proportional to the adsorption, suggesting that different forms of oxides and hydroxides could have different reactivities for atrazine. Hilton and Yuen (1963) found that amorphous oxides in Hawaiian soils greatly increased the adsorption of pre-emergence herbicides. However, Borggaard and Streibig (1988) reported that only negligible amounts of atrazine were adsorbed by goethite.

1.1.4 Effect of pH on Pesticide Sorption

The pH of the soil solution is the most important factor that affects both absorbents and pesticides. The proton in the soil solution causes conformational modifications of humic substances and hydrolysis of clay surfaces. Maximium adsorption of s-triazines occurs near the pKa values. Bailey et al. (1968) indicated that surface acidity was the major factor affecting the adsorption of basic pesticides on montmorillonite. They showed that adsorption occurred to the greatest extent on a highly acid H-montmorillonite.

1.1.5 Sorption Mechanisms

Calvet (1980) groups bonding or adsorption mechanisms of pesticides on soil constituents into two main categories, depending on whether the bonds are strong (> 80 kJ/mol) or weak (<80 kJ / mol). Ionic and ligand exchange bonds are examples of strong interactions, while hydrogen bonding, van der Waals attractions and charge transfer bonding are examples of weak bonds. Pesticides can be divided into ionic and non-ionic types. There are three main groups of ionic pesticides: 1) permanent charge, such as the cationic herbicides paraquat and diquat; 2) weak bases, such as the s-trizines, which become cationic by protonation; and weak acids, such as 2,4-D and picloram, which become anionic by dissociation and loss of a proton.

Ion Exchange

Since soil contains positively and negatively charged sites, ionic molecules can be adsorbed by ion exchange. Aluminum and iron oxides can carry positive charge and hence can adsorb anions, such as 2,4-D, at pH values below the point of zero charge of the oxides.

Cationic and weakly basic pesticides can be adsorbed on clay minerals and soil organic matter by cation exchange. Two common cationic pesticides are paraquat and diquat. They are adsorded very strongly by clay minerals because their geometry allows the ionic bonding to be reinforced by short range forces such as charge transfer and van der Waals forces (Hayes, 1970). This was confirmed when Philen et al.(1970) found a linear relationship between the surface charge density of vermiculite and mica and the amount of paraquat and diquat adsorbed onto the mineral surfaces.

Cation exchange mechanisms are also responsible for the adsorption of protonated weak bases, such as the s-trizine herbicides, but these reactions are pH-dependent. Weakly basic pesticides such as 1,3,5-triazine can accept protons and become positively charged. The pK_a varies from 1.65 to over 4 for some of the methoxy and methylthio analogues. Although these values seem low compared with the pH values of normal soil suspensions, the surfaces of clays are much stronger proton donors than would be indicated by the pH of their aqueous suspensions

(Mortland and Meggitt, 1966). Therefore, ion exchange could make a significant contribution to the adsorption of triazines in some situations. Weber (1970) reported that the adsorption of a large number of triazines increased with decreasing solution pH, reaching a maximum at the pH value close to the pK_a of each organic compound.

Related to pH is the ionic balance of the system. Nearpass (1967) found that atrazine and simazine adsorption declined as the base saturation of the soil increased. Triazines are also adsorbed to a great extent on clays with high cation exchange capacities. Triazines appear to be adsorbed on cation exchange sites of soil organic matter, particularly humic acids (McGlamery and Slife, 1966; Gaillardon, 1975). Infrared spectra indicate that protonated triazine herbicides formed ionic bonds with the carboxylate anions of soil humic acids (Senesi and Testini, 1982).

Ligand Exchange

Ligand exchange onto partially chelated metals on clays and humic acids has been proposed as a possible binding mechanism for triazines, EPTC, and perhaps substituted ureas (Calvet and Thompson, 1980; Hayes, 1970). The water of hydration of the metal ion, acting as a ligand, may be displaced by a pesticide molecule.

Hydrogen Bonding

Hydrogen, from a hydroxyl group on the edge of a clay or from the carboxyl and amino groups on organic matter, can be electrostatically attracted to an electronegative atom, usually N or O, of a pesticide molecule, to form a bridge.

However, the pesticides will be in competition with water molecules for such bonding sites.

Charge Transfer

Charge transfer complex formation occurs when partial overlap of the molecular orbitals of an electron rich and an electron-dificient molecule produce a partial exchange of electrons, and form a resonance structure of ionic forms of donor and acceptor. There is spectroscopic evidence for charge transfer complexes existing between paraquat and diquat with montmorillonite and humic acid (Khan, 1980). Senesi and Testini (1982) studied the adsorption of four triazine pesticides on humic acids using elemental, thermal, infrared, and spin resonance analysis, and presented experimental and theoretical evidence for the occurrence of electron donor-acceptor processes involving free radical intermediates. They concluded that the higher the formation of ionic or hydrogen bonds, depending on the basicity of the pesticides, the lower the tendency to form electron-transfer complexes.

Charge-Dipole and Dipole-Dipole Bonding

Electron charges of exchangeable ions on absorbents, such as Na^+, Ca^{2+}, and Mg^{2+} on montmorillonite, can attract polar molecules. Some large pesticide molecules are easily polarized. Mortland (1970) found that the adsorption of some amides and amines on clay minerals is dependent on the type of exchangeable cations, not only because the cations affect the extent of dissociation of water molecules but they also affect the cation-dipole interactions between organic molecules and exchangeable cations.

van der Waals Forces

In the context of solute adsorption, van der Waals forces may be the principle attractive forces causing adsorption of nonionic and nonpolar molecules. These forces may include short-range forces called charge-induced dipole interactions, dipole-induced dipole interactions, and transient dipole-induced dipole interactions. The latter interaction is sometimes called London-van der Waals forces. A determination of the magnitude of these interactions is not possible, except from quantum mechanical computations. Therefore, a knowledge of their existence is of little help in explaining the behavior of pesticide adsorption. However, the additive nature of van der Waals forces between the atoms of adsorbent and adsorbate may result in considerable attraction for large molecules.

Hydrophobic bonding

Hydrophobic sorption is the partitioning of nonpolar pesticides out of the polar aqueous phase onto hydrophobic surfaces in soils. The hydrophobic surfaces are primarily due to soil organic matter, but may also include -Si-O-Si- groups at the mineral surfaces. The major feature of hydrophobic sorption is the weak interaction between the solute and the solvent. The primary force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the solute from solution. The entropy change is largely due to the destruction of the cavity occupied by the solute in the solvent and the destruction of the structured water shell surrounding the solvated organics.

1.1.6 Pesticide Desorption from Soils

To completely characterize the environmental fate of a given pesticide it is also necessary to evaluate pesticide desorption. It has been generally assumed that the sorption and desorption reactions for a given pesticide-soil system are reversible and can be described by a single isotherm (Rao and Davidson, 1980). This assumption simplifies pesticide transport modeling, but is not always valid. If the sorption and desorption reactions are not described by a single isotherm, then non-singularity or hysteresis, is said to exist. The general result of this non-singularity is that for a given equilibrium concentration, more pesticide will be retained in the desorption phase than in the sorption phase (Rao and Davidson, 1980). The implications of this are significant. Van Genuchten et al. (1974) investigated the transport of picloram in a Norge loam soil and noted that if desorption hysteresis was not accounted for in the transport model, then a significant overprediction of both breakthrough time and concentration occurred. When these effects were considered, the experimental results were successfully described.

Several researchers have investigated the cause of hysteresis and concluded that in many cases it was of methodological origin. Rao and Davidson (1980) have identified three major causes of hysteresis: 1) artifacts created due to some aspect of the experimental method, 2) failure to establish complete equilibrium during the sorption phase and, 3) chemical or biological transformation of the pesticide during the course of the experiment. The centrifugation-resuspension step of the batch method has also been identified as a potential source of hysteresis. Rao et al. (1979) reported that for certain pesticide-soil combinations, the extent of hysteresis could be reduced or eliminated by employing a dilution method in place of the standard batch method. These observations were confirmed by Bowman and Sans (1985), who studied the sorption/desorption of parathion and fensulfothion. Use of the dilution method decreased observed hysteresis for both pesticides on Ca-illite, a sandy loam and organic soils.

1.1.7 Sorption - Desorption Equilibrium Models

Sorption experiments are typically conducted by the batch equilibrium method. In this method a solution of the pesticide of interest is equilibrated with a known amount of solid. The solid and solution phases are then separated and the difference between the initial and final supernatant solution concentration is assumed to be the amount of sorbate sorbed.

Numerous equilibrium models have been developed and applied to pesticide sorption data. The most commonly applied models are:

Freundlich $$x/m = KC^{1/n} \quad (1)$$

Linear $$x/m = KC \quad (2)$$

Where: x/m = the solute sorbed per unit weight of solid

C = the equilibrium solution concentration.

K, n = empirical constants.

The Freundlich equation is an empirical relation that was used to describe sorption from dilute solution. It has been generally used to describe pesticide sorption on soils (Huang et al., 1984; Clay et al., 1988; Bowman and Sans, 1985). However, as Fisher (1922) emphasized, it is an empirical relation and adherence to the Freundlich equation alone does not yield mechanistic information. The linear model, Eq. (2), has also been widely applicable for describing pesticide sorption on soils (Karickhoff et al., 1979 and Weber et al., 1983). Voice and Weber (1983) stressed that the Freundlich equation reduces to a linear relation under low sorptive concentrations frequently found in soils.

In an attempt to simplify the presentation of pesticide sorption data Talbert and Fletchall (1965) introduced the distribution coefficient (K_d) to describe sorption of several s-triazine on soils, where

$$K_d = \frac{\text{pesticide in sorbed phase}}{\text{pesticide in solution phase}}$$

The distribution term was taken from Samuelson (1953) who used K_d to describe the relative affinity of selected ions for an ion exchanger. Talbert and Fletchall (1965) emphasized that while the K_d remained relatively constant for different concentrations in their study, this behavior should be examined in each individual case. If serious deviations from linearity occur, another more appropriate model should be considered.

The objectives of this equilibrium study were: to measure atrazine adsorption on major soil constituents, humic acid, montmorillonite, goethite, these constituents coated with humic acid, and on two Delaware soils; to determine adsorption-desorption reversibility; and to investigate the factors affectting these processes, i. e., pH values.

1.2 Materials and Methods

1.2.1 Soils and Soil Constituents

Two soil horizons were used in the equilibrium studies, a surface soil obtained from the Ap horizon of a Pocomoke sandy loam from Delaware which has a high content of organic matter and a subsurface Bt horizon of a Matapeake silt loam which has low organic matter and high Fe/Al oxide contents. Some of the chemical and physical properties of these two soils are shown in Table 1.1 and 1.2. The soil samples were air dried, and passed through a 2 mm sieve.

Goethite, montmorillonite, vermiculite, and humic acid were also used in the equilibrium studies. Goethite was prepared by adding 2.5 N NaOH to a 0.15 M $Fe(NO_3)_3$ solution until the final suspension pH was 11-12. The suspension was aged

Table 1.1 Chemical and physical characteristics of the Bt horizon of the Matapeake silt loam.

Organic matter (%)	0.31
pH (0.01M $CaCl_2$)	4.8
CEC (cmol kg^{-1})	5.71
AEC (cmol kg^{-1})	0.42
Particle size, %	
Sand	6
Silt	75
Clay	16
Fe (%)	1.98
Al (%)	0.79

Table 1.2 Chemical and physical characteristics of the Ap horizon of the Pocomoke sandy loam.

