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DISSERTATION

SORPTION AND DESORPTION OF METRIBUZIN WITH SOIL AND SEWAGE BIOSOLIDS ORGANIC MATTER: INTERPRETATIONS BASED ON MECHANISTIC AND KINETIC MODELS

Submitted by

Cary Burton Jackson

Department of Soil and Crop Sciences

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY CARY BURTON JACKSON ENTITLED SORPTION AND DESORPTION OF METRIBUZIN WITH SOIL AND SEWAGE BIOSOLIDS ORGANIC MATTER: INTERPRETATIONS BASED ON MECHANISTIC AND KINETIC MODELS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Committee on Graduate Work

Adviser

Department Head

ABSTRACT OF DISSERTATION

SORPTION AND DESORPTION DYNAMICS OF METRIBUZIN WITH SOIL AND SEWAGE BIOSOLIDS: INTERPRETATIONS BASED ON MECHANISTIC AND KINETIC MODELS

Soil sorption and release mechanisms for pesticides are central to predicting their transport, bioavailability, and biodegradation. It was hypothesized that sewage biosolids added to soil would affect pesticide sorption and desorption and that the sorptive characteristics of biosolids would enhance the release of sorbed metribuzin.

Two sandy loam soils containing differing amounts of soil organic matter (1% and 3%) and sewage biosolids (37.5 and 125 mg g^{-1}) were used to evaluate sorption characteristics of metribuzin. The herbicide (^{14}C-ring labeled) was added to soil and soil plus biosolids to obtain six concentrations ranging from 0 to 5.0 ug cm^{-3}. Sorption was measured after 24 h. Desorption was studied using the highest equilibrium concentration from sorption isotherms and was measured over 120 h at 24-h intervals.

The sorption and desorption data fit the Freundlich model. More metribuzin was sorbed with the soil with greater amounts of organic matter and with increasing amounts of biosolids. Sorption linearity (n_f) increased with

increases in organic matter. Sorption decreased with the addition of extracted organic carbon from sewage biosolids, and residual biosolids after removal of labile organic carbon.

Desorption was described by an initial linear, fast-release process, followed by an exponential, slow-release process. The magnitude of metribuzin release increased with increasing amounts of biosolids. The differences in desorption and sorption isotherms (hysteresis) decreased with increasing amounts of added biosolids.

Sorption characteristics and hysteresis for these soils and the biosolids treatments were explained using the Freundlich and glassy/rubbery models. Reaction kinetic models were used to describe the mechanism of desorption. The organic matter of the soil and amended soil was described as having two-compartments. The first compartment exhibited instantaneous and reversible sorptive sites, with a second compartment exhibiting slow-release kinetic sorptive sites.

These results support the theory that the sorptive characteristics of organic matter are responsible for not only the sorptive capacity of the soil but also the mechanisms of sorption and rates of release of sorbate.

Cary B. Jackson
Department of Soil and Crop Sciences
Colorado State University
Fort Collins, Colorado 80523
Spring Semester, 2000

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I appreciate the mentoring and guidance of my advisor, Kennith G. Doxtader. I am indebted to the opportunity that was afforded to me.

DEDICATION

I dedicate this work to my wife Kristy, and my children, Nathan, Matthew, and Celeste for their support. The demands of a family provided a balance and release from the frustration of being a graduate student.

I can do everything through him
who gives me strength.

Philippians 4:13

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CHAPTER 1

INTRODUCTION

The sorption characteristics of pesticides in soil are important factors affecting the fate of these compounds in the environment. As a result of discovery of the herbicide 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one (metribuzin) in the groundwater of San Luis Valley in Colorado, attention has focused on the use of organic matter additions to increase retention of the compound by soil. Several organic amendments have been evaluated, including green animal and composted manure, plant residue, and municipal biosolids (Dunn, 1995). Among these amendments, municipal sewage biosolids appear to have the greatest propensity for sorption and thus, the greatest potential for increasing the soil retention of metribuzin.

In using the sorption isotherm value (K) to predict pesticide fate in soil (persistence, movement, retardation, etc.), one often finds predicted results that significantly differ from actual experimental results. The difference is attributed to the dynamic characteristics of soil organic matter, both stationary and mobile. An increase in stationary organic carbon would be expected to increase sorption. An increase in the mobile dissolved organic matter could increase the water solubility of the sorbate, thus decreasing stationary sorption. Once equilibrium of

the sorbate to sorbent is achieved, a fraction of the sorbent could then be irreversibly sorbed to the soil.

While the Freundlich and advection-dispersion models are most frequently used to describe solute distribution and transport, between water and through soil, they often overstate sorption and understate transport distance and rate of movement. The models carry an assumption that the pesticide sorption process is reversible and that sorption/desorption processes are in equilibrium throughout the system. But these assumptions are often misleading and not justified (Savage and Waschope, 1974, Koskinen et al., 1979. Calvet, 1980., and Clay et al., 1988).

Study Objectives

The objectives of this study were to investigate and model sorption and desorption characteristics of the herbicide metribuzin in soil amended with organic polymer-treated biosolids.

In this study, the following questions were addressed:

1. Does metribuzin sorption and desorption with soil amended with polymer-treated biosolids differ from what is predicted by conventional models?
2. Are K_f, K_d, and K_{oc} good predictive constants for characterizing the sorption of metribuzin in soil amended with polymer-treated sewage biosolids?

3. What organic matter characteristics (properties and structures) control sorption and desorption?

4. Is the use of organic polymer-treated sewage biosolids likely to be an effective treatment to impede and slow down the transport of metribuzin in soil?

Hypothesis

It was hypothesized that sewage biosolids added to soil will affect pesticide sorption and desorption and that the sorptive characteristics of biosolids will enhance the release of sorbed metribuzin.

Experimental Approach and Expected Benefits

Two sandy loam soils containing differing amounts of organic carbon were used to investigate differences in sorption, desorption, and hysteresis. Studies of metribuzin sorption and desorption were conducted at constant temperature, pH, and ionic strength. The amounts of biosolids applied to soil varied among herbicide concentration treatments. ^{14}Carbon-labeled metribuzin was used to quantify sorption and desorption compartments.

Isotherms (Langmuir, 1918; Freundlich, 1926) are often used to describe changes in pesticide sorption to soil. The most common usage of isotherms is to describe the changes in pesticide solution concentration in soil as affected by the concentrations of added pesticide (sorption). In the field, pesticide sorption and

desorption are continual processes. Therefore, for this study both sorption and desorption isotherms are included to improve the description of the system.

The knowledge gained from this research should benefit decisions about organic matter amendments when the environmental fate of pesticides is of concern

CHAPTER 2

LITERATURE REVIEW

Soil sorption and release mechanisms for pesticides are central to predicting pesticide transport, bioavailability, and biodegradation. In an attempt to better understand how pesticides move through the soil to groundwater, extensive research has been undertaken to understand sorption processes.

Various aspects of the sorption of pesticides to soil organic matter have been presented over the past several decades by numerous researchers. (Baily and White, 1964; Hamaker and Thompson, 1972; Karickhoff et al.1979; Rao and Davidson 1980; Karickhoff, 1981; and Chiou et al. 1979, 1981, 1983, 1984). There are considerable data to support the concept that partitioning of nonionic organic compounds to soil organic matter is the major process of soil uptake from solution. Of particular importance to sorption are the specific soil organic substrates that interact with pesticides. Wershaw et al. (1969) inferred that water-soluble soil organic material would enhance the solubility of certain pesticides. Ogner and Schnitzer (1970) showed that fulvic acid (FA) combines with organic chemicals to form stable complexes that are soluble in water. Ballard (1971) indicated that water-soluble humic-like substances act as carriers of DDT in the enriched organic horizons of forest soils. Poirrier et al. (1972) showed that naturally occurring organic colloids are capable of sorbing and

concentrating trace amounts of DDT at levels far in excess of that expected for pure water. Pierce et al. (1974) suggested that suspended humic particles in solution serve to transport and accumulate chlorinated hydrocarbons in sediments. Stevenson (1982) suggested that organic substances that control sorption are mainly in the form of humic acid (HA) and FA.

Pesticide Sorption by Soil

To better understand the fate of organic pesticides in a soil-water system, sorption isotherms are used to quantify pesticide distribution (EPA, 1975; Rao and Davidson, 1980). A sorption isotherm shows the amount of pesticide sorbed to soil as a function of its equilibrium concentration in solution. For a sorption isotherm to be representative of distribution, equilibrium must be achieved without secondary precipitation. Although nonlinear sorption is frequently observed, in the absence of experimental information, it is common to assume a linear isotherm. Furthermore, it is usually assumed that sorption and desorption follow the same isotherm (referred to as sorption-desorption singularity) (Brusseau and Rao, 1989).

The sorption of nonionic non-polar organic compounds is known to be correlated with soil organic matter content (Karickhoff et al., 1979). Haset and Banwart (1989) contend that sorption of nonionic, non-polar organic chemicals is largely unaffected by clay type and amount or soil pH unless the soil is low in organic carbon. Based on the understanding and correlation of soil organic matter and sorption, Brown and Flagg (1981) developed an empirical relationship

between octanol/water partition coefficients (K_{ow}) and sediment sorption coefficients normalized to organic carbon (K_{oc}), suggesting that octanol models organic matter with respect to sorption. The authors concluded that reasonable estimates of K_d or K_{oc} could be determined from a single determination of the octanol/water partition coefficient and knowledge of the organic carbon content of the sediment.

Sorption to Soil Organic Matter

Typically, in the soil science curriculum we are taught that an increase in organic matter results in increased pesticide sorption and retention by soil (Bohn et al., 1985; Sposito, 1989; Sparks, 1997). The foundation for this fundamental concept was first brought forth by Lambert (1966, 1967, 1968), who demonstrated that for a given soil, the sorption of neutral organic pesticides can be well correlated with organic matter content of soil. His approach was to normalize soil sorption of a known compound to that of a reference soil system. Lambert further suggested that the role of soil organic matter was similar to that of an organic solvent and that the partitioning of a neutral organic compound between soil organic matter and water should correlate well with its partitioning between water and an immiscible organic solvent. Briggs (1973) developed a regression model relating soil sorption of pesticides to octanol-water partitioning (K_{ow}). Karickhoff et al. (1979) normalized sorption coefficients to percent organic carbon (K_{oc}) and showed a direct dependency on sorbent properties. They also showed that K_{oc} was correlated with K_{ow} and that a reasonable estimate (within a

factor of 2) of hydrophobic pollutant sorption could be determined from the particle size distribution and organic carbon content of sediment and the octanol/water distribution coefficient of the pollutant.

Traditional Sorption Models

There are three main models used to describe sorption: Langmuir, Freundlich, and Brunauer-Emmett-Tellar (BET). The BET equation (Brunauer, Emmett, and Tellar, 1938) is commonly used to determine the surface area of solids from gas adsorption results. While the BET has been used to describe ion adsorption, the Langmuir equation (Langmuir, 1918) is preferred.

The Langmuir equation is based on three main assumptions:

(i) There are specific sorption sites with no interaction between sorbate molecules.

(ii) There is constant energy of sorption that is independent of the extent of the surface coverage.

(iii) A maximum sorption exists that is equal to a complete monomolecular layer on the adsorbent surface.

The Langmuir equation is in the form:

$$x/m = \frac{KCb}{(1+KC)} \qquad (1)$$

where x/m is the mass of adsorbate per unit mass of adsorbent; C is the equilibrium concentration of adsorbate; *K* is an empirical constant thought to be

related to the binding strength; and b is the maximum amount of adsorbate that can be adsorbed on the monolayer of the soil particle. The linear form equates to

$$\frac{C}{\left(x/m\right)} = \frac{1}{Kb} + \frac{C}{b} \qquad (2)$$

A plot of C/(x/m) versus C yields a straight line with a slope 1/b and intercept $1/Kb$. K is the quotient of the slope and intercept. An advantage of the Langmuir equation is that it defines a limit to sorption for a given array of sorption sites of the soil particle. It is of particular use for estimating the sorption capacities of inorganic and organic ions.

The Langmuir equation has also been extended to consider multiple-site sorption distribution on soil particles. The extended form is given as

$$x/m = b_1 - \frac{\left(x/m_1\right)}{K_1C + b_2} - \frac{\left(x/m_2\right)}{K_2C} \qquad (3)$$

The subscript b_1 and b_2 represent the different sorption type regions or mechanisms. The sorption maxima are the sum of b_1 and b_2. If more than two regions or mechanisms are involved, the equation can be further extended.