Organic matter (%)	18.6
pH (0.01M $CaCl_2$)	3.5
CEC (cmol kg^{-1})	4.21
AEC (cmol kg^{-1})	1.56
Particle size, %	
Sand	67
Silt	21
Clay	12
Fe (%)	0.05
Al (%)	0.34

in an oven at 60°C for 24 h and dialyzed with deionized water (Atkinson, 1967). A Wyoming montmorillonite and a Llano vermiculite from the University of Missouri Source Clays Depository were fractionated by centrifugation to an equivalent diameter of 1 to 2 µm. The <2 µm clay fractions were then suspended in a HCl solution of pH 5.0 at a temperature of 315K to remove carbonates. Homoionic Ca-montmorillonite and Ca-vermiculite were obtained by saturating the clays with 1M $CaCl_2$ four times, followed by dialysis in deionized water to wash out excess electrolyte. Humic acid was obtained from Aldrich Chemical Company Inc. It was used without further purification except for precipitating it in a $CaCl_2$ solution of pH 1.0. Humic acid-coated goethite was prepared by mixing 15 g of freeze-dried goethite with 500 mL of a 0.05% humic acid solution which was adjusted to a pH of 7.0. The suspension was shaken for 24 h, centrifuged, and the supernatant solution decanted. This equilibration procedure was repeated three times to obtain the maximum adsorption of humic acid on goethite. Then the coated sample was washed with deionized water until free of humic acid detected by UV spectrophotometry. Humic acid-coated montmorillonite was also prepared using the same procedure as for goethite. The coated samples were then freeze-dried.

1.2.2 Adsorption Equilibrium Studies

A series of atrazine solutions with concentrations ranging from 5×10^{-6} M to 1×10^{-4} M were prepared in a background solution of 0.01 M $CaCl_2$. The solutions were adjusted to desirable pH's ranging from 3.0 to 9.0. The ^{14}C-labeled solutions were prepared by adding ^{14}C-labeled atrazine to each of the solutions to yield a specific activity of 400 Bq mL^{-1}. Duplicate samples of 0.1g humic acid, 0.5g of the clay and humic acid-coated samples, and 1g of the soils were equilibrated with 15 mL of each of the above ^{14}C labeled atrazine solutions in glass centrifuge tubes. The tubes were sealed with Teflon-lined caps, shaken at 298K for 24 h, and centrifuged at 10,000 RPM for 20 min. We chose 24 h as the equilibrium time since this time has been the typical period used for equilibrium studies. Triplicate aliquots (1.0 mL) of the supernatant were carefully withdrawn and counted using a liquid scintillation spectrophotometer. The difference between atrazine concentrations before and after equilibration was assumed to be the amount of atrazine adsorbed (after correction for solid, solvent and tube blanks). Quenching corrections were also made for these determinations.

1.2.3 Desorption Equilibrium Studies

Desorption studies were conducted on the samples initially equilibrated with 1 X 10^{-4} M ^{14}C labeled atrazine for 24 h. The atrazine pre-equilibrated samples were diluted with 2, 5, 10, 15, and 20 mL of 0.01 M $CaCl_2$ solutions which were adjusted to pH's of 3.0 and 6.0. The suspensions were shaken for 24 h at 298K and centrifuged as above. The atrazine concentration in the supernatant was measured also by liquid scintillation counting. The amount of atrazine desorbed was obtained from the difference in atrazine concentrations between the supernatant solutions of initial and diluted samples.

1.3 Results and Discussion

1.3.1 Adsorption Equilibrium Studies

The adsorption equilibrium studies show that the adsorption of atrazine on soil constituents was in the order of humic acid > vermiculite = montmorillonite >> goethite (Figure 1.1). Adsorption conformed to linear isotherms in the concentration range which was employed in the experiments. Humic acid had a much greater affinity for atrazine than the clay minerals, indicating that organic matter content could be a major factor controlling the sorption of atrazine on soils. In fact, quite often the organic matter content of soils is the only parameter that correlates with atrazine adsorption on soils (Hance, 1967; Weed and Weber, 1974; Hermosin, 1989). As shown in Figure 1.2, humic acid-coatings significantly increased the adsorption of atrazine on montmorillonite and goethite. The Pocomoke surface soil, which has a high content of organic matter adsorbed much more atrazine than the Matapeake subsoil (Figure1.3). There was an insignificant amount of atrazine adsorbed on goethite. The degree of atrazine adsorption on soil oxides is not well understood. Huang et al. (1984) found that atrazine adsorption on soil was significantly decreased after removing Al- and Fe- oxides. Hilton and Yuen (1963) showed that amorphous oxides contained in some Hawaiian soils greatly increased the adsorption of pre-emergence herbicides. However, these authors used dithionite-citrate-bicarbonate (DCB) to extract soil Fe-oxides and H_2O_2 was used to remove soil organic matter. Since complete removal of soil organic matter by H_2O_2 is very difficult, a trace amount of soil organic matter could possibly have accounted for the atrazine adsorption on the DCB-treated soil samples. Borggaard and Streibig (1988) reported only negligible amounts of atrazine adsorption on goethite.

As shown in Table 1.3 and also in Figures 1.4 and 1.5, adsorption of atrazine on all the adsorbents greatly increased as pH decreased, especially when the pH decreased from 6.0 to 3.0. This finding agrees with the results of other researchers (Weber, 1966; Bailey, 1968; Calvet, 1980). Atrazine is a weak basic pesticide. Increasing surface acidity of adsorbents as the result of decreasing pH enhanced hydrogen bonding between atrazine and the adsorbents. The maximum adsorption of s-triazines occurs in the pH range near their pK_a (Weber, 1969; Adams, 1973). Since the pK_a of atrazine is as low as pH 1.4, it is expected that increasing acidity would increase atrazine adsorption. However, at such low pH's, disintegration of soils and soil constituents occurs and any experimental results on atrazine adsorption could be artifactual.

1.3.2 Desorption Equilibrium Studies

The desorption equilibrium studies showed that adsorption-desorption of atrazine on montmorillonite was completely reversible at pH 6.0 (Figure 1.6) while nonsingularity was observed for vermiculite (Figure 1.7). This is also illustrated in the magnitude of the distribution coefficients for the soil constituents at pH 3.0 (Table 1.4). The latter were higher for desorption than for adsorption with vermiculite, humic acid, and Pocomoke sandy loam.

While sorption hysteresis in soil pesticide systems has been often observed (Swanson and Dutt, 1973; Van Genuchten, 1974; Rao and Davidson, 1980; Bowman and Sans, 1985; Clay et al.,1988), little research has been conducted to establish the relationship between hysteresis and soil properties other than soil carbon content. Van Genuchten (1974) has indicated that the extent of hysteresis can be related to the total adsorbed concentration of a given pesticide. The greater the amount of pesticide adsorbed, the greater the extent of hysteresis. Rao and Davidson (1980) suggested three possible causes of pesticide hysteresis in soil systems: 1) artifacts created by the methodology that was employed, 2) failure to achieve equilibrium, and 3) chemical or microbiological transformations during equilibration. The commonly used batch or centrifugation-resuspension method may cause hysteresis (Bowman and Sans, 1985). In our study, the dilution method, rather than the centrifugation-resuspension technique, was employed and hence methodological artifacts should be minimized. Moreover, microbiological transformation of atrazine was negligible in our study as determined by UV spectrophotometry. However, there was not enough evidence indicating that the nonsigularities observed in this study were true hysteresis between atrazine adsorption and desorption since the results were based on a 24 h equilibrium time. Most of the systems probably did not reach equilibrium in a 24 h time period. This was confirmed later in the long-term kinetic study presented in Chapter 3.

Table 1.3 Distribution coefficients (K_d) calculated for atrazine adsorption at pH 3.0, 6.0, and 9.0.

pH	3.0	6.0	9.0
		$L Kg^{-1}$	
Humic acid (HA)	95.61		
Montmorillonite	18.52	16.10	16.04
Vermiculite	23.45	20.91	20.39
Goethite	0.00	0.00	0.00
HA-Montmorillonite	30.28	28.81	
HA-Goethite	6.84	5.34	
Matapeake silt loam	2.18	1.01	0.97
Pocomoke sandy loam	5.34	3.67	3.65

Table 1.4 Distribution coefficients (K_d) calculated for atrazine adsorption and desorption on soil constituents at pH 3.0.

	Adsorption	Desorption
	$L Kg^{-1}$	
Humic acid	95.61	126.90
Montmorillonite	18.52	18.50
Vermiculite	23.45	29.78
Goethite	0.00	0.00
Matapeake silt loam	2.18	2.20
Pocomoke sandy loam	5.34	6.01

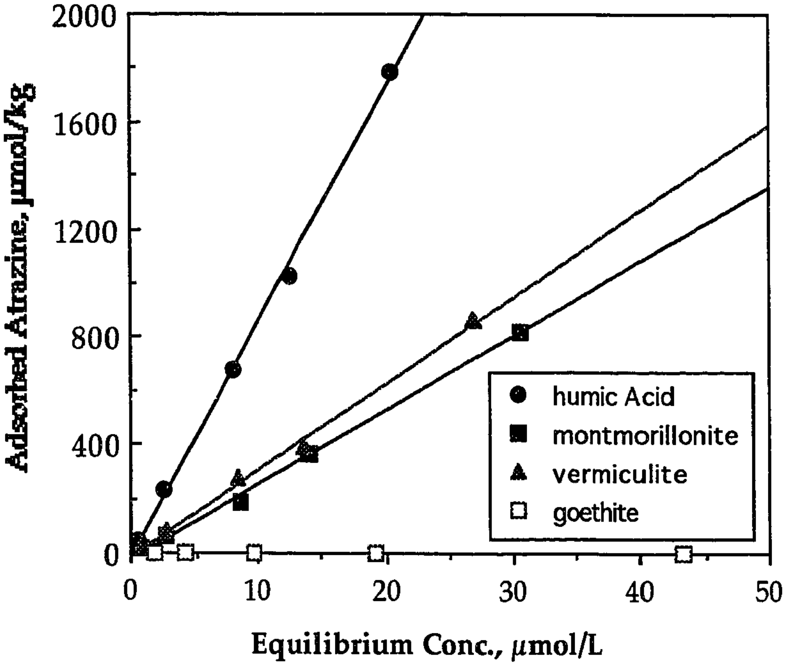

Figure 1.1 Atrazine adsorption on humic acid, montmorillonite, vermiculite, and goethite at pH 3.0.

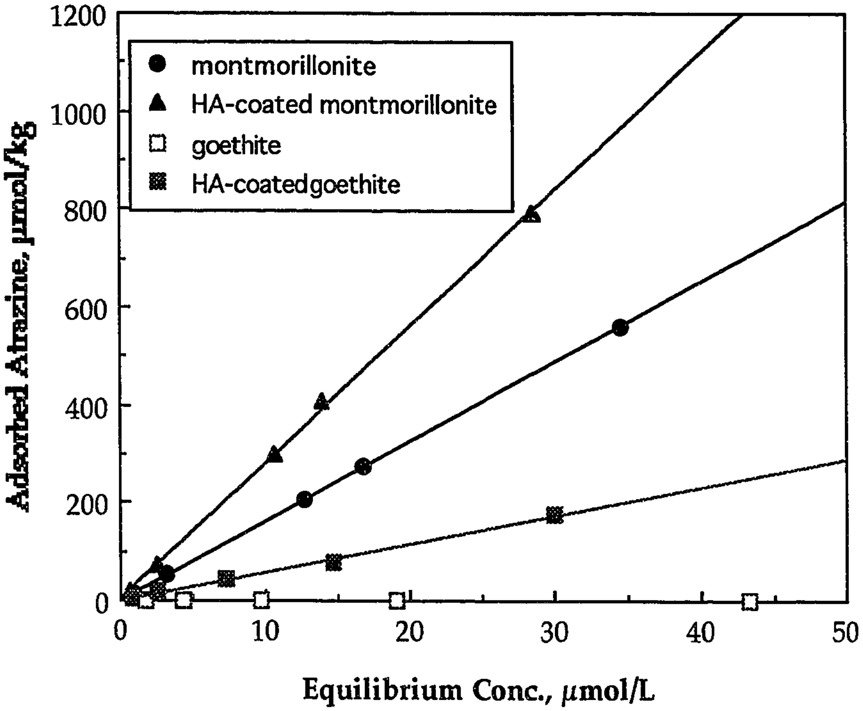

Figure 1.2 The effect of humic acid coatings on atrazine adsorption on montmorillonite and goethite at pH 6.0.