The sorption of nonionic pesticides are typically modeled using the Freundlich equation (Freundlich, 1926):

$$x/m = K C^n \quad (4)$$

where K and n are empirical constants. When n is $\geq$ 1, K becomes the partition coefficient (K_d) and is a function of (x/m)/C. Inherent in this equation is (i) a decrease in energy of sorption with increasing surface coverage is due to surface-heterogeneity, and (ii) the maximum sorption capacity is not quantified.

Because most if not all pesticides that are nonionic and, of low solubility in water can be fitted linearly to the Freundlich model, sorption at low concentrations from aqueous solution can be exponential. When this occurs, sorption becomes multi-mechanistic. That is, K is exponential at low concentrations and becomes linear at higher concentrations.

Sorption and Desorption Phenomena

Despite the popularity of the use of batch isotherm methods, the translation of the results obtained from these methods to real world sorption phenomena in dynamic systems remains in question (Green and Corey, 1971; Huggenberger et al., 1972; Elabd, 1984). The batch method is idealized because the measurement assumes equilibrium and maximizes sorbent-solute contact. For solutions flowing through structured soil, however, two basic types of non-equilibrium sorption-desorption behavior are recognized. Physical non-equilibrium (a transport related phenomena) occurs where the rate limiting step of the sorption reaction is the movement of chemical to and from the sorbent surface. Chemical non-equilibrium (a surface chemistry phenomena) occurs if

the reaction rate(s) itself is the limiting step (Brusseau and Rao, 1989; Nkedi-Kizza et al., 1989; Farrell and Reinhard, 1994; Schrap et al., 1994; Spurlock and Biggar, 1994; McGinley et al., 1996; Aroca et al., 1996, Aochi and Farmer, 1997; Huang et al., 1997). The nonlinear sorption/desorption behavior results from biphasic sorption kinetics and proceeds with an initial "fast" rate followed by a subsequent "slow" rate. Brusseau and Rao (1989) point out that nonlinear sorption occurs when chemical concentrations are sufficiently high enough that the activity coefficient is not constant and sorption mechanisms other than hydrophobic binding are present.

In addition to nonlinearity of sorption, research on hysteresis (difference between sorption and desorption) has been reported (Pignatello, 1990; Pignatello et al., 1993; Hunter et al., 1996; Aochi and Farmer, 1997; Huang and Weber, 1997). Hysteresis results from slow release of hydrophobic organic chemicals from sorption sites. Pignatello and Huang (1991) studied desorption of several pesticides from soil and sediment materials and found desorption occurred at two different rates. They defined these rates as the "fast" fraction and the "slow" fraction. The "fast" fraction or compartment was found to be linear while the "slow" fraction or compartment followed an exponential desorption. Barriuso et al. (1992), developed an empirical, two-compartment model

$$C_s = K_{f1} C_e + C_{sn}\left(1 - e^{-K_{f2} C_e}\right) \tag{5}$$

which more accurately described desorption over that of the Freundlich model,

especially for extreme high concentration points of the isotherm.

Xing and Pignatello (1997) suggested that the Freundlich model is too simplistic for describing sorption of hydrophobic organic chemicals to organic matter sorbents. They state that:

(1) There is a concentration dependency of "dissolved" compounds inside the organic matter sorbent structure.

(2) There is site specific and size structure factors that influence sorption.

(3) Sorption potentials are not constant.

(4) Organic matter sorbents have internal surface sorption sites (de Jonge and Mittelmeijer-Hazeleger, 1996).

Increased exposure time for organic matter sorbents and solute leads to stronger sorption (Huang and Weber, 1997) and greater resistance to desorption (Pignatello et al., 1993). Most sorption and desorption studies are conducted using short equilibration times, usually less than one week. However, sorption studies by Brusseau (1989), Nkedi-Kizza et al. (1989), Brusseau et al. (1991), Pedit and Miller (1996), Pignatello and Xing (1996), Weber and Huang (1996), and Xing and Pignatello (1996) suggest that sorption equilibrium be achieved only after substantially longer periods of time.

Soil Organic Matter Structures

The dominant sorbents within soil organic matter are humic substances. Humic substances are ultimately derived from microbially mediated poly-condensation reactions from plant exudates and animal wastes and dead plant

and animal tissue (Stevenson, 1992). Humic substances consist of physically and chemically heterogeneous mixtures of high molecular weight compounds (generally from 200 to 30,000 Da) that contain aliphatic, aromatic, and hetero-atomic cyclic structures substituted with amines, alcohols, phenols, ketones, and carboxylic acid groups.

Humic substances can be chemically and physically separated into two main fractions, humic acid (HA) and fulvic acid (FA). These fractions are extracted from soil with alkali. HA is precipitated under acid conditions. FA is soluble in both alkali and acid. FA has lower molecular weights and higher O to C ratios as compared to humic acids. HA and FA act similarly to synthetic organic polymers and behave in a manner predicted by charged particle colloid or "DLVO" theory. That is, they undergo stabilization-destabilization (flocculation or dissolution) by attractive and repulsive particle forces. Structurally, HA and FA are rigid "spherocolloids" at high concentration, low pH, and high concentrations of neutral electrolytes (Ghosh and Schnitnzer, 1980). In contrast, at low HA and FA concentrations, low ionic strength, and moderate pH, they are flexible linear colloids. Young and Weber (1995) and Xing and Pignatello (1997) describe humic substances as having expanded and condensed regions within their structures. The presence of such regions would have considerable implications for sorption and desorption and are analogous to glassy and rubbery states of synthetic organic polymers (Pignatello, 1997).

Wershaw (1993) described humic substances as having separate hydrophilic and hydrophobic surfaces (amphophile) that form pseudomicelles.

Humic substances are viewed as ordered aggregates of amphophiles, composed mainly of plant polymer segments attached to functional carboxylic acid groups (Stevenson, 1994). The humic aggregates are arranged in such a way that the hydrophobic surfaces are in the interior pores of the molecule and the hydrophilic surfaces are on the exterior. The ordered aggregates exist as bilayer membranes, adhering to mineral surfaces and acting as micelles in soil solution. The hydrophobic interior acts as a partitioning environment for neutral organic compounds, while the hydrophilic exterior can exist as a highly charged state, adsorbing cations and positively charged chemical species from solution.

Advances in the Understanding of Sorption Mechanisms

Pignatello and Xing (1996) describe "specific" or chemisorption and molecular diffusion as causation for "slow" sorption. However, chemisorption does not appear to be a major role with hydrophobic organic chemicals. Brusseau et al. (1991) concluded that specific sorbate-sorbent interactions do not contribute to rate-limited sorption of hydrophobic organic chemicals by natural organic matter.

Based on the structures of soil organic matter proposed by Stevenson (1982 and 1994), Schnitzer (1978), Ghnosh and Schnitzer (1980), Swift (1989), Chen and Schnitzer (1989), Young and Weber (1995), Xing and Pignatello (1997), and Wershaw (1993), there are two possible diffusion mechanisms to explain the sequestration of hydrophobic organic chemicals by organic matter. The first mechanism is diffusion of hydrophobic organic chemicals into the lattice

or structural voids of HA and FA. This mechanism is called intraorganic matter diffusion (IOMD) and has been studied extensively by de Jonge and Mittelmeijer-Hazeleger (1996). The second mechanism is diffusion of hydrocarbons into the hydrophobic interior of the pseudomicelle structure of HA and FA (Chien, 1997).

Intraorganic Matter Diffusion (IOMD) Theory

Using surface area techniques similar to that of Brunauer, Emmett, and Tellar (1938), de Jonge and Mittelmeijer-Hazeleger (1996) studied and described the physical structures of soil organic matter. Their study revealed that organic matter consists of a network of microporus structures that are not hydrated. Based on concentration gradients and pore size dimension, they concluded that configurational diffusion is the primary transport mechanism for the movement of nonionic organic contaminants to organic matter micropores. The studies of Nkedi-Kizza (1989), Brusseau et al. (1991), Schlautman and Morgan (1993) Hu and Brusseau (1995), Weber and Huang (1996), Xing et al. (1996), and Aochi and Farmer (1997) further support this theory. Hydrophobic organic chemicals are subject to diffusivity constraints throughout the sorption/desorption process.

Experimental observations that support IOMD theory are as follows:

(1) Biphasic or two-compartment sorption/desorption isotherms are observed with hydrophobic organic chemicals and organic matter (Schrap et al., 1994 and Aochi and Farmer, 1997).

(2) The "slowness" of desorption is a function of residence time with organic matter (Alexander, 1995 and Loehr and Weber, 1996).

(3) The presence of organic cosolvents increases the rate of sorption and desorption due to swelling effects of the organic matter (Brusseau et al., 1991 and Xing et al., 1996).

(4) There is solute pair competition (Xing and Pignatello, 1997).

(5) Rate of sorption/desorption is a function of temperature changes and contraction and expansion of organic polymer structure (Carroll et al., 1994, Young and Weber, 1995; Xing and Pignatello, 1997; and Lebouf and Weber, 1997).

(6) Sorption capacity is a function of dimensional structure of the organic matter (Young and Weber, 1995; Chin et al., 1997; Iglesias-Jimenez et al., 1997; and Xing and Pignatello, 1997).

(7) Sorption to organic matter is influenced by its chemical structure (Hu et al., 1995 and Chiou et al., 1998).

(8) Symmetrical breakthrough curves are observed for displaced solutes (Nkedi-Kizza et al., 1989).

(9) Gas adsorption studies with organic matter show internal micropore sites accessible only by diffusion through the solid phase (de Jonge and Mittelmeijer-Hazeleger, 1996).

Pseudomicellar Theory of Soil Organic Matter

The studies of Chien et al. (1997) suggest the applicability of pseduomicellar theory to describe sorption of hydrophobic organic chemicals to humic substances. By studying the effects of hydrophilic and hydrophobic

paramagnetic probes on the nuclear magnetic relaxation of atrazine in humic acid solution, they found evidence to confirm the existence of a hydrophobic domain.

Engebretson and Wandruszka (1994) monitored the fluorescence of a pyrene probe in five different HA solutions. They found that in a HA solution of low ionic strength, hydrophobic domains exist that are accessible to both solvent and solvent-borne quenchers. Hydrophobic organic chemicals in proximity to this region can undergo diffusive motion and come into contact with the solvent quenchers. They also found that temperature played a role similar to ionic strength in affecting HA microorganization. However, this observation was found not to be universal and was a function of aromaticity and aliphatic content of HA. For example, a marine HA derived from algae is mostly aliphatic (Stuermer and Harvey 1977), whereas terrestrial HA, derived from higher plant material, is rich in aromaticity. At increasing ionic strengths, they found the formation of hydrophobic colloids. Based on the fluorescence anisotropy of a diphenyloxazole probe, Engebretson et al. (1996) further evaluated association indices of HA with nonpolar organic compounds. Their index of variations provided further support for the presence of pseudomicelles that sequester hydrophobic organic chemicals from solution. They concluded that the sorptive capacity of HA is related to its molecular size distribution and conformational configuration.

Glassy/Rubbery Model of Soil Organic Matter

Recently, studies have been undertaken to explain two-compartment sorption and desorption of organic chemicals using the concept of the polymeric glassy/rubbery model (Carroll et al., 1994; Young and Weber, 1995; Pignatello and Xing, 1996; Xing et al., 1996; Xing and Pignatello, 1997; and Graber and Borisover, 1998). According to the model, humic substance colloids are viewed as having two different and distinct structures or regions where sorption takes place. The first region consists of a hard, condensed organic material analogous to the glassy state of synthetic organic polymers. The diffusion rate of solute to this type of site would be "slow", and sorption and desorption would follow nonlinear hysteretic isotherms, with competition between cosolutes for sorption. The second region consists of soft, amorphous organic material analogous to the rubbery state of synthetic organic polymers. At this type of site, there would be linear isotherms, rapid diffusion, no hysteresis, and no cosolute competition for sorption (Luthy et al., 1997).

Carroll et al., (1994) first used the glassy/rubbery model concept to describe two-compartment desorption with polychlorinated biphenyls (PCBs) from Hudson River sediments. Their data suggest a "fast" desorbing labile fraction (24 h desorption) and a "slow" desorbing resistant fraction (170 h desorption). They concluded that the labile and resistant fractions develop from different diffusion rates of PCBs associated with two structurally distinct compartments or phases of the organic matter. One was conceptualized as a swollen phase and the other as a condensed phase.

In another study by Xing et al. (1996), competitive sorption between polar and non-polar organic cosolutes to differing organic matter was investigated. The sorbents chosen for this study included a mineral soil (3% organic matter), a peat soil (93% organic matter), "rubbery" polymers (polyethylene, cellulose, and chitin), a "glassy" polymer (poly[2,6-diphenyl-*p*-phenyleneoxide]), and a mesoporus silica gel. The isotherms for single solutes on the "rubbery" polymers were linear, and no competition between solutes for sorption sites was observed in multi-solute systems. For other sorbents, the isotherms were nonlinear, there was significant competition between chemical analogs and no competition between non-analogs. The results also indicated that like a "glassy" polymer, soil organic matter is a dual-mode sorbent. With sorption mechanisms that were both simple partitioning and hole filling. The author concluded that dual-mode sorption with soil organic matter is applicable to both polar and non-polar chemicals.

Dual-mode Sorption

The findings of Xing and Pignatello (1997) supported the dual-mode sorption, in which partitioning and hole filling mechanisms occur concurrently as in "glassy" polymers. They studied the sorption of chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 2,4-dichlorophenol, and the herbicide metachlor from water to high organic soils, humic acid particles, native peat, humin, and poly(vinyl chloride). Sorption was found to be non-linear, competitive, and affected by temperature and cosolute addition for all sorbents.

With each sorbent, the dual-mode sorption mechanism seemed applicable. Sorption became progressively non-linear and competitive following the order of humic acid, native peat, and humin. This suggested that the order reflected the increasing "glassy" characteristics (high rigidity and condensation) of the organic material. Xing and Pignatello (1997) further conceptualized that soil organic matter is an amalgam of glassy- and rubbery-type regions, with each phase or having its own dissolution (partitioning) domain. Based on this model, the glassy region contains holes or structural voids in which IOMD processes take place. The holes would vary in size and would normally be filled with water and small natural organic molecules. The number, size, steric, and electronic properties of the void structure would confer sorption specificity.

The earlier research of Young and Weber (1995) also supports the glassy/rubbery model of soil organic matter. They measured isosteric heats of phenanthrene sorption to three natural soils of varying degrees of organic carbon diagenesis. With either increasing temperature or solid phase loading, the isotherms became increasingly linear and the sorption reactions less exothermic. While these observations are expected with classical surface sorption reaction models, they do not explain decreases in exothermic reactions for a surface sorption process at high sorption capacity. These findings are consistent with a model that considers soil organic matter as a macromolecule that is gradually transformed diagenetically from a loose amorphous structure to a condensed and highly microcrystalline structure.

Weber and Huang (1996) measured and characterized the rates of

sorption of phenanthrene to four different types of soils and sediments by examining the time dependence of solute phase distribution relationships (PDRs) in mixed batch reactors. Their experiments were conducted using a range of concentrations to obtain a time series of non-equilibrium PDRs. They found that the non-equilibrium PDRs were increasingly non-linear as reaction time increased. They postulated a three-domain particle-scale model (exposed inorganic surfaces and amorphous and condensed soil organic matter) to explain the sorption behavior and functional relationships underlying the time dependence of the PDRs.

Huang and Weber (1997) further examined the sorption and desorption of phenanthrene with ten natural sorbents of different diagentic age and organic matter composition. They found that the sorption affinities of these materials, the isotherm non-linearity, and the hysteretic patterns of these organic materials were inversely correlated with the O/C atomic ratios of the organic matter. With more physically condensed and chemically reduced soil organic matter, there was the greater solute affinity, more non-linear sorption isotherm, and more pronounced hysteresis.

Pesticide Transport in Soil

Because of the importance of the interaction of pesticide movement to sorption and desorption processes, soil-leachate columns have become a standard tool for evaluating the fate of these compounds in soil (Bouchard et al., 1989, Hutzler et al., 1989). With column studies, a common approach in

assessing sorption is through comparison of the breakthrough curves of the pesticide of interest and of a non-reactive solute (often bromide ion). Numerous examples of non-equilibrium sorption during transport have been reported in the literature (Selim et al., 1976; van Genuchten et al., 1977; Bouchard et al., 1988; Brusseau and Rao, 1990; Ptacek and Gillham, 1992). Early breakthrough and/or long tailing of effluent concentration versus time curves are typical signatures of non-equilibrium processes. Butters and Bandaranayke (1993) reported non-equilibrium sorption with a dye that was non-reactive in structured soil and reactive under "repacked" soil conditions.

Numerous transport models have been described that predict the movement of chemicals through soil. The simplest of these models is the advection-dispersion equation. For a solute that has a minimal vapor phase and neither reacts or adsorbs to soil particles, the advection- dispersion equation (Bigger and Nielsen, 1967) takes the form

$$\frac{\partial C_l}{\partial t} = D \frac{\partial^2 C_l}{\partial z^2} - V \frac{\partial C_l}{\partial z} \qquad (6)$$

where C_l is the dissolved solute concentration; t is time; D is the effective diffusion-dispersion coefficient divided by the soil water content θ; z is the distance or length; and V is water velocity.

For chemicals that adsorb to the stationary phase (soil particles), the equation is written as

$$\frac{\rho_b}{\theta}\frac{\partial C_a}{\partial t}+\frac{\partial C_l}{\partial t}=D\frac{\partial^2 C_l}{\partial z^2}-V\frac{\partial C_l}{\partial t} \tag{7}$$

where ρ_b is bulk density; and Ca is the adsorbed soil concentration. This equation differs from the previous equation by considering the rate change of mass storage in the sorbed phase ($\rho_b/\theta\ \partial Ca/\partial t$). Both equations assume that water is flowing uniformly at steady state, through a homogeneous soil column, with constant water content.

By assuming that a linear isotherm exists in the soil at all times, the time derivative Ca may be written as

$$\partial C_a/\partial t = K_d\,\partial C_l/\partial t \tag{8}$$

From this equation, the adsorbing chemical transport equation can be written as

$$\left(1+\rho_b K_d/\theta\right)\partial C_l/\partial t = D\,\partial^2 C_l/\partial z^2 - V\,\partial C_l/\partial z = R\,\partial C_l/\partial t \tag{9}$$

where $R = (1 + \rho_b K_d/\theta)$. Now dividing both sides by R, the equation is reduced to the simplest form of the advection-dispersion equation

$$\partial C_l/\partial t = D_R\,\partial^2 C_l/\partial z^2 - V_R\,\partial C_l/\partial z \tag{10}$$

where D_R, the retardation dispersion coefficient; is equal to D/R, and V_R the solute velocity, is V/R.

The equation can now be solved to predict breakthrough time of an adsorbing chemical through soil

$$t_{br} = L/V_R = RL/V = Rt_o \quad (11)$$

where t_{br} is the solute breakthrough time for the adsorbed chemical; and L is the distance of a chemical to be transported.

Transport as a Function of Dissolved Organic Carbon

In addition to evaluating pesticide sorption and transport for systems that are non-homogeneous and dynamic, an emerging research area is the study of transport carriers, in the form of dissolved organic carbon (DOC), especially with regard to accelerated movement of pesticides by DOC transport (Ballard, 1971; McCarthy and Jiminez, 1985; Dunnivant et al., 1992; Jardine et al., 1992). Madhun et al. (1986), and Chiou et al.(1986) have examined sorption and transport as they relate to DOC in the form of HA and FA. As DOC, HA can bind with the mineral fraction of soil to become immobilized. The stationary mineral-HA complex can sorb pesticides from the soil solution. Mineral complexed HA can act as a solvent to partition free pesticide from the aqueous phase. FA in the soil solution can act as a partition solvent to increase the apparent water

solubility of pesticides and forms a FA-pesticide complex.

Recent Compartmentalized Sorption and Transport Models

The continuing interest in sorption and transport as a function of DOC has led to the development of several new models that better describe pesticide interactions with soil and water. Barriuso et al. (1992) developed a sorption model that estimates the permanently adsorbed quantities of pesticide by introducing a desorption coefficient into a Freundlich sorption isotherm model:

$$x/m = \left[\left(x/m\right)_{irr}\right] d^{-K} + \left(x/m\right)_{irr} \tag{12}$$

where $(x/m)_0$ is the initial amount of pesticide adsorbed before the start of desorption; $(x/m)_{irr}$ is the nondesorbable amount of pesticide adsorbed; k is a coefficient related to desorption efficiency; and d is the dilution factor for replacement of the sorption aqueous phase.

For a bi-mechanistic isotherm, for which one compartment is linear and the second compartment is exponential, Barriuso et al. (1992) introduced a second model

$$x/m = K_1 C + \left(x/m\right)_n \left(1 - e^{-K_2 C}\right) \tag{13}$$

where C is the equilibrium pesticide concentration; K_1 is a linear parameter and K_2 an exponential parameter; and $(x/m)_n$ is the total amount of pesticide adsorbed in the exponential compartment.

Ding et al. (1997) modified the advection-dispersion transport equation to include a free-moving DOC component. The assumption is made that DOC in the form of HA, can act as a carrier for the transport of pesticides through soil. While this modified transport model better predicted the sorption of DOC over the standard two-compartment models, it was only accurate in the first seven pore volumes of leaching. Discrepancies occur, beginning at the eighth pore volume, led to an underestimation of the sorption of DOC to the soil. The data suggest that non-singular hysteresis may be playing a significant role in the movement of DOC. Also, the concentration of DOC used to leach the columns (949 mg C/L) is unrealistic in a natural soil environment and may be a significant artifact in the simulation model.

Ding et al. (1997) developed their simulation model for aldrin using an estimate of the partition coefficient of pesticide between DOC and water based on a water-solubility enhancement method (Ding and Wu, 1995). The resulting K_{doc} is approximately 0.5 log units smaller than the K_{ow} value and 0.3 log units smaller than the K_{oc} value. Because these coefficient parameters are for sorption and do not consider desorption, the model may continue to understate true values.

Characteristics of Sewage Biosolids

Sewage biosolids are the solids (inorganic and organic) that settled during sewage treatment. The surfaces of the colloidal particles present in the biosolids possess or acquire electrical charges that lead to forces that cause the colloids to be repulsed (stabilization). As a result of the presence of these electrical charges colloidal particles are surrounded with a shell of ions of opposite charge, thereby maintaining electric neutrality. Such suspensions are completely stable in the absence of external influences on the system. To facilitate the removal of solids, the system is treated with chemical agents (metal coagulants or synthetic organic polymers). These chemical agents destabilize dissolved colloids and promote coagulation and flocculation.

Chemistry of Metal Coagulants

Colloid destabilization is carried out most frequently with trivalent salts. For example, when an aluminum salt is added to a wastewater system, several hydrolysis reactions occur to form a series of multivalent charged hydrous oxide species. Depending on pH, their charges may range from positive at acidic pH values to negative at more basic pH values. These reactions are represented as follows:

$$[Al(H_2O)_6]^{3+} + H_2O \leftrightarrow [Al(H_2O)_5OH]^{2+} + H_3O^+$$

$$[Al(H_2O)_5OH]^{2+} + H_2O \leftrightarrow [Al(H_2O)_4(OH)_2]^{+} + H_3O^+$$

The reactions proceed until the neutral species $Al(H_2O)_3(OH)_3$ or the negative charged species $Al(H_2O)_2(OH)_4^-$ is formed. However, it is thought that these monomeric aluminum species are transient and that a second type of reaction (called olation) is more important in coagulation. In this process a series of polymerization reactions occurs, resulting in complexes containing several aluminum ions bridged by two hydroxyl groups. This complex is illustrated as follows:

$$[Al_2(H_2O)_8(OH)_2]^{4+}$$

Another complex important in coagulation is a polynuclear complex containing aluminum ions of tetrapositive charge, is

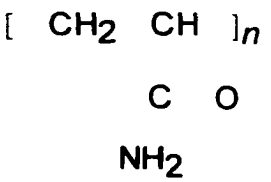
$$[Al_8(OH)_{20}]^{4+}$$

One of the most significant points about these reactions is that both hydroxide and hydrogen ions are involved; thus, pH plays a substantial role in coagulation. The pH is of primary importance in establishing the average charge of the hydrolysis products and consequently, is significant in determining the degree and rate of coagulation. Secondary to pH, the chemical composition of the solution also influences the species of complex being produced, since negative ions other than hydroxide (di- and trivalent) may enter the complex and significantly change its properties.