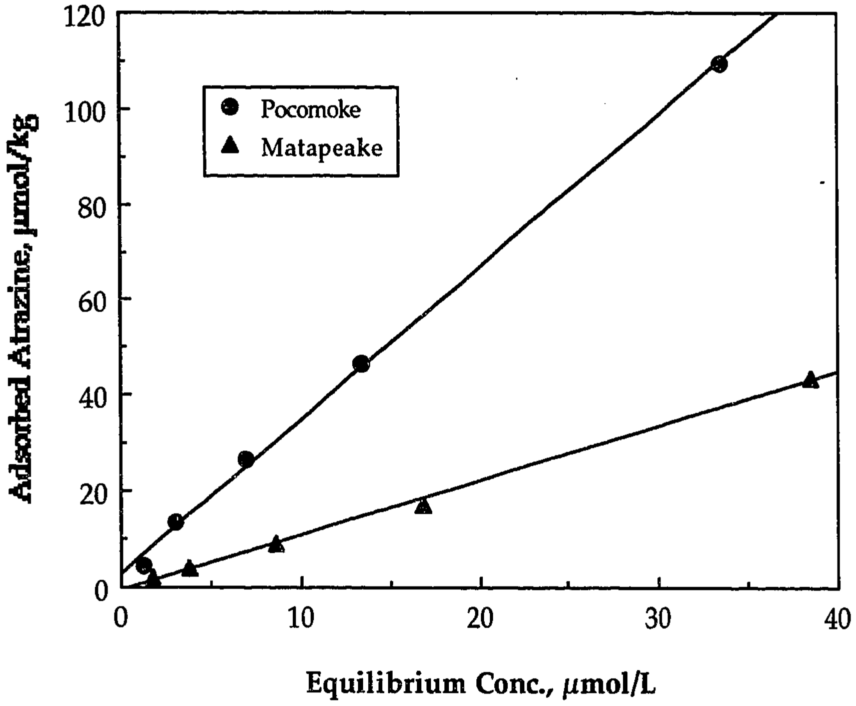

Figure 1.3 Atrazine adsorption on two Delaware soils: Pocomoke surface soil and Matapeake subsoil at pH 6.0.

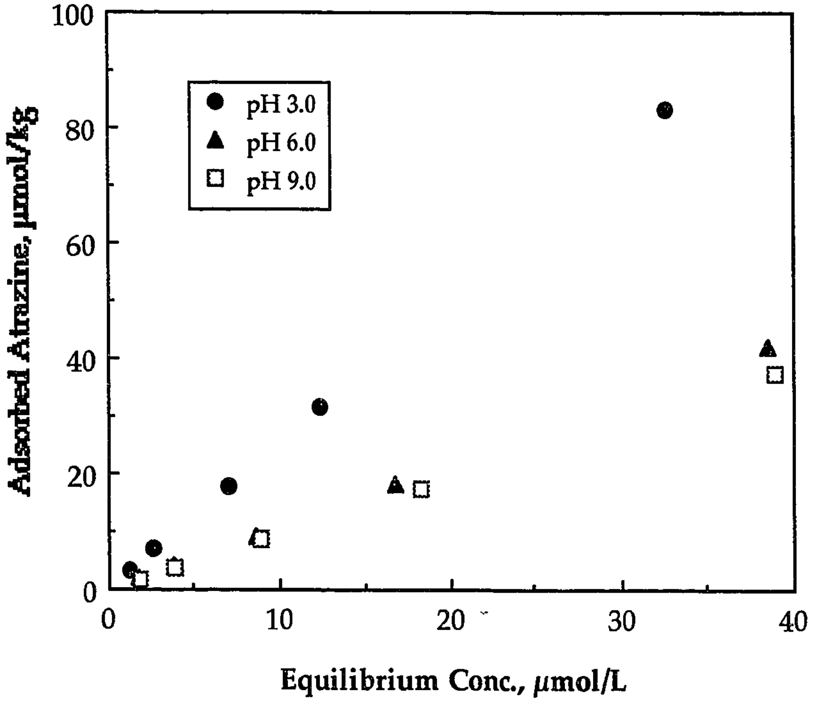

Figure 1.4 Effect of pH on atrazine adsorption on Matapeake silt loam.

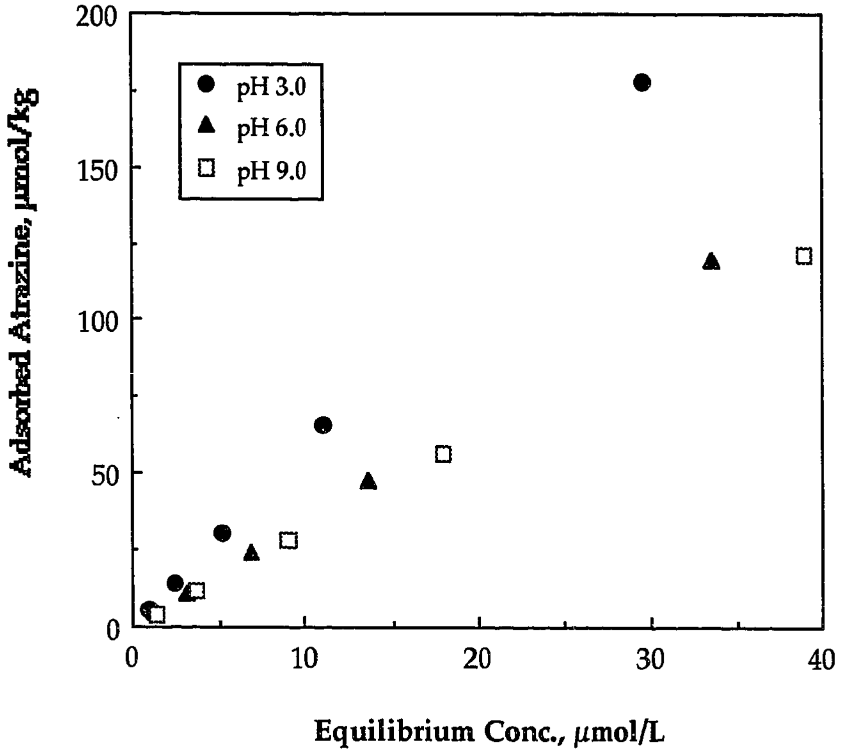

Figure 1.5 Effect of pH on atrazine adsorption on Pocomoke sandy loam.

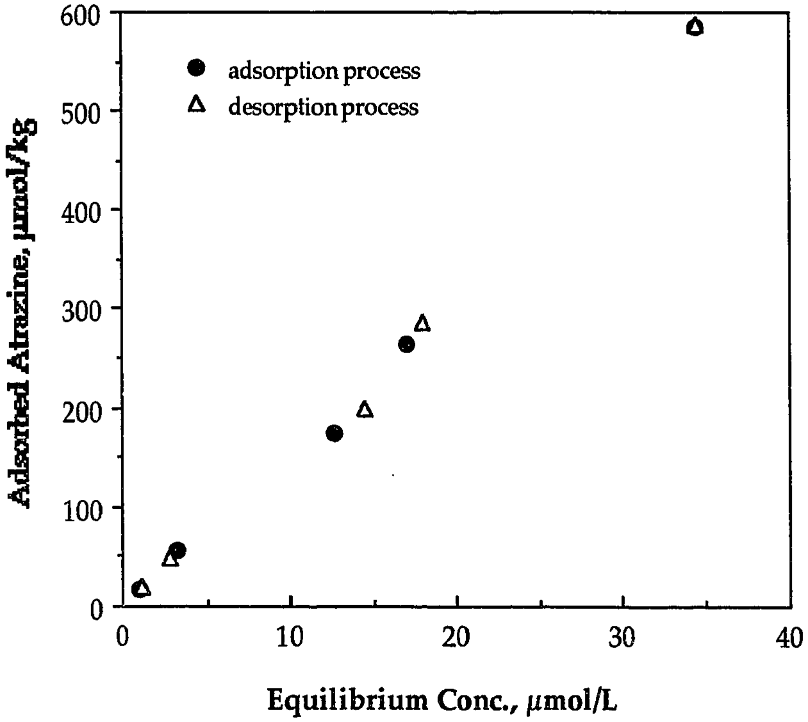

Figure 1.6 Reversibility of atrazine adsorption-desorption reactions on montmorillonite at pH 6.0.

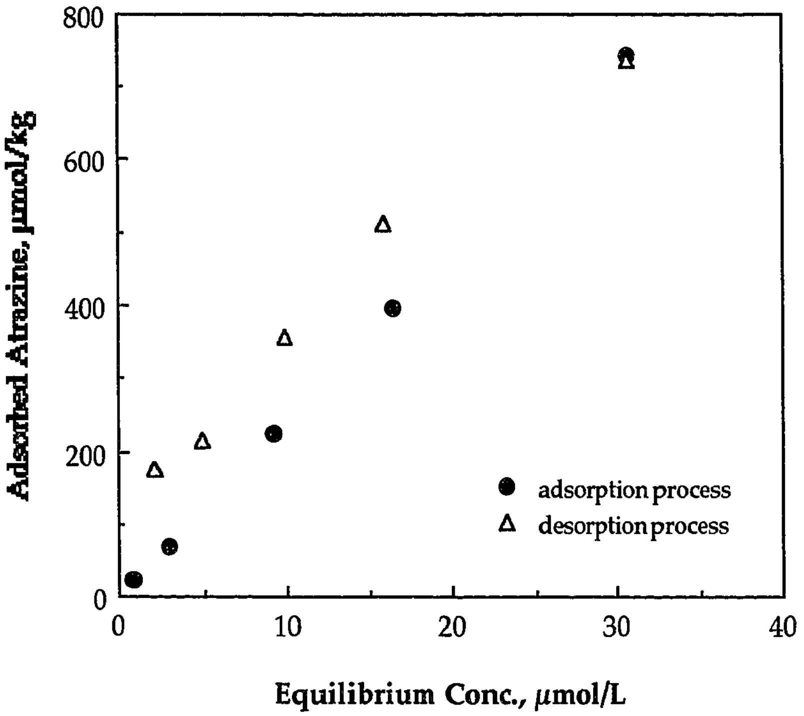

Figure 1.7 Nonsingularity of atrazine adsorption-desorption reactions on vermiculite at pH 6.0.

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Chapter 2

SHORT-TERM KINETICS OF ATRAZINE ADSORPTION

2.1 Introduction

Sparks et al. (1980) introduced a continuous flow method that is quite similar in principle to liquid-phase chromatography. Using this technique, one can measure reactions at rapid intervals (1 min). This method may also be preferable if one wishes to simulate solute transport in soils. In this method, samples can either be injected as suspensions or spread as dry samples on a membrane filter. The filter holder is capped securely and then is attached to a fraction collector and a peristaltic pump, which maintains a constant flow rate. Samples are leached with sorptive solutions, and effluents are collected at various time intervals.

For sorption /desorption studies, the sorption reaction is followed by monitoring the increasing concentration of leachate with time. At an apparent equilibrium, the effluent concentration equals to that of the initial sorption solution. The desorption reaction is studied in a similar way, the reaction being followed by monitoring the decreasing concentration of the previously sorbed ion or other sorbate with time. In either case, the reaction is followed by determining the sorptive concentration in solution. This means that any process that effects a change in concentration will be interpreted as adsorption or desorption.