Once the coagulating multipositive hydroxo and polynuclear complexes are produced, they are adsorbed on to the negatively charged colloids. The net result is that repulsive electrical charges on the colloids are reduced to a potential that allows van der Waals attractive forces to promote destabilization, leading to flocculation.

Chemistry of Organic Polymer Flocculants

As an aid to the flocculation of colloids, the use of synthetic organic polymers such as polyacrylamide (PAM) has become increasingly popular. Polyacrylamide in the form



have molecular weights from 50,000 to several million Da. Due to the degree of polymerization, the molecules exist as "thread-like" coils when hydrated. The PAM molecules, because of their great length in solution and charge density, attach themselves to multiple colloid particles simultaneously. This "bridging" mechanism accounts for the aggregate behavior of PAM. Overall coagulation and flocculation of the system is dependent on solution chemistry and type of metal coagulant and synthetic organic polymer employed. These variables ultimately influence organic matter content of the biosolids.

CHAPTER 3

MATERIAL AND METHODS

Soils

Two sandy-loam soils (Table 3.1) of contrasting soil organic carbon contents were used for the investigation of sorption and desorption, of metribuzin. The Paoli series consists of deep, well-drained soils that formed in alluvium (Pachic Haplaustoll). These soils are mainly used for irrigated crops such as corn, sugar beets, small grains, and pasture grass. The San Arcacio series consists of well drained soils 51 to 102 cm deep over sand and gravel and formed in alluvium on old flood plains and broad alluvial fans (Typic Haplargid). The acreage is used for potatoes, small grain, alfalfa, and vegetables. Both soils are annually planted to crops and irrigated using flood and center-pivot techniques, respectively. The upper most 10 cm of soil was sampled. The soils were air dried and passed through a 2-mm sieve, then stored for later chemical analysis and sorption experiments.

Biosolids

Biosolids were obtained from a municipal sewage treatment plant (Fort Collins, CO, USA). The biosolids were anaerobically digested and destabilized with polyacrylamide. Water removal was by filter press and air-drying.

Table 3. 1. Classification and chemical properties of two soils used to investigate metribuzin sorption and desorption.

Soil series	Classification	Soil texture	OM§	TOC‡	pH
Paoli	Pachic Haplaustoll	Sandy loam	2.88	1.62	7.34
San Arcacio	Typic Haplargid	Sandy loam	1.07	0.62	7.51

§ organic matter
‡ total organic carbon

The biosolids were received in granular form and ground to powder with a ball mill.

Dissolved Organic Carbon

Extracts from the biosolids containing dissolved organic carbon were obtained by mixing 12.5 g biosolids with 200 mL of demineralized water, followed by shaking (24 h with a Burrell Wrist Action Shaker, Model 75, Pittsburgh, PA, USA), centrifugation (20 min at 10,000 rpm x g, with a Sorvall RC-5B centrifuge; Dupont Co., New Town, CT, USA), and collection of the supernatant. The extracts were preserved with mercuric chloride, 0.05 *m*M.

Characterization of Soil, Biosolids, and Dissolved Organic Carbon

The soil and biosolids were analyzed for total organic carbon (LECO), dissolved organic carbon (Shimadzu TOC500 Carbon Analyzer, Nippon, Japan), and pH (2 g soil or biosolids in 4 mL 0.05 M $CaCl_2$). The amounts of dissolved organic carbon (DOC) and pH were measured using unspiked samples.

Classification of these two soils was based on the soil surveys of Larimer County (Soil Survey Staff, 1980) and Rio Grande County (Soil Survey Staff,1977).

Chemical properties of the soil are presented in Table 3.1. The biosolids contained 58.6% organic matter and 32.9% total carbon, with a pH value of 7.18.

Metribuzin

The high-purity metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one) was received from Sigma Chemical Company (St. Louis, MO, USA). The compound was ^{14}C-ring labeled and had a specific activity of 4.07×10^{8} Bq $mmol^{-1}$ and radiopurity > 98.8%.

Sorption of Metribuzin on Soil and Biosolids-Amended Soil

Metribuzin sorption isotherms were obtained by the batch equilibration procedure using 30-mL Corex centrifuge tubes with 6 g of air-dried soil or 6 g of soil amended with 0.225 or 0.750 g of biosolids. All samples were pre-equilibrated for 24 h in 0.05 M $CaCl_2$-0.05 *m*M $HgCl_2$, and then 2 mL of ^{14}C-metribuzin aqueous solutions at different concentrations were added to obtain initial metribuzin concentrations of 0, 0.05, 0.10, 0.50, 1.0, 2.5, and 5.0 ug cm^{-3}. Spiked suspensions were agitated using a wrist shaker (23 ± 3° C for 24 h), then centrifuged (10,000 rpm) for 20 min. The concentration of metribuzin remaining in solution was determined by measurement of the radioactivity in the supernatant using a Tricarb 2500 TR scintillation counter (Packard Instruments, Meridian, CT, USA) using1 mL of soil solution mixed with 15 mL of scintillation cocktail, and counted from 1 to 20 min. The amount of herbicide sorbed to soil

for each initial concentration was calculated from the difference between the initial and final solution concentrations.

Sorption of Metribuzin on Soil in the Presence of Dissolved Organic Carbon

The effects of DOC from biosolids on herbicide sorption to soil was studied by pre-equilibrating 6 g of soil with 10 mL of DOC that contained 0.05 *m*M $HgCl_2$ solution for 24 h at 23 ± 3° C. After pre-equilibration, metribuzin was added, suspensions were shaken for 24 h, and the concentration of metribuzin was determined as above.

Sorption of Metribuzin on Soil Amended with Biosolids After Extraction

The biosolids remaining after extraction of labile organic carbon (2:1 water/soil, shaken for 24 h then centrifuged as above) were air-dried and added to soil.

Desorption Studies

Metribuzin desorption was studied using the highest equilibrium concentration used with the sorption isotherms. The supernatant was removed and replaced with are approximately equal volumes of fresh 0.05 M $CaCl_2$-0.05 mM $HgCl_2$ solution. The suspensions were shaken at 23 ± 3° C for 24 h, centrifuged, and metribuzin concentrations determined in the supernatant as described above.

Sorption-Desorption Water Balance Measurements

Measurement of added solution and removal of soil supernatant from the Corex tubes was by the gravimetric water balance technique, assuming the density of all solutions was 1.000 g cm^{-3}.

Sorption-Desorption Isotherm Algorithms

Sorption and desorption isotherm data were fit to the Freundlich equation

$$\left(x/m\right) = K_f C^n \tag{14}$$

where x/m is the weight of the adsorbate per unit of adsorbent, C is the equilibrium solution concentration of adsorbate, n_f is an empirical exponential constant, and K_f is the Freundlich binding constant. When n = 1, the isotherm is said to be linear leading to the following expression:

$$K_d = \frac{x/m}{C} \tag{15}$$

Hysteresis Algorithm

The hysteresis coefficient, H, for the sorption-desorption isotherms was calculated according to the following equation:

$$H = \frac{n_{fd}}{n_f} x 100 \tag{16}$$

where the subscripts of *n* define the Freundlich desorption and sorption empirical constants.

Statistical Analysis

Statistical analysis of data from studies of amended soil were compared to corresponding results from unamended soil using the General Linear Models Procedure (SAS System). The model tested the null hypothesis that the lines of sorption and desorption were coincident (slopes and intercepts of the lines were the same. For desorption, the data were log transformed according to the linear form of the Freundlich equation:

$$\log\left(\frac{x}{m}\right) = \frac{1}{n}\log C + \log K \tag{17}$$

where 1/n is the slope and log*K* is the y-intercept of the equation.

CHAPTER 4

RESULTS AND DISCUSSION

Sorption

The reaction of metribuzin with soil treated with sewage biosolids was evaluated from a series of laboratory partition sorption and release experiments. The sorption dynamics were studied to evaluate the effectiveness of biosolids for reducing advection transport of metribuzin through soil. The consequences of sorption dynamics were considered important because of the major role that sorption plays in the fate of pesticides. Various thermodynamic algorithms modeled the experimental data and provided a mechanistic picture of metribuzin sorption and release.

Paoli Soil and Amendments

The sorption data for the Paoli soil fit well to Freundlich isotherms across a range of three orders of magnitude of initial water phase concentration (Fig. 4.1). Both K_f and n_f empirical constants increased with increasing organic carbon (OC) content (Table 4.1). The sorption linearity resulted from sorption to soil organic matter (SOM) for which the sorption domain is likely dominated by fast sorption, rubbery sites. Metribuzin sorption to the rubbery domain occurs by a partition mechanism, which is independent of concentration, resulting in a linear isotherm

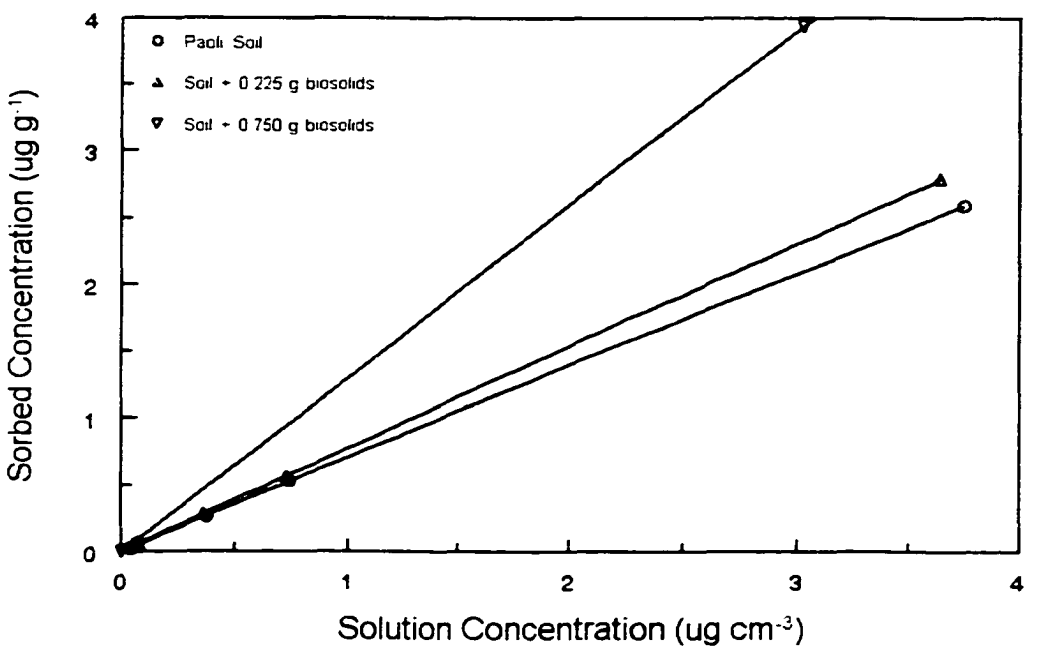


Fig. 4. 1.The sorption isotherms of metribuzin for the Paoli soil and Paoli soil amended with biosolids(0.225 or 0.750 g added to 6 g of soil).

Table 4. 1. Soil organic carbon (OC) content, Freundlich empirical constants (K_f and n_f), probability of K_f significance, regression values (r^2), dissolved organic carbon at equilibrium, and normalized organic carbon constants (K_{oc}).

Soil	Treatment	OC	K_f	Statistical Significance	n_f	R^2	K_{oc}	Equilibrium DOC
		%	$cm^3\ \mu g^{-1}\ \mu g^{1-n}$					$\mu g\ cm^{-3}$
Paoli	Unamended	1.62	0.71 ±(0.00)§	-	0.976	0.999	44	427
Paoli	Biosolids, 0.225 g	2.85	0.78 ± (0.03)	0.020‡	0.986	0.999	27	402
Paoli	Biosolids, 0.750 g	5.74	1.3† ± (0.1)	<0.001‡	1.00†	1.00†	23	835
San Arcacio	Unamended	0.62	0.49 ± (0.01)	-	0.877	0.996	79	46
San Arcacio	Biosolids, 0.225 g	1.85	0.59 ± (0.01)	0.001¶	0.920	0.999	32	195
San Arcacio	Biosolids, 0.750 g	4.74	0.90 ± (0.00)	<0.001¶	1.01	0.999	19	727

† isotherm based on two data points where n was assumed to be 1 and K_d = (x/m)/C.
$K_{oc} = K_d$ / % OC
‡ probability that the K_f of treatment is the same as untreated Paoli soil.
¶ probability that the K_f of treatment is the same as untreated San Arcacio soil.
§ Standard error of the mean in parentheses.
# Threshold of statistical significance ($P \leq 0.05$).

(Pignatello et al., 1996). The isotherm shape was of the C-type ($n_f \approx 1$), which results from the solute penetrating the sorbent more readily than the solvent (Weber & Miller, 1989).

San Arcacio Soil and Amendments

Sorption for unamended San Arcacio soil was non-linear but became linear with the addition of 0.750 g biosolids (Fig. 4.2). As with the Paoli soil, both K_f and n_f empirical constants increased with increasing OC content (Table 4.1). The isotherm shape was curve-linear ($n_f = 0.877$) and was a result of low soil OC content having a glassy structure, characteristic of slow sorptive sites (Pignatello and Xing, 1996). The non-linear isotherm observed with unamended soil can be characterized as being of the L-type. The L-type isotherm has an initial slope of $n_f < 1$, is characteristically nonlinear, and occurs with soils having low OC (Giles et al., 1960). This type of sorption isotherm could indicate minimum competition between metribuzin and water molecules for sorption sites (Giles et al., 1960; Bansal, 1983).

Organic Carbon – Empirical Constants Correlation

Metribuzin sorption correlated well with total organic carbon of the biosolids-amended soils (Fig. 4.3). The empirical K_f values for each soil increased with increasing levels of OC (Table 4.2). Surprisingly however, the increase in added OC (Table 4.2) did not result in an appreciable increase in sorption. This may have resulted from the overall heterogeneity in sorptive

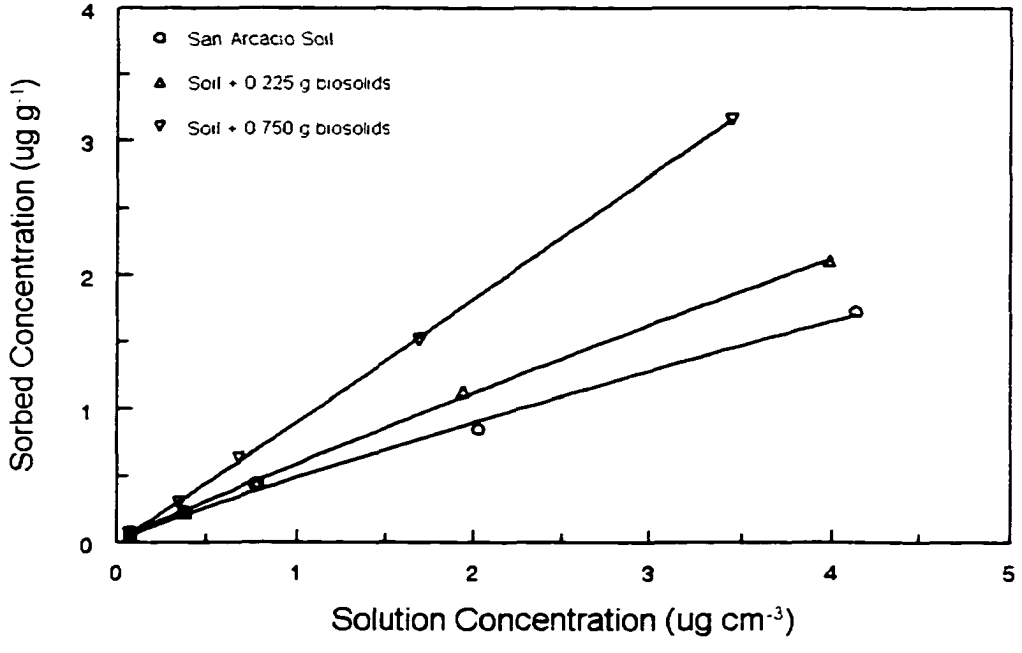


Fig. 4. 2. **The sorption isotherms of metribuzin for the San Arcacio soil and San Arcacio soil amended with biosolids.**

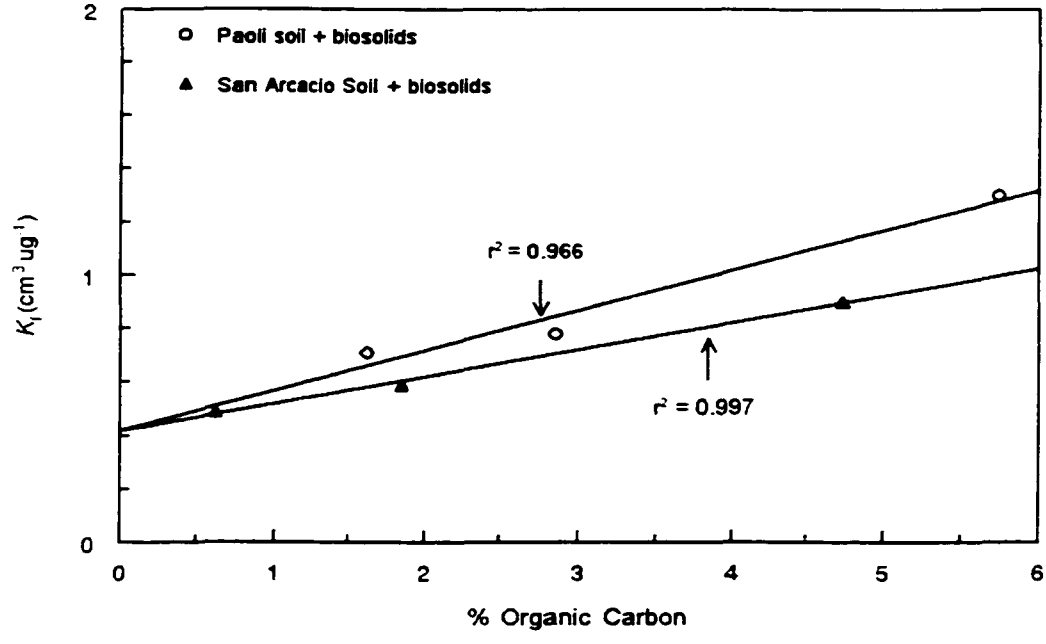


Fig. 4. 3. The sorption coefficients of metribuzin as a function of total organic carbon in the Paoli and San Arcacio soils amended with biosolids.

behavior of the organic material from biosolids (Pignatello and Xing, 1996; Pignatello et al., 1996; Pignatello and Xing, 1997; Weber and Leboeuf, 1997; Weber et al., 1997; Weber and Huang, 1997) and the low sorptivity of metribuzin. While the biosolids may contribute a significant fraction of OC to soil, it appeared that much of this OC was unreactive with regard to its sorptive characteristics. This would indicate that in addition to the quantity of organic carbon present in soil, sorptive characteristics play an important role in determining the degree of association between soil and metribuzin.

Table 4. 2. Increases in total organic carbon (TOC) and sorption (K_f), and dissolved organic carbon (DOC) concentrations for amended and unamended Paoli and San Arcacio soil.

Soil	Treatment	Increase in TOC	K_f Change	DOC at equilibrium
		%		µg cm^{-3}
Paoli	Unamended	-	-	427
Paoli	Biosolids, 0.225 g	76	10	402
Paoli	Biosolids, 0.750 g	254	83	835
San Arcacio	Unamended	-	-	46
San Arcacio	Biosolids, 0.225 g	198	20	195
San Arcacio	Biosolids, 0.750 g	665	84	737

The increase in n_f as a function of soil and biosolids OC content (Table 4.1) can be explained by the dual-mode glassy/rubbery model for soil organic matter (SOM) (Pignatello et al., 1996; Pignatello and Xing, 1996; and Pignatello

and Xing, 1997). Accordingly, the SOM of both Paoli and San Arcacio soils are viewed as having rubbery (expanded) and glassy (condensed) organic carbon domains. Sorption to the rubbery domain is thought to be analogous to dissolution in organic solvents (Pignatello et al., 1996). As described earlier, metribuzin sorption to the rubbery domain occurs by a partition mechanism, which is independent of concentration, resulting in a linear isotherm. The glassy domain is characteristic of non-linearity (slow sorption) and exhibits co-solute competition. Sorption here could occur by a hole-filling mechanism and solute diffusion, both being rate limited (Pignatello, 1989; Pignatello et al., 1993; and Pignatello and Xing, 1996).

Sorption of Metribuzin for Soil Amended with Biosolids Separates and Polyacrylamide

To characterize the sorptive domains of soil amended with biosolids, Paoli soil was treated with the separates from biosolids and polyacrylamide (PAM). Separates are defined as the organic carbon extracted by water from biosolids (dissolved organic carbon), and the residual biosolids after water-soluble organic carbon had been extracted. PAM was a polymer used as a flocculent during sewage treatment.

Metribuzin sorption data for soil amended with biosolids separates and PAM were fit to the Freundlich model (Table 4.3). Based on the linear sorption results for Paoli soil amended with biosolids (Table 4.1), it was assumed that soils amended with biosolids separates and PAM would also yield linear results

(*n* approaching 1). Therefore, sorption experiments were conducted at only two initial metribuzin solution concentrations and sorption coefficients (K_d) were calculated using the linear form of the Freundlich equation (K_d = (x/m)/C).

The concentration of DOC solution added to soil was measured from the extraction of biosolids with reagent water as described in Methods and Materials (Chapter 3). It should be noted that the amount of DOC obtained from the extracted biosolids or the ratio of DOC to biosolids might be somewhat different from that of DOC obtained from the sorption experiments of soil with whole biosolids. The soil-biosolids sorption experiments were conducted in the presence of a constant amount of $CaCl_2$. The presence of calcium in solution may affect the stabilization of OC. Humic and fulvic acids (major sorptive components of organic matter) act in a manner predicted by charged particle colloid or "DLVO" theory (see Chapter 2). That is, they undergo stabilization-destabilization (flocculation or dissolution) by attractive and repulsive particle forces. Free calcium in solution affects the attractive and repulsive forces between humic and fulvic acids, resulting in a lower concentration of DOC in solution.

Dissolved Organic Carbon Treatment

The propensity for sorption significantly decreased for both soils when amended with DOC from extracted biosolids (Fig. 4.4). However, there was no difference in the K_d values for the two DOC treatments (2.94 and 13.2 mg). The resulting K_d value for both treatments was 0.47 cm^3 μg^{-1}. This was surprising as

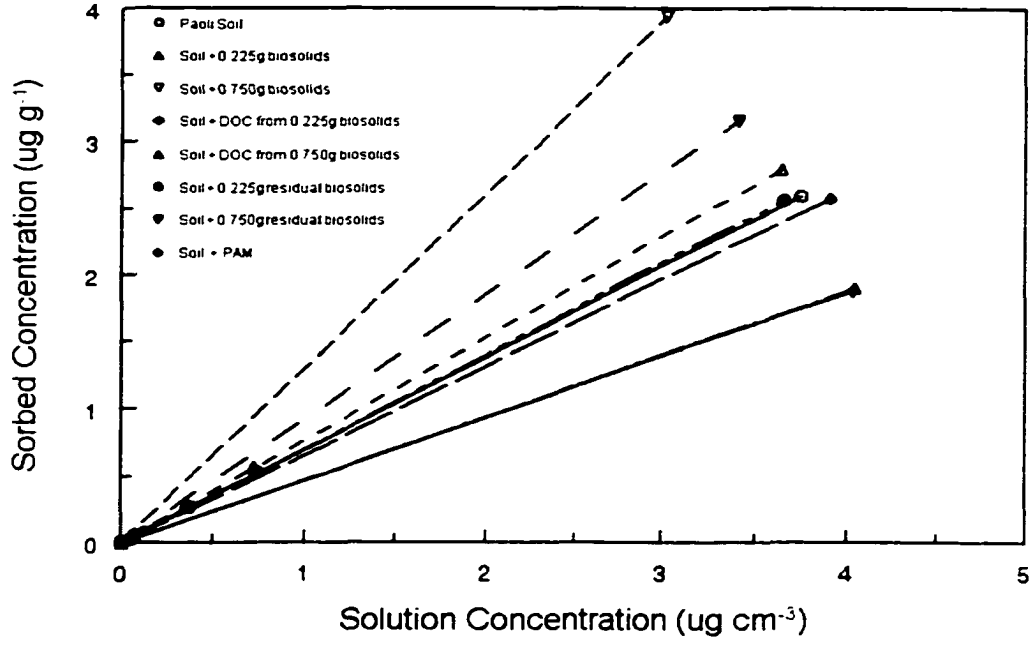


Fig. 4. 4. The sorption isotherms of metribuzin for the Paoli soil and Paoli soil amended with biosolids separates and polyacrylamide (PAM).

the soil receiving 13.2-mg DOC had a equilibrium DOC concentration 2.2 times greater than that of the 2.94-mg treatment (Table 4.3). This observation could support the conclusion that much of the DOC contributed by biosolids was un-reactive and had little or no affinity for metribuzin.