With the continuous flow method of Sparks et al. (1980), the dilution of incoming sorptive solution by the liquid used to load the sorbent onto the filter, or the washing out of leftover sorptive solution during desorption can cause a concentration change. This concentration change is not due to sorption or desorption and is a potential source of error, as shown by Carski and Sparks (1985). Regardless of the sorbent used, some solution will be held back or entrained on the top of this filter. This entrained solution cannot be completely removed by suction, and the total amount will be dependent on the water-holding capacity of the sorbent. Fortunately, the dilution problem and other shortcomings of continuous flow techniques can be eliminated in a stirred-flow method (Carski and Sparks, 1985) which was used in this study.

The basic components for the construction of the stirred-flow device include a barrel and plunger from a 10 ml B-D plastic syringe and a 15 mm filter holder. The filter holder is modified and glued to the top of the syringe barrel, and the base of the barrel is threaded to provide a plunger height adjustment. The device enables one to add and to maintain a known quantity of fluid to a known amount of absorbent, regardless of the absorbent used. Operation of the apparatus is simple, a magnetic stirring bar is placed in the chamber above the plunger, a known amount of absorbent is loaded into the reaction chamber, a membrane filter and the top are attached, and a known amount of entrained fluid is added using a hypodermic syringe. The plunger is then used to displace the excess air from within the reaction chamber, thus enabling a known volume to be diluted or washed out. This volume is maintained throughout the adsorption and desorption study. A peristaltic pump is used to maintain a constant flow rate and a fraction collector is used to monitor the reactions. A magnetic stirrer is used to ensure adequate mixing in the reaction chamber, and stirring speed is kept to a minimum, about 100 rpm, to minimize abrasion of the sorbents. A diagram of the stirred-flow technique apparatus is shown in Figure 2.1.

2.2 Materials and Methods

Short-term adsorption kinetic studies with vermiculite were conducted using a stirred-flow reaction chamber first described by Carski and Sparks (1985) and modified by Seyfried et al. (1989). A magnetic stir bar was placed in the chamber above the rubber plunger. One-half g of dry solid Ca-vermiculite was then placed in the chamber. A known amount of 0.01 M $CaCl_2$ (8.5 mL)was added using a hypodermic syringe and this volume was maintained throughout the reaction period. A 0.2 μm membrane filter was placed beneath the outlet port to prevent any loss of the sorbents. The influent which contained ^{14}C labeled atrazine was pumped into the chamber using a peristaltic pump at flow rates of 1 mL and 2 mL min^{-1}. The effluent was collected using a fraction collector at 4-min intervals for a period of 2 h.

Triplicate aliquots of 1.0 mL of effluent were placed in a scintillation cocktail and the activity of the solution was counted. A blank curve was determined for a known chamber volume, using the same initial chamber solution and adsorptive

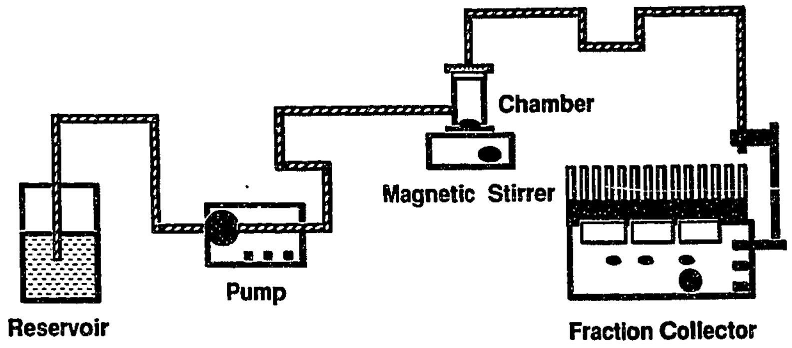

Figure 2.1 Diagram of the stirred-flow technique apparatus.

solution as described above, but without adsorbent in the chamber. This curve was used to calculate adsorbed quantities of atrazine.

2.3 Results and Discussion

Bar-Tal et al. (1990) suggested three simple but necessary tests, using the stirred-flow method (Carski and Sparks, 1985) to distinguish between (i) instantaneous equilibrium and kinetically controlled reactions, and (ii) solution concentration-dependent kinetic models vs. those that are independent of solution concentration. These tests are: stopping the flow for at least 15 to 60 min, varying the flow rate, and using two or more influent concentrations. The assumption of the stop-flow test is that, if nonequilibrium conditions are present, stopping the flow for a time period sufficient for 50% of the reaction to be completed will allow the system to attain equilibrium (Seyfried et al., 1989). If the reaction is time dependent, the solution concentration in the stirred-flow chamber in an adsorption study should decrease and, when flow is restarted, a discontinuity in the curve (drop in concentration) of relative effluent concentration vs. effluent volume will be observed. If the reaction is instantaneous, no drop in relative effluent concentration will be observed and the curve should be continuous (Bar-Tal et al., 1990). Varying the flow rate can also distinguish between instantaneous equilibrium and time-dependent reactions. If an instantaneous equilibrium reaction is assumed, the relative effluent concentration or the adsorbed fraction as a function of effluent volume should not be affected by flow rate because adsorption is a function of the concentration and independent of time.

Both stopped-flow and varying flow rate tests were conducted on Llano Ca-vermiculite to ascertain that the atrazine adsorption reaction was kinetically controlled and could be measured using the stirred-flow method. As shown in Figure 2.1, the effluent atrazine concentration as a function of effluent volume was affected by the flow rate. Although not shown here, plotting effluent atrazine concentration vs. effluent volume resulted in a sharp drop in effluent concentration after flow was stopped for 30 min. Therefore, both tests indicated that adsorption of atrazine on vermiculite was time dependent.

Two influent concentrations, 20 and 50 μM, were employed to determine whether a solution-concentration-dependent kinetic model or one that is independent of concentration is suitable to describe the atrazine adsorption reaction on vermiculite (Figure 2.2). Our results clearly indicated that adsorbed atrazine is significantly dependent on the influent solution concentration. Since diffusion in the bulk solution was substantially reduced with the stirred-flow method, the time-dependent adsorption may be due to diffusion in the partially collapsed interlayers of vermiculite.

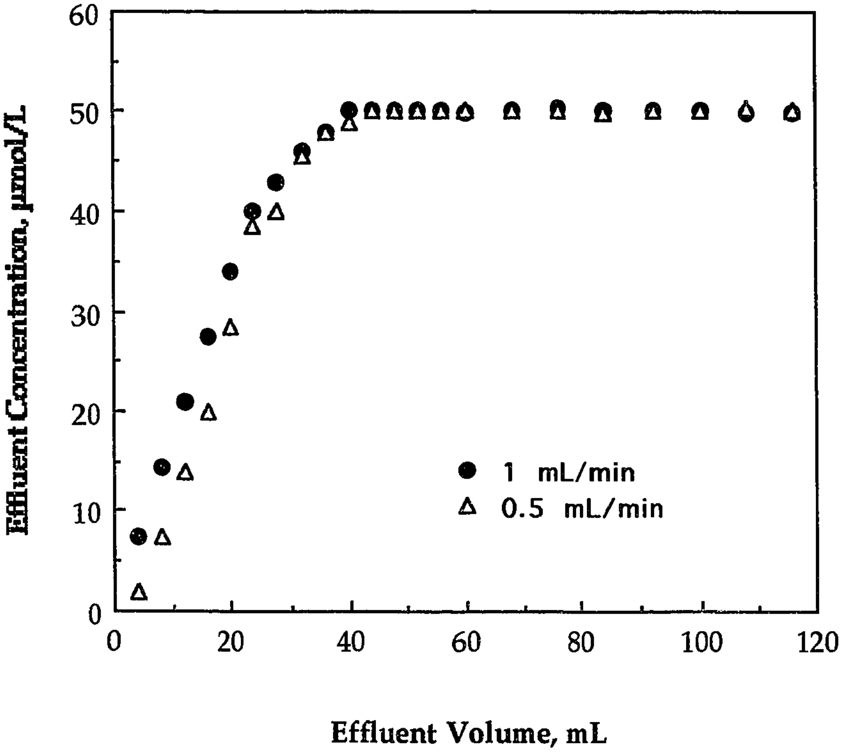

Figure 2.2 The effect of flow rate on atrazine effluent concentration as a function of effluent volume for vermiculite.

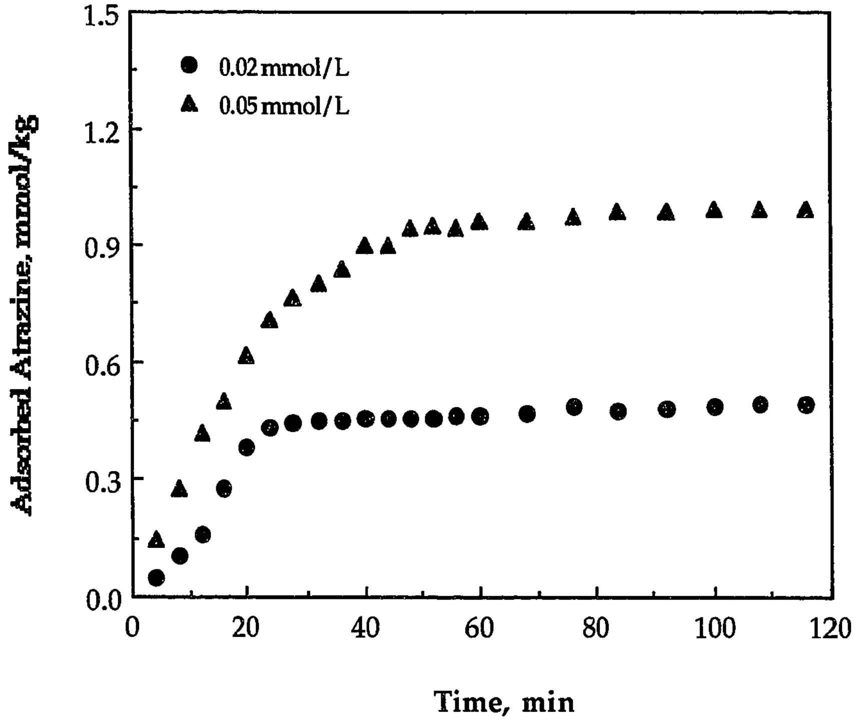

Figure 2.3 The effect of influent concentration on adsorbed atrazine as a function of time for vermiculite.

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Chapter 3

LONG-TERM KINETICS OF ATRAZINE ADSORPTION-DESORPTION

3.1 Introduction

The thermodynamics of pesticide sorption on soils and soil constituents has been studied extensively. Unfortunately, sorption kinetics and especially desorption kinetics have not been extensively studied. One reason for this inattention is a widely held view that sorption equilibria are established rapidly; that is, on time scales that are shorter compared to other fate processes. Reflecting this view, fate and transport models usually include only equilibrium terms to describe sorption. It is becoming clear, however, that sorption is not necessarily instantaneous, particularly as "equilibrium" is approached. In order to develop efficient strategies to remove or immobilize pesticide contaminants from the soil matrix a more complete understanding of sorption/desorption kinetics is necessary. The study of sorption/desorption kinetics can lead to a better understanding of pesticide retention mechanisms. This will in turn improve the ability to predict contaminant fate in the natural environment.

Recently a number of studies have been conducted on the kinetics of organic contaminant adsorption-desorption on natural soils and sediment systems. Many of these investigations have shown that adsorption-desorption is characterized by a rapid, reversible stage followed by a much slower, nonreversible stage (Karickhoff et al., 1979; DiToro and Horzempa, 1982; Karickhoff and Morris, 1985) or biphasic kinetics. The rapid phase has been ascribed to retention of the organic chemicals in a labile form that is easily desorbed. However, the much slower reaction phase involves the entrapment of the chemicals in a nonlabile form that is difficult to desorb. These slower sorption/desorption reactions have been ascribed to diffusion of the chemical into micropores of organic matter and inorganic soil components (Wu and Gschwend, 1986; Steinberg et al., 1987; Brusseau and Rao, 1989; Ball and Roberts, 1991). The labile form of the chemical is available for microbial attack while the nonlabile portion is resistant to biodegradation.