Residual Biosolids Treatment

Paoli soil receiving residual biosolids from which water-soluble organic carbon had been extracted had lower sorption values (Table 4.3) than the soil amended with whole biosolids (Table 4.1). The sorptivity (K_f) for soil amended with 0.225 g residual-biosolids (0.70) was similar to that of the unamended Paoli soil (0.71). However, the equilibrium DOC in the 0.225 g residual biosolids treatment (370 μg cm^{-3}) was somewhat less than the soil amended with 0.225 g whole biosolids (402 μg cm^{-3}). The sorption value (K_f) for the soil amended with 0.750 g residual biosolids (0.90) was significantly different than soil amended with 0.750 g whole biosolids (1.3). Part of the difference may be attributed in comparing the K_f sorption value from residual biosolids to the K_d sorption value from whole biosolids. In earlier discussions, it was assumed that the *n* coefficient for whole-biosolids treatment was 1 and therefore, sorption would follow the linear form of the Freundlich equation (K_d = (x/m)/C). While it is likely that *n* approached 1 and sorption was linear, comparison of K_f and K_d sorption values may not be valid. The actual K_f value for soil amended with 0.750 g biosolids may be closer to that of soil amended with 0.750 g residual biosolids. A study of sorption with soil and whole biosolids with five initial aqueous solution

Table 4. 3. Freundlich sorption constants, dissolved and residual organic carbon additions, and dissolved organic carbon for Paoli soil separates and PAM.

Additions to soil	K_d	Initial DOC Added	Residual OC added	Equilibrium DOC
	$cm^3\ \mu g^{-1}$	——— mg ———		$\mu g\ cm^{-3}$
DOC from biosolids, 0.225 g	0.47	2.94	-	454
DOC from biosolids, 0.750 g	0.47	13.2	-	1014
Residual biosolids, 0.225 g	0.70	-	67.5	370
Residual biosolids, 0.750 g	0.93	-	225	734
PAM	0.66	-	-	214

Residuals = biosolids remaining after extraction of water-soluble organic carbon.
PAM = polyacrylamide.

concentrations would resolve this question. The equilibrium DOC in the 0.750 g residual-biosolids treatment (734 $\mu g\ cm^{-3}$) was also less than the soil amended with 0.750 g whole biosolids (835 $\mu g\ cm^{-3}$).

Polyacrylamide Treatment

The addition of PAM to Paoli soil resulted in a slight decrease of metribuzin sorption (Table 4.3) from that of unamended soil (Table 4.1). Interestingly, the DOC concentration (217 $\mu g\ cm^{-3}$) was reduced by nearly half from that of the unamended soil (427 $\mu g\ cm^{-3}$). Metribuzin sorption to soil was expected to increase because PAM should remove OC from solution. It is possible that the addition of PAM caused a fraction of the soil sorptive sites to

become unavailable to metribuzin. More likely, however, the DOC from the soil had few sorptive sites that could influence sorption.

Sorption Characteristics

The magnitudes of metribuzin sorption for whole biosolids and biosolids separates experiments can be explained by describing the sorptive compartments for organic carbon and mineral domains:

$$\text{soil} + H_2O \quad \text{yields } \text{mineral}_{soil}OC_{soil} + \text{mineral}_{soil} + DOC_{soil}$$

$$\text{biosolids} + H_2O \quad \text{yields } \text{mineral}_{bios}OC_{bios} + \text{mineral}_{bios} + DOC_{bios}$$

$$\text{soil} + \text{biosolids} + H_2O \quad \text{yields } \text{mineral}_{bios}OC_{soil} + \text{mineral}_{soil} + DOC_{soil}$$
$$+ \text{mineral}_{soil}OC_{bios} + \text{mineral}_{bios} + DOC_{bios}$$
$$+ \text{mineral}_{bios}OC_{soil} + \text{mineral}_{soil}OC_{bios}$$
$$+ \text{mineral}_{soil}OC_{soil,bios} + \text{mineral}_{bios}OC_{soil,bios}$$

where mineral_{soil} = mineral compartment of soil;

$\text{mineral}_{soil}OC_{soil}$ = soil mineral complexed with soil organic carbon;

$DOC_{soil.}$ = dissolved organic carbon of soil;

mineral_{bios} = mineral compartment of biosolids;

$\text{mineral}_{bios}OC_{bios}$ = mineral compartment of biosolids complexed with biosolids organic carbon;

DOC_{bios} = dissolved organic carbon from biosolids;

$mineral_{bios}OC_{soil}$ = mineral compartment from biosolids complexed with soil organic carbon;

$mineral_{soil}OC_{bios}$ = mineral compartment from soil complexed with biosolids organic carbon;

$mineral_{soil}OC_{soil,bios}$ = mineral compartment from soil complexed with soil and biosolids organic carbon;

and $mineral_{bios}OC_{soil,bios}$ = mineral compartment from biosolids complexed with soil and biosolids organic carbon.

From these expressions, ten compartments could be identified, each with its own uniqueness (distribution and type of sites) for sorption of metribuzin.

For the experiments conducted with unamended and whole biosolids amended-soil, the $mineral_{soil}$OCsoil and $mineral_{bios}$OCbios compartments influenced metribuzin sorption. The reduction of sorption for soil amended with DOC from biosolids appeared to be due to an increase in sorptive sites for the DOC_{bios} compartment. The DOC_{bios} compartment had sufficient affinity for metribuzin to increase the apparent metribuzin solution concentration above that of unamended, whole-biosolids and residual-biosolids amended soil.

The decrease in metribuzin sorption for soil receiving residual biosolids from that of soil receiving whole biosolids could be due to a decrease in sorptive sites for the $mineral_{bios}OC_{bios}$ compartment. $Mineral_{bios}OC_{bios}$ sorptive sites may have been removed during the water extraction of whole biosolids.

In comparing sorption the residual-biosolids and DOC amended soil (Table 4.3), metribuzin sorption was greater with the soil-residual biosolids amendment. This was not surprising, as the equilibrium DOC concentration for soil amended with residual biosolids was considerably lower than for soil amended with DOC (Table4.3). These results also suggest that DOC added to soil was stable and did not complex with the mineral domain. For this to occur, the equilibrium DOC concentrations in soil amended with DOC would have been less than 454 and 1014 μg cm^{-3}, respectively, and their sorption coefficients (0.47) would likely be closer to that of the soil amended with 0.225 and 0.750 g residual-biosolids (0.70 and 0.93, respectively).

While the compartment approach could identify the direction or location of sorption, it does not explain why K_d values between the two DOC-soil treatments were significantly different. Also, the compartment approach fails to qualitatively differentiate DOC_{bios} from DOC_{soil} and sorptive OC from non-sorptive OC.

Desorption

Studies of sorption with soil organic carbon are common, but few studies characterize desorption. The fate of pesticides is dependent upon the extent to which they are retained in soil. In field practices, pesticide sorption and desorption are a continual process. Therefore, metribuzin desorption isotherms were studied to improve the description of the soil-pesticide interaction. A single-compartment (Freundlich) and two-compartment (Barriuso et al., 1992)

algorithms were used to model the data and provide a mechanistic picture of metribuzin release.

Soil and Biosolids-Amended Soil

The decreases in the amounts of metribuzin remaining sorbed over the course of the repeated desorption cycles were described by an exponential function of the number of desorption cycles with an asymptotic term representing a fraction of the herbicide irreversibly sorbed.

Desorption curves were fitted to the Freundlich model to represent the isotherms of each soil and amendment (Table 4.4). An initial linear fast-release compartment of metribuzin was observed (first two desorption cycles), followed by an exponential, slow-release (Fig. 4.5 to 4.7). The isotherms followed the two-compartment, biphasic desorption models of Brusseau et al. (1991), Carrol et al. (1994) Schrap et al. (1994), Young and Weber (1995), Pignatello and Xing (1996), Xing et al. (1996), Aochi and Farmer (1997), Xing and Pignatello (1997), and Graber and Borisover (1998). The linear compartment exhibited weak retention for metribuzin. That is, the linear compartment released a relatively substantial amount of sorbed metribuzin in a short period of time. The exponential compartment exhibited intense sorption with release of metribuzin being slow.

Desorption isotherms were also described using the two-parameter model of Barriuso et al. (1991) (Table 4.5) along with isotherms calculated by the

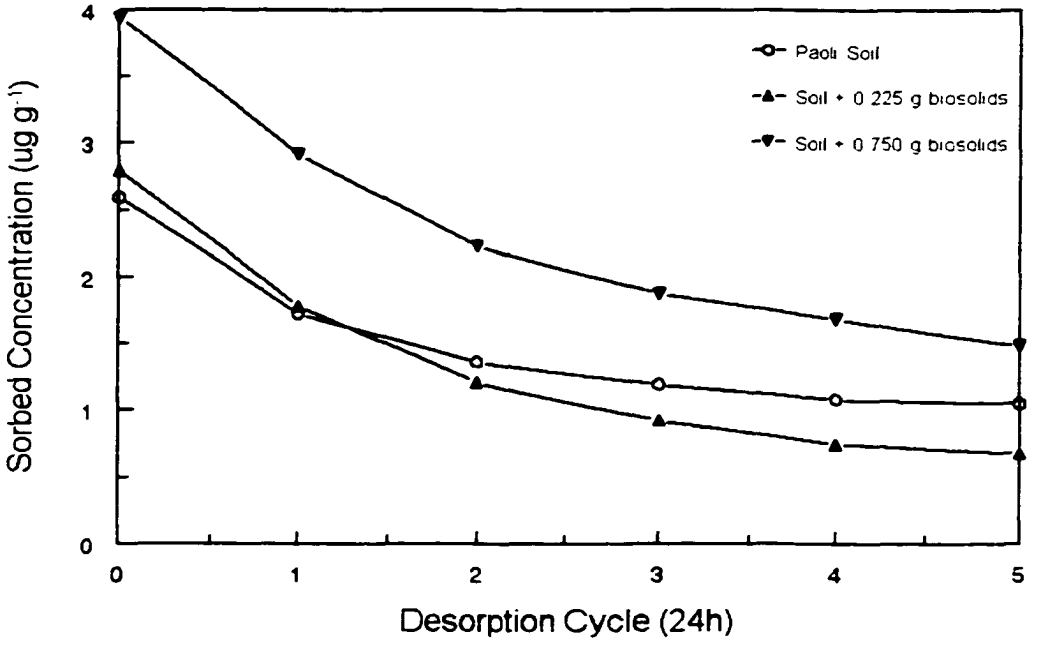


Fig. 4. 5. **The desorption cycle isotherms of metribuzin for the Paoli soil and Paoli soil amended with biosolids.**

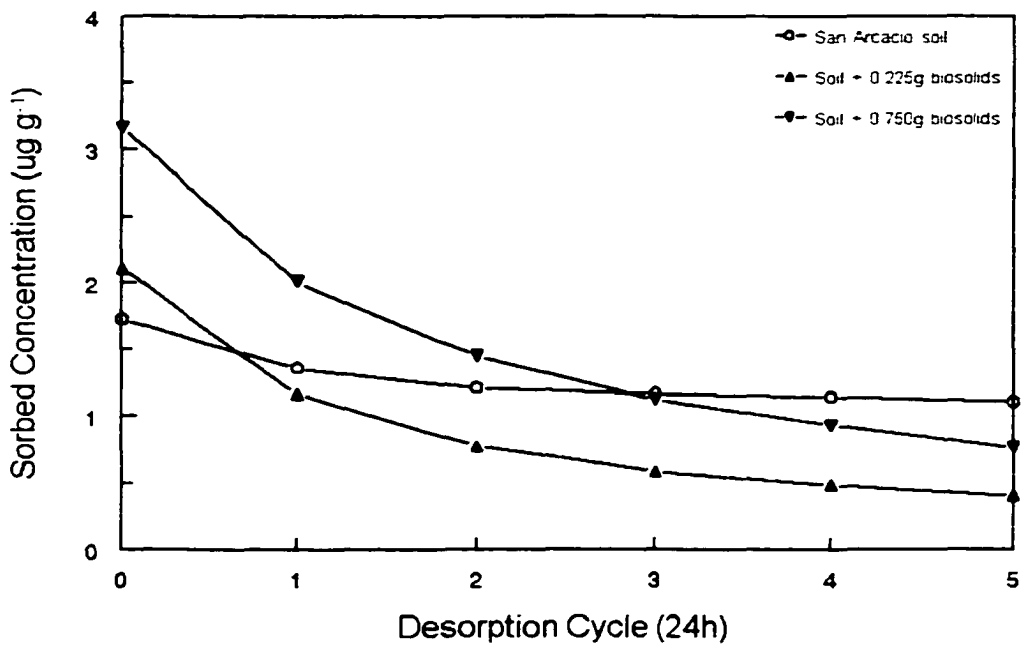


Fig. 4. 6. The desorption cycle isotherms of metribuzin for the San Arcacio soil and San Arcacio soil amended with biosolids.