Coates and Elzerman (1986) predicted desorption time periods of weeks for polychlorinated biphenyls (PCBs) with low chlorine content, and months to years for PCBs with significantly higher chlorine content. Rogers et al. (1980) demonstrated the resistance of benzene to desorption in two soils and a montmorillonite clay. Pavlostathis and Mathavan (1992) studied the simultaneous desorption of trichloroethylene, tetrachloroethylene, toluene, and xylene from five field-contaminated soils. The study indicated that a significant fraction (48%-94%) of the sorbed contaminant mass resisted desorption in a deionized water-soil mixture following 7 d of contact time.

A number of studies have also shown that with "aging" the nonlabile portion of the organic chemicals in the soil/sediment becomes more resistant to desorption (McCall and Agin, 1985; Steinberg et al., 1987; Pavlostathis and Mathavan, 1992, Scribner et al., 1992; Pignatello et al., 1993). However, Connaughton et al. (1993) did not find that the nonlabile fraction increased with aging for naphthalene contaminated soils. Steinberg at al. (1987) and Pignatello et al. (1990) demonstrated that residues of 1, 2-dibromoethane (EDB) in soils with a long contamination history were resistant to desorption, compared to recently added EDB in the same soil samples. Pignatello and Huang (1991) studied the sorptive reversibility of herbicide residues (atrazine and metolachlor) in field soil samples 2 to 15 months after their last applications. They found that samples collected from the field had a large fraction of the contaminant in a slowly reversible sorbed state and that this fraction increased with contaminant residence time. Pavlostathis and Jaglal (1991) investigated the desorptive behavior of trichloroethylene from a long-term contaminated soil. The trichloroethylene in the soil was not easily desorbed, demonstrating the high persistence of the nonionic organic contaminant. As part of a field study of a water-table aquifer contaminated with trichloroethene for over 20 yr, Smith et al. (1990) concluded that the desorption of trichloroethene from the unsaturated-zone soil to the soil gaseous phase was kinetically limited. Specifically, measurement of the concentration of trichloroethene in the unsaturated-zone soil and the soil gaseous phase indicated that the ratio of the sorbed trichloroethene to the vapor concentration was one to three orders of magnitude greater than equilibrium ratios determined in the laboratory and by other researchers.

Another major finding from sorption-desorption studies conducted on "freshly aged" and "aged" samples is the variability of the distribution coefficients (K_d values). Most of the K_d values obtained from the laboratory were based on an equilibration time of 24 h. When these values are compared to K_d values for field soils previously reacted with the organic chemicals ("aged" samples) for extended periods of time, the latter have much higher K_d values, indicating that much more of the organic chemical is in a sorbed state. For example, Pignatello and Huang (1991) measured K_d values in "freshly aged" (K_d) and "aged" soils (K_{app}, apparent distribution coefficient) reacted with atrazine and metolachlor. The "aged" soils had been treated with the herbicides 15-62 months before sampling. The K_{app} values ranged from 2.3-42 times higher than the K_d values. Scribner et al. (1992), studying simazine desorption and bioavailability in "aged" soils, found that K_{app} values were 15 times higher than K_d values. They also showed that 48% of the simazine added to the "freshly aged" soils was biodegradable over a 34 day incubation period while none of the simazine in the "aged" soil was biodegraded.

Slowly reversible sorption can be defined as sorptive processes that are slow relative to concurrent transport processes, such as advection and dispersion in the subsurface (Pignatello and Huang, 1991; Szecsody and Bales, 1989). The resistence to desorption of organic contaminants from the field soils indicates that the rate of desorption is proportional to the residence time of the contaminant. Conditions of equilibrium and complete reversibility are typically assumed when simulating sorption or desorption in soil-water systems. However, this assumption may be invalid for soils with a long-contamination history (Pavlostathis and Jaglal, 1991).

3.2 Adsorption- Desorption Kinetic Modeling

Many models have been developed and applied to simulate organic sorption/desorption kinetics. Most of these models can be divided into two categories: 1) chemical models including one-site and two-site reaction models; and 2) physical models which include the pore diffusion model, surface-diffusion model, and the combined pore and surface diffusion model or dual resistance model. Ball and Roberts (1991) provide a good review of diffusive processes in natural solids and sediments.

Brusseau and Rao (1991) indicated that the chemical nonequilibrium caused by the rate-limited interactions between hydrophobic organic chemicals (HOC) and natural sorbents is usually unimportant and may be eliminated as a probable mechanism, since sorption of HOC is generally considered to be rapid physical adsorption (e.g., partitioning). Often, sorption at the sorbent-solvent interface is assumed to be instantaneous, the rate at which the solute is transported to and from the interface controls the sorption rate. Several mechanisms are involved in the solute-transport process: (1) advective-dispersive transport from bulk solution to the boundary layer; (2) diffusion across the adsorbed water (film diffusion); (3) diffusion within intra-particle micropores and dead-end pores (intra-particle diffusion). Any or all of these three mechanisms may be a rate-limiting step. In most well- mixed systems, intra-particle diffusion is usually the rate-limiting step. The diffusion process can be modeled either by Fick's law for a well-defined geometry or a first-order mass transfer approximation. Fick's law often assumes that the sorption process is controlled by pore or surface diffusion into a well-defined particle geometry, usually a sphere.

Intra-particle diffusion may occur by pore diffusion, surface diffusion, or both. As these processes act in parallel, the slower one will be the predominant mechanism and will, therefore, control the sorption rate. Most models for the kinetics of sorption by activated carbon assume that surface diffusion is dominant. This dominance is a result of the large tortuosity associated with the internal pore structure of activated carbon, which results in very slow diffusion. This dominance may not hold, however, for soil/sediment systems, as the tortuosities of soil aggregates (2-3) are likely to be less than that of activated carbon (>6). Therefore, pore diffusion may be important for soil/sediment systems.

3.2.1 One-site and two-site reaction models

The one-site or one-box model is the simplest model in which sorption rate is a first-order function of concentration difference between the sorbent and the solute and is quantified by a single rate constant. This model implies that the sorption process is limited by only one of many conceivably important processes including binding on a single class of sorbing site. However, the one-site model does not fit experimental data well (Rao and Jessup, 1983; Wu and Gschwend, 1986; Boesten and Van Der Pas, 1988). Sorption of organic chemicals on sorbents exhibits a two-stage approach to equilibrium: a short initial phase of fast sorption or release, where roughly 30 to 50% of the total sorption occurs within minutes to hours, followed by an extended period of much slower sorption or desorption occurring over periods of days or months (Hamaker and Thompson, 1972; Leenheer and Ahlrichs, 1971; Khan, 1973; Karickhoff, 1980; Karickhoff and Morris, 1985; McCall and Agin, 1985; Wu and Gschwend, 1986).

A common method to deal with the observed deviation from a simple one-site model is to use bicontinuum conceptulized models which sometimes have been called "two-site", "two-compartment", or " two-box" models (Brusseau and Rao, 1989; Jardine, et al. 1992; van Genuchten and Wagenet, 1989). This model divides sorbent into two sorption sites or domains, where sorption is essentially instantaneous for one domain (fast) and is rate-limited for the other (slow). Sorption for the kinetically-controlled domain is described by a first-order rate equation, wheres the other domain is represented by an equilibrium isotherm equation. Karickhoff (1980) has proposed a two-box release model to describe the desorption of nonionic organic compounds from sediments. This model has two fitting parameters: the fraction of sites at local equilibrium and the kinetic rate constant. Another disadvantage of this model is that it is not easy to relate these parameters to known properties of the colloidal material. Wu and Gschwend (1986), found, for example, that two totally different sets of parameters for tetrachlorobenzene sorption on a Charles River sediment were obtained if different sediment mean aggregate sizes were used. This indicates that the parameters would have to be experimentally estimated for each type of sediment, which is not practical. It is widely recognized that natural porous materials contain many different sorptive compartments. As a result, it is unlikely that the fitting parameters for the two-site model can correspond to the actual rates for the mixture of sorptive sites in a soil. An alternative approach that has recently been employed is to experimentally characterize the sorptive properties of significant soil components and to use this information to predict aggregate soil behavior. In effect, this approach increases the number of compartments in the sorptive model of the soil. However, each compartment that was added would introduce two more adjustable model parameters. Numerous other mass transfer approaches similarly suffer in having no fundamental basis on which to predict the values of the model parameters.

3.2.2 Pore Diffusion Models

Pore diffusion is envisioned to occur in the intraparticle pore spaces of minerals and aggregates. Several investigators have used the pore diffusion approach to model batch systems (Ball and Roberts, 1991; Steinberg et al., 1987; Harmon et al., 1992; and Pignatello et al., 1993).

Wu and Gschwend (1986) developed a radial diffusive penetration model modified by a retardation factor considering microscale partitioning of the sorbate between intraggregate pore fluids and the solids making up the aggregate grains. This model assumes that the sediment and soil particles are aggregates of the mineral grains and organic matter and that the organics diffuse through the pore fluids between the interstitial regions of the aggregates. Also, their penetration is retarded by microscale partitioning of the organics between essentially mobile (dissolved in particle pore fluids) and immobile (in/on particle solids) states of the chemical.` The authors found that sorption of organic pollutants, 1,4-dichlorobenzene, 1,2,3,4-

tetrachlorobenzene, and pentachlorobenzene, on the sediments was described very well with the retarded/radial diffusion model by adjusting only the effective intraparticle diffusivity parameter. An additional benefit of this model is that the effective diffusion coefficient (D_e) can be estimated a priori by correlation with chemical and sediment or colloidal properties and this is the only parameter required for model simulation.

Applications and Limitations of Pore Diffusion Model

It is clear that the deterministic radial diffusion model can be applied to a variety of environmental situations by adjusting the D_e according to easily measured or estimated environmental parameters. Therefore, once it is incorporated in the fate model it will certainly improve our capability to predict the fate of organic pollutants and the related governing equations if the particle size distribution is sufficiently narrow that we can choose a reasonable average particle size. Soil scientists have recently demonstrated the effectiveness of this physical view for transport of conservative chemicals through soils in their natural aggregate state.

Because pore diffusion occurs through the aqueous phase, the rate of pore diffusion can be related to the aqueous diffusivity of the adsorbate if the effects of tortuous paths and steric hindrance are taken into account. Steric hindrance results from pore constrictions and pore walls shortening the mean-free path of the diffusing molecules. Steric hindrance increases with decreasing pore size and becomes very large as pore size approaches molecular dimensions. Tortuous and dead-end pores lead to longer diffusional paths to travel a given radial distance within a particle or aggregate.

Although the pore radial diffusion model is the most commonly used model in soil and sediment systems, it has many limitations. A serious limitation of the pore diffusion model is the assumption that the distribution of pores can be characterized by a representative, average D_e. Implicit in this assumption is that there exists a continuum in properties and behavior across the entire pore size spectrum. This continuum assumption, however, breaks down as pore diameters approach molecular dimensions.

Because pore size can influence both the amount and kinetics of adsorption, pores have been classified according to size. Cylindrical pores with diameters < 20 Å or slit-shaped pores of this width are classified as micropores, pores with diameters between 20 and 500 Å are classified as mesopores, while pores > 500 Å are classified as macropores. Capillary condensation is associated with mesoporosity, while solids possessing only macroporosity show little or no capillary effects. Because micropores are of molecular dimensions, several additional factors govern sorption in these pores.

Molecules adsorbed in micropores are subject to stronger field strengths than those adsorbed on flat surfaces. Adsorption energies are substantially increased because of the superposition of interaction potentials of opposing walls. Higher adsorption energies lead to increased adsorption and contribute to isotherm nonlinearity for sorbents with pores less than several adsorbate diameters in size (Farrell, 1994),.

In micropores, increased sorption leads to reduced diffusive transport rates through the effect of isotherm slope on the internal ratardation factor (R_{int}). Aside from increased adsorption, there are two additional contributions to reduced transport rates in micropores. The first contribution is that steric hindrance increases exponentially as the pore size approaches the size of the solute. The second contributing factor is that as pore size decreases, the ratio of pore surface area to pore volume increases. Even if the K_d remains the same, the ratio of sorbate mass on the surface to sorbate mass in solution is greater in smaller pores. The result is that a given sorbate molecule spends relatively more time sorbed on the surface than in solution for smaller pores compared to larger pores. If diffusion occurs only through the solution phase, the D_e, is reduced in smaller pores because the sorbate spends less time diffusing. Even in the presence of surface diffusion, transport rates are still reduced because of the relative slowness of surface diffusion compared to aqueous diffusion. Therefore, even for a constant partitioning coefficient, smaller pores lead to higher internal retardation.

In light of these factors, assuming homogeneity among the pores can be a significant oversimplification for microporous sorbents. Sorbent microporosity leads to three effects: increased steric hindrance, increased sorption energies, and greatly increased surface area to volume ratios, all of which contribute to reduced desorption rates.

Although a number of researchers have found success in applying the pore diffusion model to the sorption and the desorption of organic contaminants (Ball and Roberts, 1991; Wu and Gschwend, 1986), the fits may be based on an inappropriate physical model. A major shortfall in previous investigations is that sorption or desorption rates were measured over limited concentration ranges. Mechanisms such as sorption in micropores that may be dominant at one concentration range but contribute only marginally at another may be obscured. Wu and Gschwend (1986) found that the pore diffusion model was adequate to describe both adsorption and desorption kinetics for several nonpolar organic sorbates on soils and sediments. However, the range of concentrations investigated was less than two orders of magnitude, and the resolution of slow phenomena was not possible. Where the range of experimental data is limited, mechanisms may be overlooked although models may fit the data. However, these models may lead to erroneous conclusions since they may not be applicable if extrapolated beyond the range for which the parameters were determined. Data from some studies indicate that, for limited concentration ranges, fits can be made with the pore diffusion model, but the best fit parameters for a given sorbent are concentration dependent and, are therefore, not mechnistically representative of the true phenomena. Ball and Roberts (1991) found that a pore diffusion model fit data for PCE uptake on Borden sand if an instantaneously adsorbed fraction was assumed. Assuming an instantaneously adsorbed fraction is an a priori limit on the concentration range investigated and provides a second fitting parameter- both of which obscure the early time mechanisms for sorptive uptake.

In order to obtain meaningful physical parameters, the length scale over which the characteristic D_e applies must be the particle radius. If this is not the case, the pore diffusion model defaults to a nonmechanistic model with a fitting parameter, X_e. Nonmechanistic bases for fits to the pore diffusion model may explain inconsistent observations on the effects of particle size on adsorption rates. Ball and Roberts (1991) found that pulverization of their adsorbent particles increased adsorption rates, but the increase was less than expected based on pore diffusion parameters derived from the original material. Additionally, Steinberg et al. (1987) observed that pulverization greatly increased desorption rates of ethylene dibromide (EDB) from two soils, but for the original material, rates of release were only weakly dependent on particle size. Therefore, although the pore diffusion model may fit experimental data, if the underlying physical mechanisms do not correspond to the model formulation, the model will not be useful for predictive purposes under different circumstances.

3.2.3 Surface Diffusion Model

Surface diffusion is envisioned to occur along intraparticle pore walls. It is commonly invoked to explain pore diffusion that appears to be faster than could be accounted for by aqueous diffusion. The surface diffusion coefficient is often assumed to be constant for the sake of simplicity or because of the lack of information on concentration dependence. Several investigators (Weber and Miller, 1988; Miller and Pedit, 1992) have used the surface diffusion model assuming a constant surface diffusion coefficient to model a batch system. Miller and Pedit (1992) attempted to explain the apparent discrepancy between sorption and desorption using a reactive surface diffusion model. While their model was successful in simulating the observed data, Miller and Pedit (1992) suggested that a pore diffusion model may be more appropriate for such systems.

3.2.4 Combined Pore and Surface Diffusion Model (Dual-Resistance Model)

This model usually is based on Fick's first law which incorporates parameters for both pore and surface diffusion. The driving force for diffusion is the concentration gradient of solute in the porewater (pore diffusion) and the concentration of sorbed solute in the pore walls (surface diffusion). Generally, the dual-resistance model is insensitive to the film diffusion component in well-mixed, batch systems, and in most cases is associated with groundwater transport. The relative contribution of surface and pore diffusion is more difficult to distinguish as the processes occur in parallel within the particle. Moreover, mass transport in solids usually occurs much more slowly than aqueous diffusion, so surface diffusion is usually neglected (Harmon and Roberts, 1994).

3.2.5 Intra-Organic Matter Diffusion Model

Intra-organic matter diffusion (IOMD) is defined as diffusion of a solute into, from, or within the interior matrix of the soil organic matter. Soil organic matter can be envisioned as a three-dimensional matrix of randomly oriented polymer chains with a relatively open, flexible structure (Brusseau and Rao, 1989). With this description of soil organic matter, an organic solute may diffuse, over a period of time, deep within the interior of the matrix. Nonequilibrium results from the slow diffusive mass transfer from the interior of the matrix to the aqueous phase. Szecsody and Bales (1989) indicated that diffusion in the organic -matter phase will be retarded relative to that in the aqueous phase as a result of the nonliquid nature of the organic phase. An example given in the study was 1, 4-dichlorobenzene, for which diffusion in the organic phase is 200-1000 times slower than that in the aqueous phase. Brusseau and Rao (1989) contend that IOMD is the primary cause for sorption of nonionic organic compounds in soil-water systems.

The organic matter in sediment is believed to be composed of both swollen and condensed humic polymers. It is known that the sorption-desorption rate process for organic contaminants in dissolved humic polymers is very fast and there is no resistant fraction. Since dissolved humic polymers are likely in a swollen state, the labile fraction of organic solute desorption may be due to desorption from a swollen, rubber-like humic polymer. In contrast, the resistant fraction may be due to desorption from a condensed, glass-like humic polymer phase. Therefore, estimations of diffusion coefficients for swollen humic polymer and condensed humic polymer couples are needed for modeling organic sorption - desorption.

The objectives of this study were: to determine atrazine long-term adsorption and desorption kinetics on selected soil constituents and soils; and to simulate the experimental results with different kinetic models.

3.3 Materials and Methods

Before conducting the long-term kinetic study, preliminary kinetic experiments were performed for all of the adsorbents used in the equilibrium study. The samples were equilibrated at 2, 4, 8, 12, and 24 h. Our results indicated that atrazine adsorption and desorption reached equilibria in 2 h on montmorillonite and Matapeake silt loam. Therefore, only the following adsorbents were employed in the long-term adsorption-desorption kinetic study: humic acid, vermiculite, humic acid-coated montmorillonite, and a Pocomoke sandy loam.

A surface horizon from a Pocomoke sandy loam from Delaware which has a high content of organic matter was air dried, and passed through a 2 mm sieve. A Llano vermiculite from the University of Missouri Source Clays Depository was fractionated by centrifugation to an equivalent diameter of 1 to 2 µm. The 2 µm clay was suspended in a HCl solution of pH 5.0 at a temperature of 315K to remove carbonates. A homoionic vermiculite were obtained by saturating the clay with 1M $CaCl_2$ four times, followed by dialysis in deionized water to wash out excess electrolyte. Humic acid, obtained from Aldrich Chemical Company Inc., was precipitated in a $CaCl_2$ solution of pH 1.0. Humic acid-coated montmorillonite was prepared by mixing 15 g of freeze-dried montmorillonite with 500 mL of a 0.05% humic acid solution which was adjusted to a pH of 7.0. The suspension was shaken for 24 h, centrifuged, and the supernatant solution decanted. This equilibration procedure was repeated three times to obtain the maximum adsorption of humic acid on montmorillonite. Then the coated sample was washed with deionized water until free of humic acid, as detected by UV spectrophotometry and then freeze-dried.

3.3.1 Adsorption Kinetics

The long-term adsorption kinetic studies were conducted by mixing duplicate samples with 15 mL of $1\mathrm{x}10^{-4}$ M ^{14}C labeled atrazine in a background solution of 0.01 M $CaCl_2$ at pH 3.0 in a series of glass centrifuge tubes. These were equilibrated in a temperature-controlled chamber at 277K. This temperature was employed to minimize microbial transformation of atrazine. The tubes were removed at different time periods (1d, 2d, 3d, etc., up to 90 days) and centrifuged at 10,000 RPM for 20 min. The concentration of atrazine in the equilibrated solution was measured using a liquid scintillation spectrophotometer. The difference between atrazine concentrations in the initial solution and the supernatant solution of the equilibrated sample was assumed to be the amount of atrazine adsorbed (after correction for solid, solvent and tube blanks). UV spectrophotometry was used to monitor microbiological transformations throughout the entire period of the kinetic studies.

3.3.2 Desorption Kinetics

The samples which were pre-equilibrated with atrazine for 90 days were diluted with 10 mL of 0.01 M $CaCl_2$ solutions. The suspensions were then equilibrated in a temperature-controlled chamber at 277K. The suspensions were removed at different time periods (1d, 2d, 3d, etc., up to 90 days) and centrifuged at 10,000 RPM for 20 min. The atrazine concentration in the supernatant was also measured using a liquid scintillation spectrophotometer. The amount of atrazine desorbed was obtained from the difference in atrazine concentrations between the supernatant solutions of initial and diluted samples.

3.4 Results and Discussion

3.4.1 Long-Term Kinetic Study

Long-term kinetic studies indicated that adsorption-desorption on humic acid is slower than on clay minerals (Figure 3.1 and 3.2). Equilibria in atrazine adsorption and desorption on montmorillonite was attained in 2 h, while equilibrium on vermiculite was reached in 6 d. For humic acid, adsorption and desorption of atrazine continued up to 90 days. The humic acid-coatings on montmorillonite decreased the reaction rates significantly. Equilibria in atrazine adsorption and desorption on the Pocomoke surface soil was attained in 10 d (Figure 3.4), while for the Matapeake subsoil, equilibrium was reached in 2 h. To compare the relative reaction rates of the adsorption and desorption among the different adsorbents, the equilibrium times required to complete 90% of the reaation were extrapolated from the long-term kinetic study (Table 3.1). Humic acid, Pocomoke surface soil, and humic acid-coated montmorillonite required a much longer equilibrium time to complete 90% of adsorption and desorption than vermiculite. This is probably due to the rate-limiting step of intraparticle diffusion in the pores and capillaries of the organic matter in the former three samples. In the solid state the humic acid is considered to have a laminated, textured makeup (Orlov and Glebova, 1972). It has been postulated that the structure of humic acid is loose and open (Kodama and Schnitzer, 1967) and contains voids or holes of different molecular dimensions. It follows, therefore, that at longer reaction times, adsorption is governed by diffusion of atrazine molecules from the exterior surfaces to the interior of the pores of the humic acid.