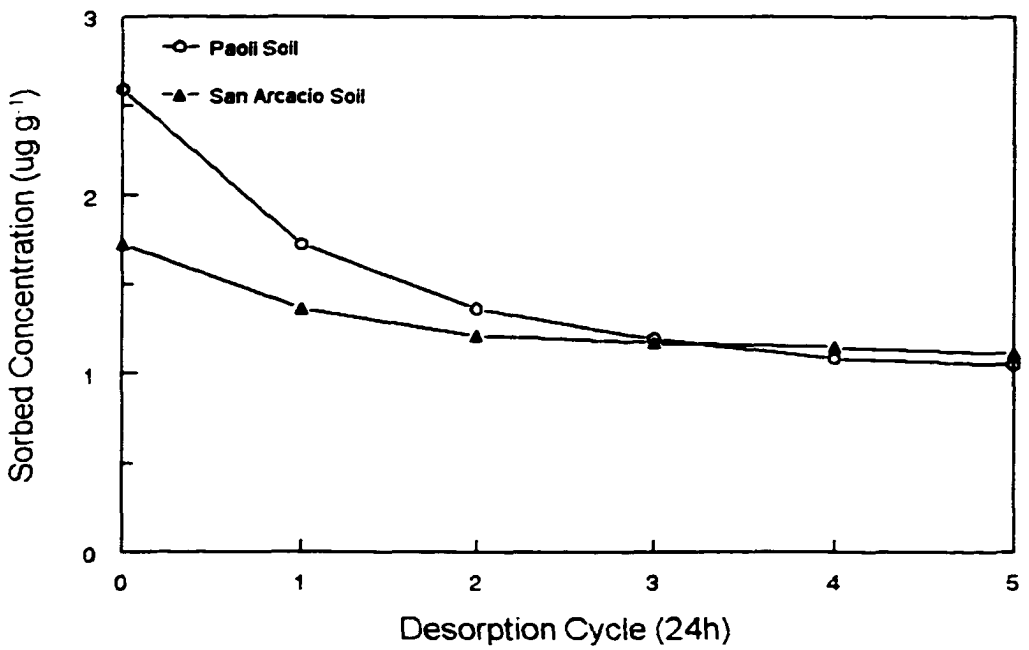


Fig. 4. 7. **Comparative desorption cycle isotherms of metribuzin for the Paoli soil and San Arcacio soil.**

Table 4. 4. Metribuzin desorption empirical parameters using the Freundlich model.

Soil	Treatment	K_{fd}	n_{fd}	r^2
		$cm^3\ \mu g^{-1}\ \mu g^{1-n}$		
Paoli	Unamended	2.0 ± (0.14)§	0.192	0.980
Paoli	Biosolids, 0.225 g	1.9 ± (0.04)	0.319	0.970
Paoli	Biosolids, 0.750 g	3.0 ± (0.42)	0.252	0.960
San Arcacio	Unamended	1.5 ± (0.00)	0.071	0.974
San Arcacio	Biosolids, 0.225 g	1.3 ± (0.07)	0.333	0.989
San Arcacio	Biosolids, 0.750 g	2.1 ± (0.12)	0.329	0.977

§ Standard error of the mean in parentheses.

Freundlich model (Fig. 4.8 to 4.13). The linear and exponential parameters of K_1 and K_2 are related to propensity of desorption for each compartment. The quantity $(x/m)_n$ describes the amount of metribuzin sorbed in the exponential compartment.

The Paoli soil desorption isotherms were better-described (goodness of fit, r^2) by the Freundlich model (Table 4.4 and 4.5 and Fig. 4.8 to 4.10). However, the goodness of fit of the two-compartment model increased with increasing OC levels (Fig.4.8 to 4.10). The Freundlich model also better described the San Arcacio unamended soil (Fig. 4.11), whereas the two-compartment model description became equivalent with 0.225 g biosolids amendment (Fig. 4.12), and exceeded the Freundlich model goodness of fit with 0.750 g biosolids amendment (Fig.4.13). These results contradict the finding of Barriuso et al. (1992) that desorption was better described with the two-compartment model.

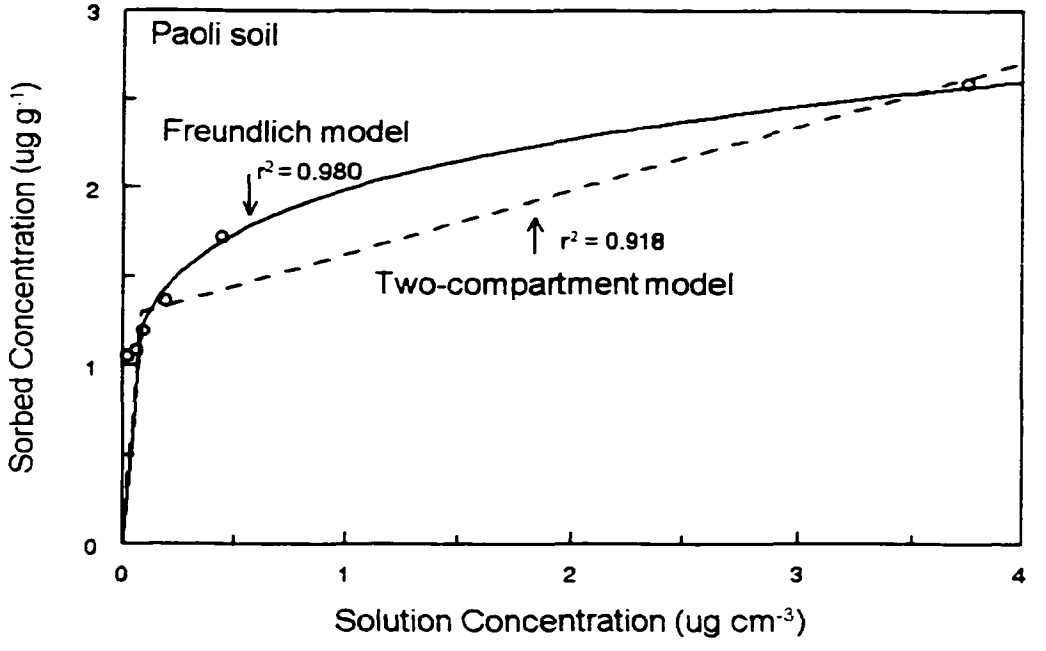


Fig. 4. 8. **Desorption of metribuzin from Paoli soil as described by the Freundlich and two-compartment models.**

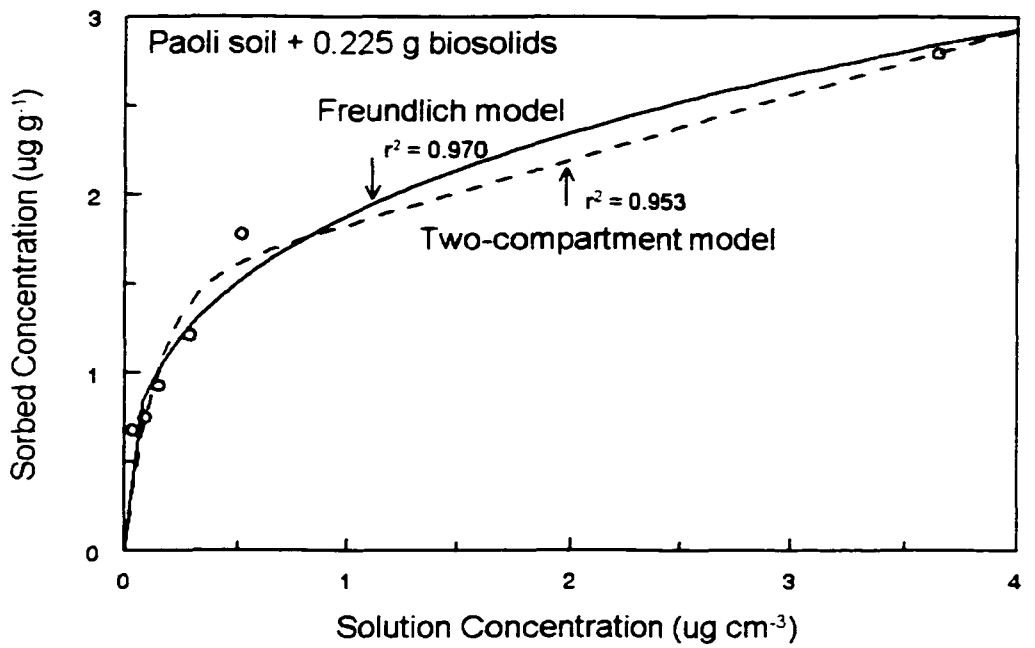


Fig. 4. 9. **Desorption of metribuzin from Paoli soil amended with 0.225 g biosolids as described by the Freundlich and two-compartment models.**

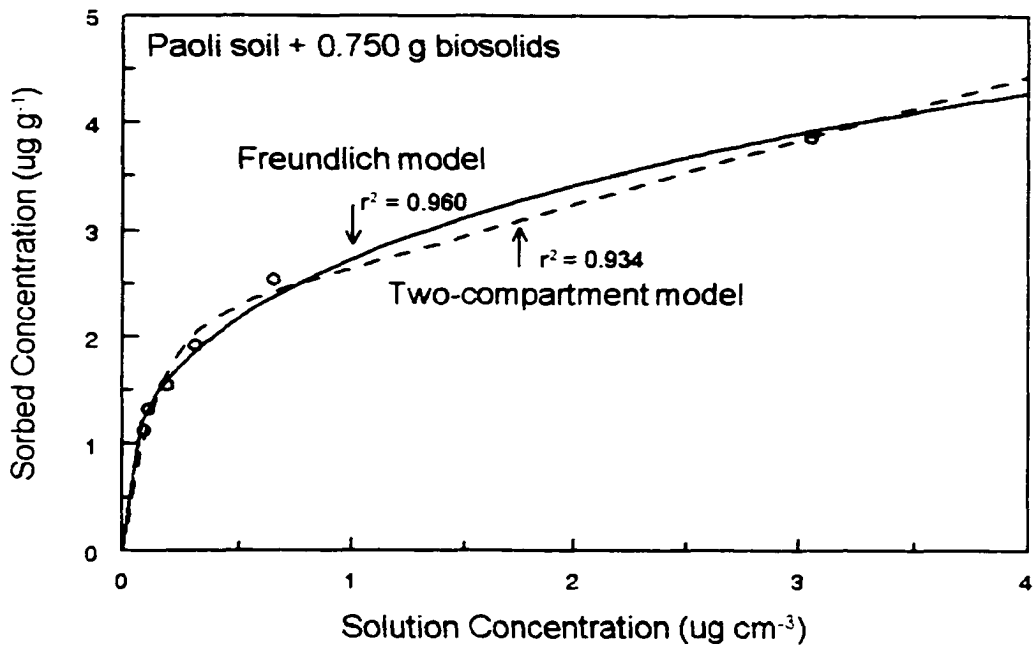


Fig. 4. 10. **Desorption of metribuzin from Paoli soil amended with 0.750 g biosolids as described by the Freundlich and two-compartment models.**