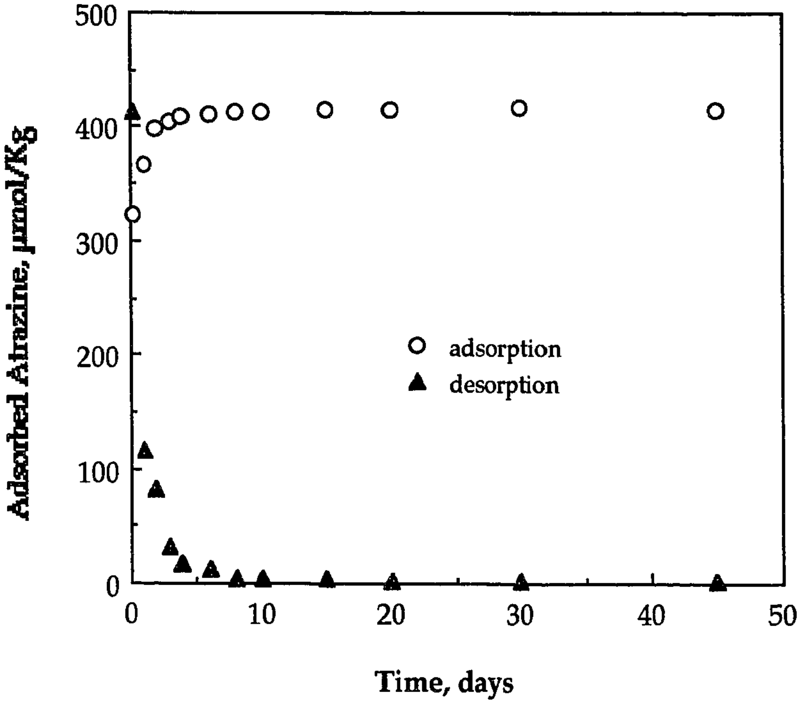

Figure 3.1 Long-term adsorption-desorption kinetics on vermiculite at 277K.

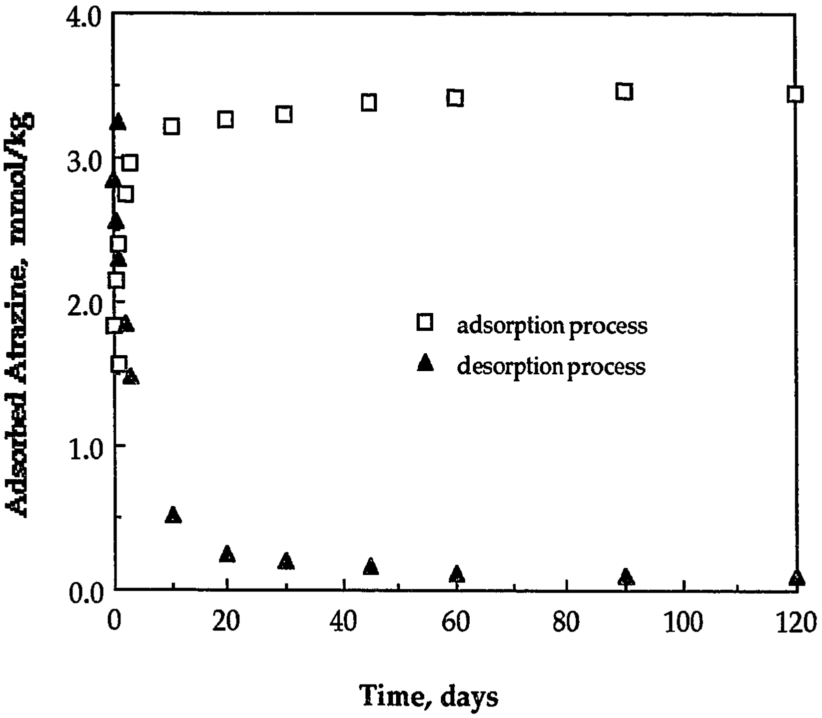

Figure 3.2 Long-term adsorption-desorption kinetics on humic acid at 277K.

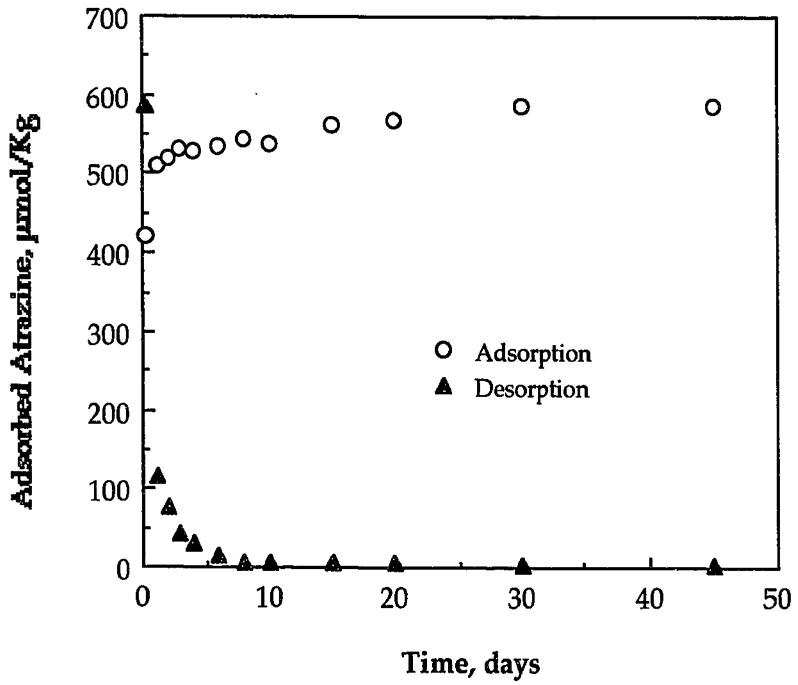

Figure 3.3 Long-term adsorption-desorption kinetics on humic acid-coated montmorillonite at 277K.

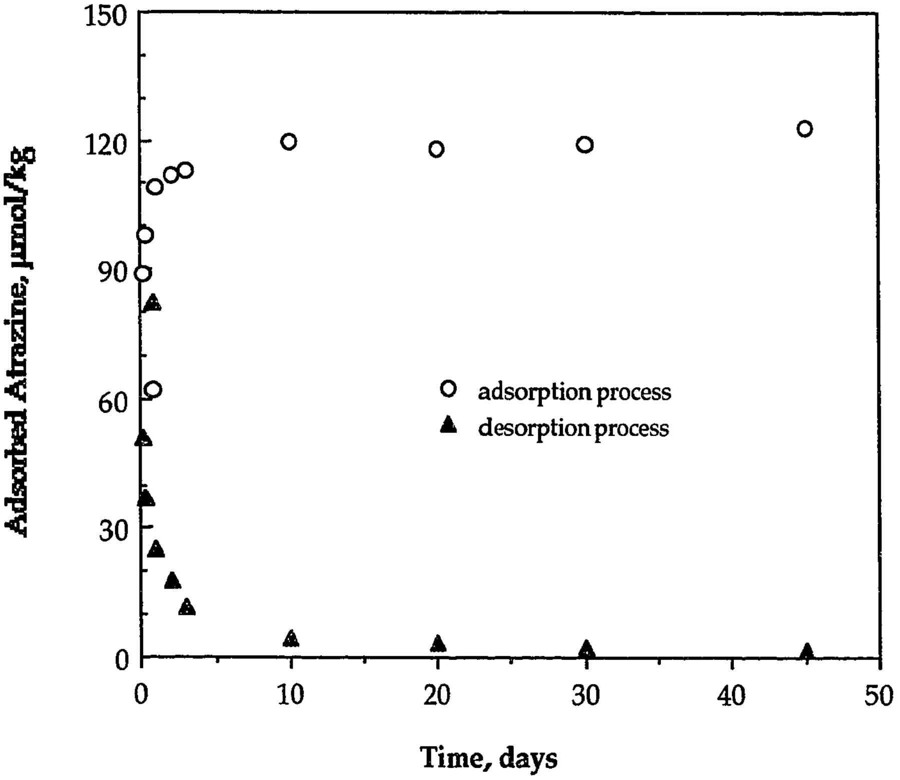

Figure 3.4 Long-term adsorption-desorption kinetics on Pocomoke sandy loam at 277K.

Table 3.1 Time (h) required to complete 90% of atrazine adsorption and desorption. *

	90% adsorption	90% desorption
	h	
Humic acid(HA)	46.5	56.2
HA-montmorillonite	19.8	21.0
Vermiculite	10.9	10.8
Pocomoke sandy loam	34.6	36.8

* These time periods were extrapolated from the long-term kinetic studies.

3.4.2 Model Simulation

The pore diffusion model provides a framework for understanding solute mass transfer within porous particles and aggregates. A mathematical description of diffusional mass transfer requires an assumption of the particle or aggregate geometry. If the particles are approximated as spheres, Fick's second law of diffusion within the particle can be expressed as

$$\rho_a \frac{\partial q_r}{\partial t} + \theta_i \frac{\partial C_r}{\partial t} = \frac{\theta_i D_p}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \qquad (3\text{-}1)$$

Where ρ_α = apparent density of the sorbing particle [$M\,L^{-3}$]

q_r = solute concentration in sorbed phase [$M\,M^{-1}$]

θ_i = fractional intraparticle porosity

C_r =immobile aqueous phase concentration [$M\,L^{-3}$]

D_p = effective pore diffusion coefficient [$L^2\,T^{-1}$]

r = radial coordinate [L]

Equation 3-1 describes the concentration of sorbate as a function of time and position within the immobile fluid which fills the internal pores of a soil particle or aggregate. As Eq. 3-1 is written, the driving force for diffusion is the concentration gradient in the aqueous phase, surface diffusion is ignored, and diffusion occurs only through the aqueous phase.

Equation 3-1 can be simplified by differentiating the expression for the equilibrium isotherm and substituting for q_r. This substitution is valid if the rate of partitioning at the pore wall is faster than the rate of diffusion though the pore water. Then, the new mass balance is in terms of the aqueous concentration:

$$\frac{\partial C_r}{\partial r} = \frac{D_p}{R_{int}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r} \right) \qquad (3\text{-}2)$$

where R_{int} = internal retardation factor, defined by

$$R_{int} = 1 + \frac{\rho_a K_d}{\theta_i} \qquad (3\text{-}3)$$

R_{int} is the ratio of the diffusion rate of a sorbing species to that of a nonsorbing solute with the same pore diffusivity. Equation 3-3 assumes a linear adsorption isotherm and shows that the rate of diffusive sorption or desorption decrease with increasing isotherm slope, K_d.

The effective diffusion coefficient, D_p, reflects the rate at which the solute appears to diffuse through the particle. It accounts for the fraction of the time that the diffusing species is adsorbed on the solid surface and is therefore immobile. The actual rate at which the solute diffuses through the pore fluid is represented by the pore diffusion coefficient, D_p. For linear partitioning, D_p, is related to D_b by the expression:

$$D_p = \frac{D_b}{\chi_e} \qquad (3\text{-}4)$$

where χ_ε = effective tortuosity factor

D_b = bulk aqueous diffusivity $[L^2T]$

D_b values are known for many organic solutes or can be accurately estimated using empirically derived correlations. Thus, with an independent estimate of the internal retardation factor, the effective tortuosity factor (χ_ε) becomes the ultimate fitting parameter for a batch system modeled using Eq. 3-2.

Wakao and Smith (1962) introduced a simplistic model that related the effective tortuosity to a single, measurable parameter. According to their model, the effective tortuosity factor is related inversely to the internal porosity of the sorbent (θ_i)

$$\chi_e = \frac{1}{\theta_i} = \frac{D_b}{D_p} \qquad (3\text{-}5)$$

This relationship has failed to adequately account for the slow rates of sorption and desorption in recent studies with some natural sorbents. More complex expressions than that in Eq. 3-5 have been presented in the past, mainly for porous catalysts.

In the absence of independent estimation of internal retardation factors, the following expression can be substituted for Eq 3-2:

$$\frac{\partial C_r}{\partial r} = D_a \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \qquad (3\text{-}6)$$

where $D_a = D_p/R_{int}$ is the apparent diffusion coefficient. The apparent diffusion coefficient can be used to describe overall sorption-desorption rates.

If the effective pore diffusion coefficient is independent of solute concentration, then the apparent diffusion coefficient for the linear isotherm is a constant value. Furthermore, it can be demonstrated via the solution of Eq. 3-6 (with Eq. 3-4) that for a given solute/sorbing system, sorption will proceed at a overall faster rate than desorption. The observed D_a values of a sorption experiment would thus be greater than the observed D_a values for a desorption experiment.

The solution to Eq. 3-2 was approximated using an implicit finite difference scheme (Crank-Nicholson) employing a predictor-corrector routine to address the nonlinear isotherm case. A computer program (FORTRAN) was developed to execute the finite difference scheme. The numerical approximation was verified using the analytical solutions to the problems of diffusion from a sphere with a constant zero boundary condition and diffusion from a sphere into a well-mixed solution of limited volume. The spherical diffusion model was coupled with a fitting routing which determined the value of the effective pore diffusion coefficient (D_p) that minimized the mean squared error about the observed data.

Figure 3.5, 3.6, and 3.7 shows the experimental and the pore diffusion model fitting results. Quantitatively, the model described the kinetics reasonably well, capturing the relatively fast initial desorption from the sample and the relatively slow process that followed. However, it is apparent that the model underestimated the desorption rate at early times and overestimates the rate at later times. This aspect of the simulations may be due, in part, to the wide range of particle sizes associated with the bulk sample. Most fits were found to be unique, based on minimizing the mean-square residuals.

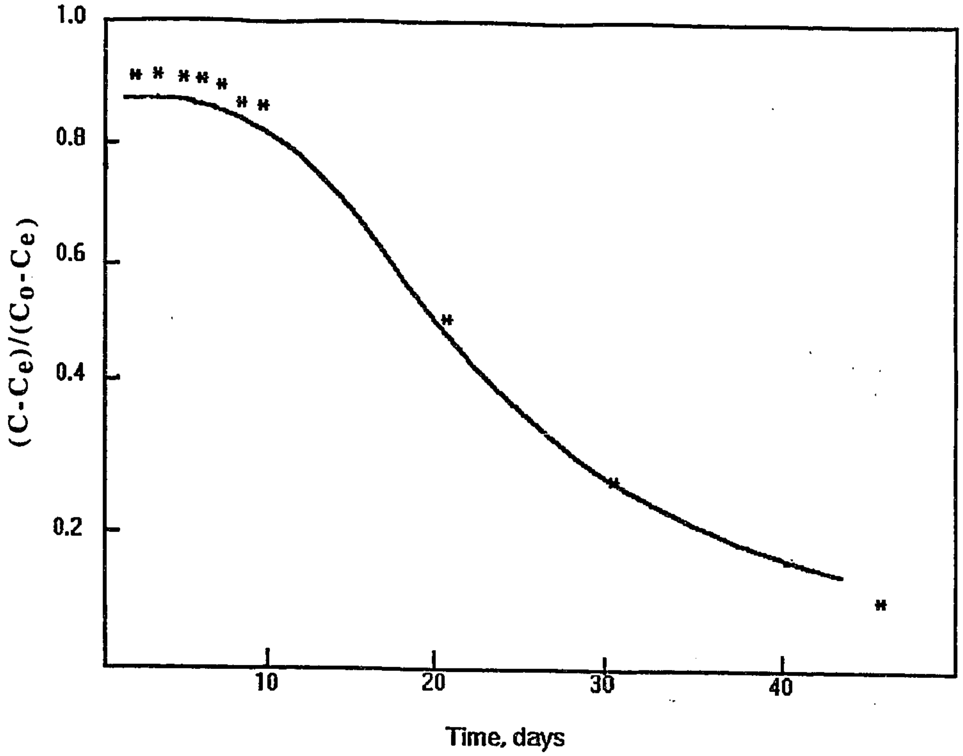

Figure 3.5 Experimental (*) and model-fitting (solid line) results for long-term desorption kinetics on vermiculite. The line represents the data fit based on the pore diffusion model.

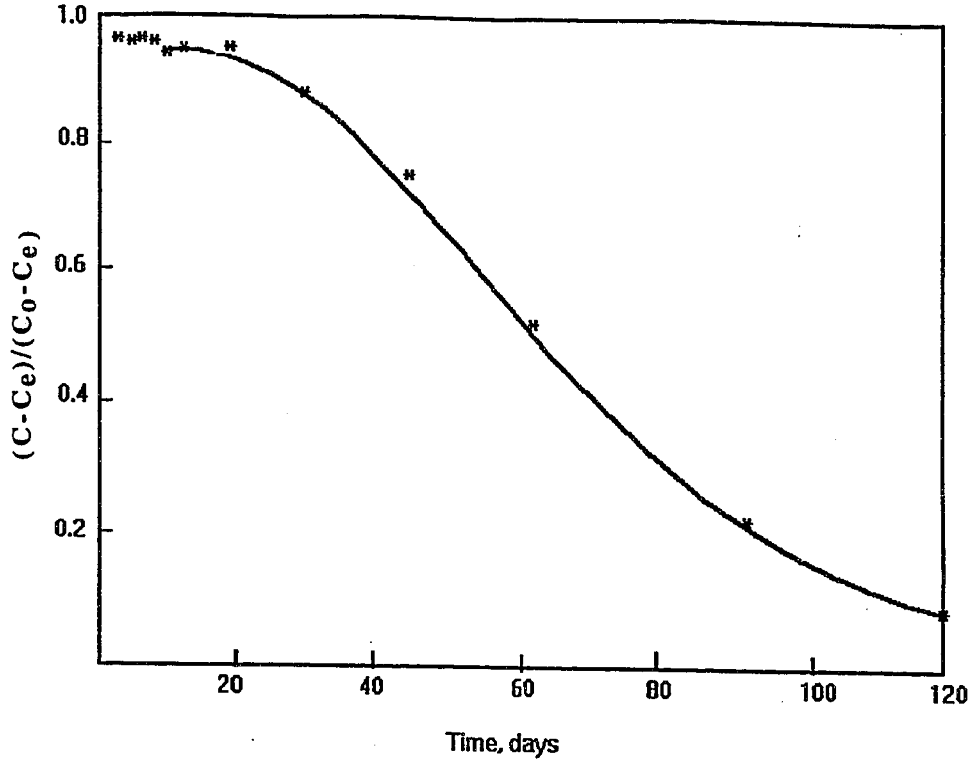

Figure 3.6 Experimental (*) and model-fitting (solid line) results for long-term desorption kinetics on humic acid. The line represents the data fit based on the pore diffusion model.

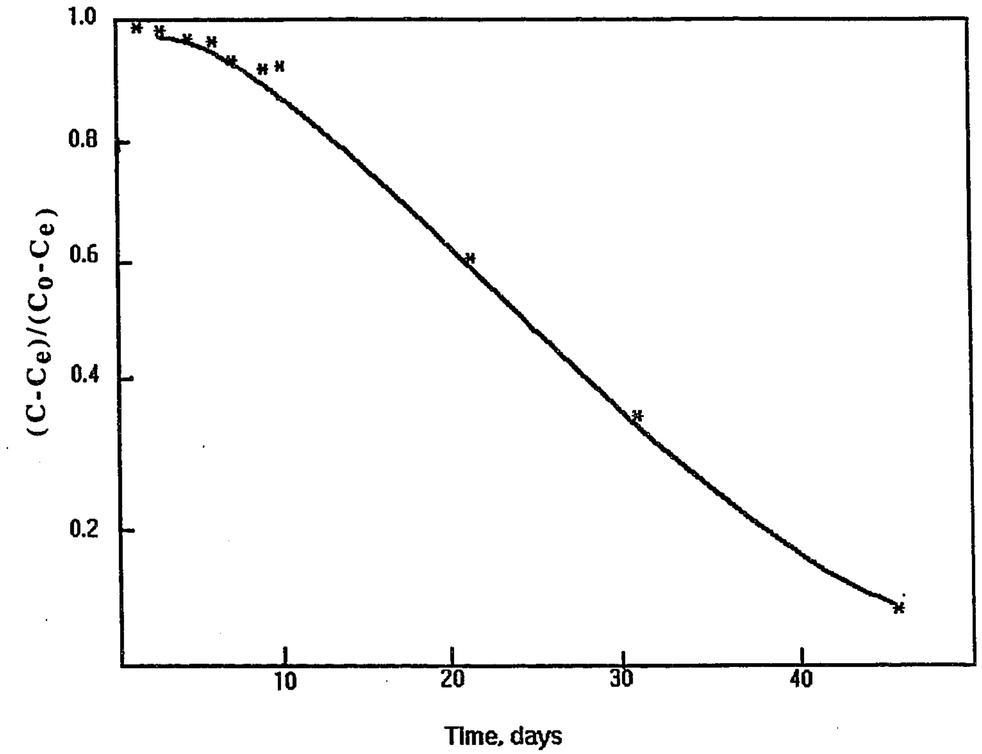

Figure 3.7 Experimental (*) and model-fitting (solid line) results for long-term desorption kinetics on humic acid-coated montmorillonite. The line represents the data fit based on the pore diffusion model.

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Chapter 4

SUMMARY AND CONCLUSIONS

All the findings of this study clearly show that the soil component that most affects atrazine retention is humic substances and that the kinetics of the reactions are important. Humic acid, a Pocomoke surface soil, and humic acid-coated montmorillonite not only have the greatest affinity for atrazine, but also have the slowest adsorption-desorption rates. This is probably due to the rate-limiting step of intraparticle diffusion of atrazine in the pores and capillaries of the organic matter in these three samples.

A number of studies have shown that with "aging" the nonlabile portion of the organic chemicals in the soil/sediment becomes more resistant to desorption (McCall and Agin, 1985; Steinberg et al., 1987; Pavlostathis and Mathavan, 1992, Scribner et al., 1992; Pignatello et al., 1993). Another major finding from sorption-desorption studies conducted on "freshly aged" and "aged" samples is the variability of the distribution coefficients (K_d values). Most of the K_d values obtained from the laboratory were based on an equilibration time of 24 h. When these values are compared to K_d values for field soils previously reacted with the organic chemicals ("aged" samples) for extended periods of time, the latter have much higher K_d values

(2 to 15 times more), indicating that much more of the organic chemical is in a sorbed state. In this study, the distribution coefficients obtained based on a 24 hour equilibrium time were much lower than those obtained from the long-term kinetic studies. As shown in Table 4.1, The K_d value of atrazine adsorption on humic acid obtained from a 24 hour equilibrium time was almost half of that from a 90 day equilibrium time.

Many of the investigations reported in the literature have shown that adsorption-desorption is characterized by a rapid, reversible stage followed by a much slower, nonreversible stage or biphasic kinetics. The rapid phase has been ascribed to retention of the organic chemicals in a labile form that is easily desorbed. However, the much slower reaction phase involves the entrapment of the chemicals in a nonlabile form that is difficult to desorb. These slower sorption-desorption reactions have been ascribed to diffusion of the chemical into micropores of organic matter and inorganic soil components. The biphasic kinetics concept was tested in this study by simulating the retarded radial pore diffusion model to our long-term atrazine desorption data. The model fitted reasonably well for humic acid, humic acid-coated montmorillonite, and vermiculite systems. Our results have important implications for modeling pesticide transport and fate in soils, since most transport models assume instantaneous equilibrium and a first-order reaction(s). Such assumptions would be incorrect for modeling pesticide sorption on soils high in organic matter and containing certain clay minerals such as vermiculite. Moreover, this assumption may be invalid for soils with a long-contamination history.

Table 4.1 Distribution coefficients (K_d) calculated for atarzine adsorption at pH 3.0 based on different equilibrium times.

Equilibrium time	24 hours	90 days
Humic acid(HA)	95.60	175.64
HA-montmorillonite	30.28	47.59
Vermiculite	23.45	28.56
Pocomoke sandy loam	5.34	8.01

Very few pesticide adsorption-desorption kinetic studies have been conducted. Most of them were carried out on soils involving time periods of only hours. Because contamination and remediation in the natural environment occurs over long times and is often characterized by slow mass-transfer reactions, long-term equilibrium and rate phenomena like those investigated in this research are important to understand.