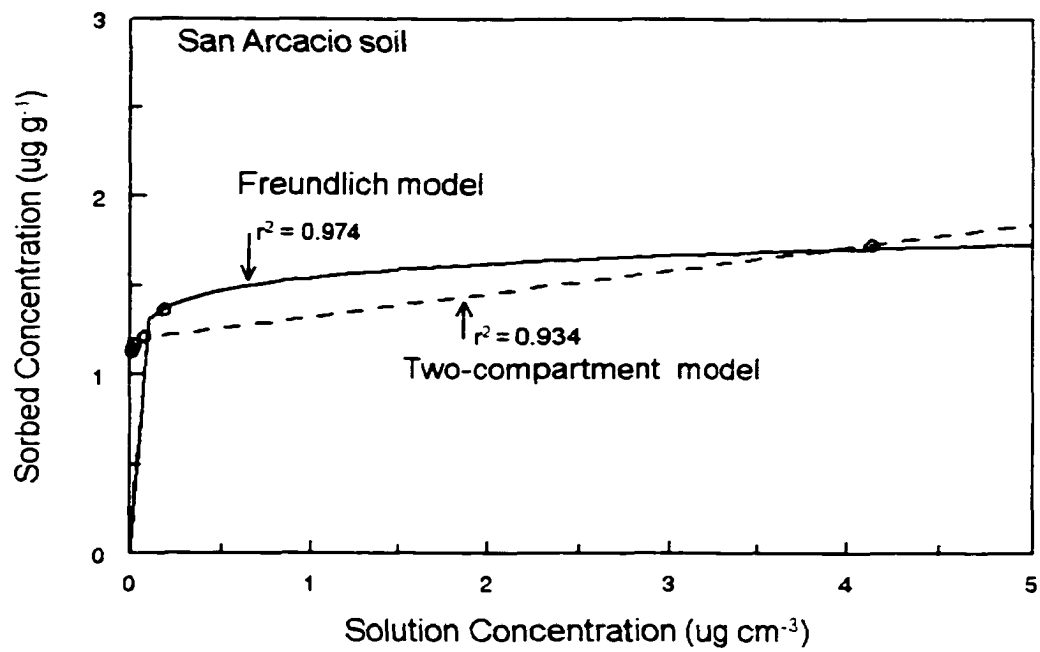


Fig. 4. 11. **Desorption of metribuzin from San Arcacio soil as described by the Freundlich and two-compartment models.**

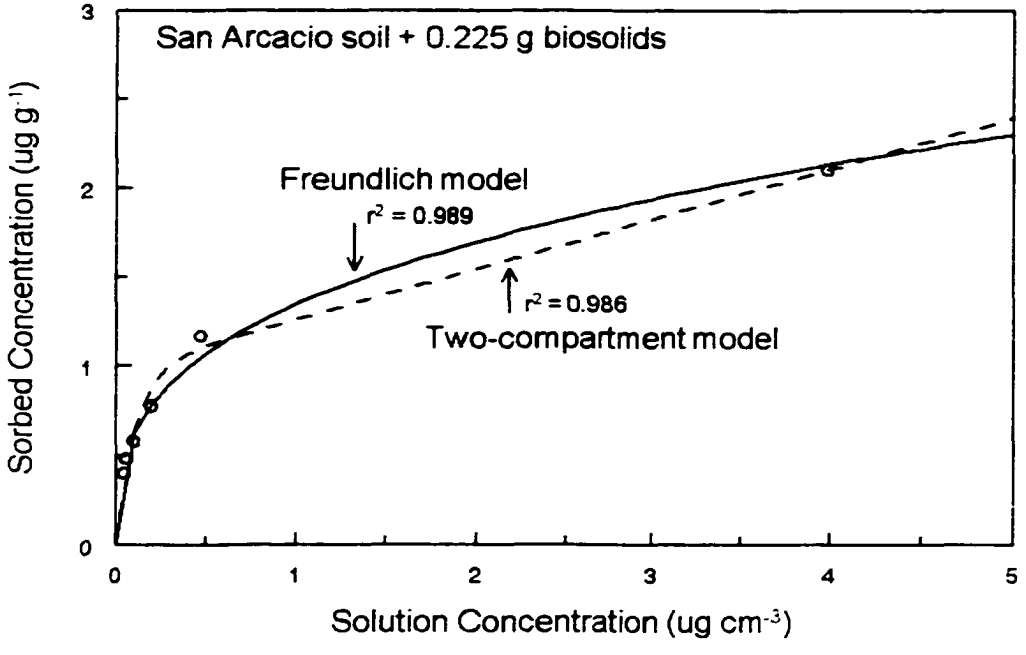


Fig. 4. 12. **Desorption of metribuzin from San Arcacio soil amended with 0.225 g biosolids as described by the Freundlich and two-compartment models.**

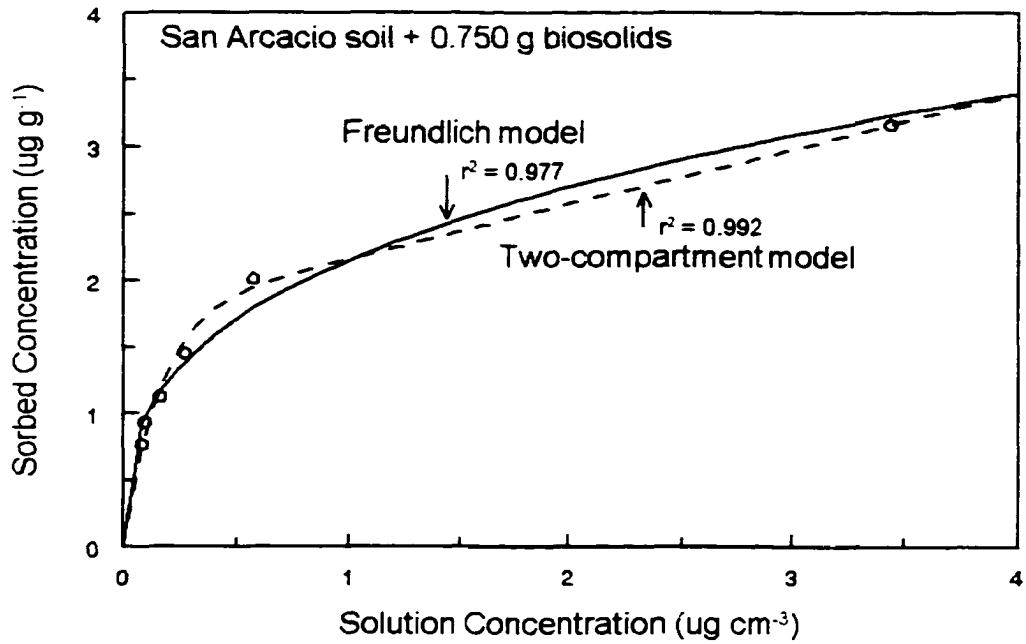


Fig. 4.13. **Desorption of metribuzin from San Arcacio soil amended with 0.750 g biosolids described by the Freundlich and two-compartment models.**

Table 4. 5. Metribuzin desorption empirical parameters using the two-compartment model.

Soil	Treatment	K_1†	K_2†	$(x/m)_n$‡	r^2
		$cm^3\ \mu g^{-1}$		$\mu g\ g^{-1}$	
Paoli	Unamended	0.36	106	1.3	0.918
Paoli	Biosolids, 0.225 g	0.37	7.38	1.5	0.953
Paoli	Biosolids, 0.750 g	0.60	2.06	7.5	0.989
San Arcacio	Unamended	0.12	281	1.2	0.934
San Arcacio	Biosolids, 0.225 g	0.28	9.72	0.98	0.986
San Arcacio	Biosolids, 0.750 g	0.41	6.48	1.8	0.992

† Propensity of metribuzin desorption for the linear (K_1) and exponential (K_2) compartments.
‡ Quantity of metribuzin sorbed in the exponential compartment.

The contradiction may be in part to due to the larger number of desorption cycles (7) and initial solute concentration range (15 to 100 $\mu g\ cm^{-3}$) used in the Barriuso et al. (1992) study. Their findings described the two-compartment isotherm fit as increasing with greater solute concentration and desorption dilution. In the present study, the fit of the two-compartment model increased with increasing OC content. Thus, application of the two-compartment model may be suited for soils of moderate to increasing organic matter, where initial solute concentrations are typical of normal agricultural practices.

Soil Amended with Biosolids Separates and Polyacrylamide

Decreases in the amounts of metribuzin remaining sorbed over the course of the repeated desorption cycles are shown in Fig.4-14. Desorption curves were

fitted to the single (Freundlich) and two-compartment models to represent the isotherms of each soil treatment (Table 4.6 and Fig. 4.15 to 4.19). The Freundlich model described the metribuzin desorption curves with greater confidence than the 2-compartment model, except for soil amended with 0.750 g residual biosolids.

Table 4. 6. Freundlich and 2-compartment desorption constants of metribuzin for Paoli soil amended with biosolids separates and PAM.

Treatment	Freundlich Model			2-Compartment Model			
	K_{fd}	n_{fd}	r^2	K_1†	K_2†	$(x/m)_n$‡	r^2
				—— $cm^3\ \mu g^{-1}$ ——		$\mu g\ g^{-1}$	
DOC from 0.225g biosolids (2.94 mg)	1.5	0.18	0.968	0.22	49	1.0	0.898
DOC from 0.750g biosolids (13.2 mg)	1.2	0.33	0.992	0.27	12	0.83	0.974
Residual biosolids, 0.225 g	2.2	0.12	0.970	0.21	41	1.8	0.926
Residual biosolids, 0.750 g	2.2	0.30	0.948	0.32	5.3	2.1	0.992
PAM	1.8	0.27	0.993	0.38	26	1.1	0.954

† Propensity of metribuzin desorption for the linear (K_1) and exponential (K_2) compartments.
‡ Quantity of metribuzin sorbed in the exponential compartment.
PAM Polyacrylamide.

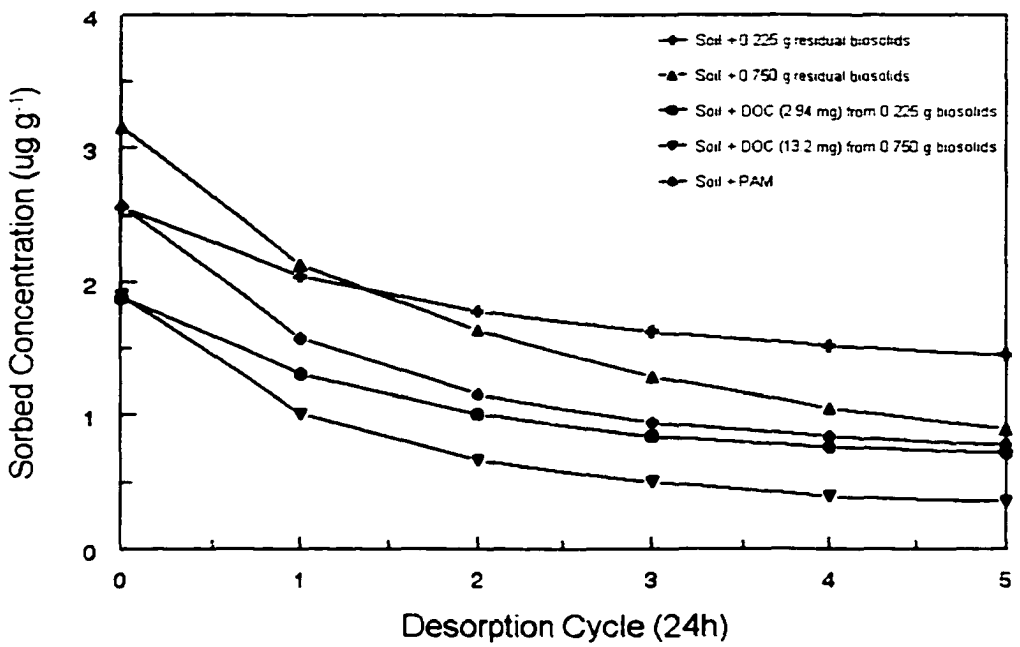


Fig. 4.14. **Desorption cycle isotherms of Paoli soil amended with biosolids separates and polyacrylamide.**

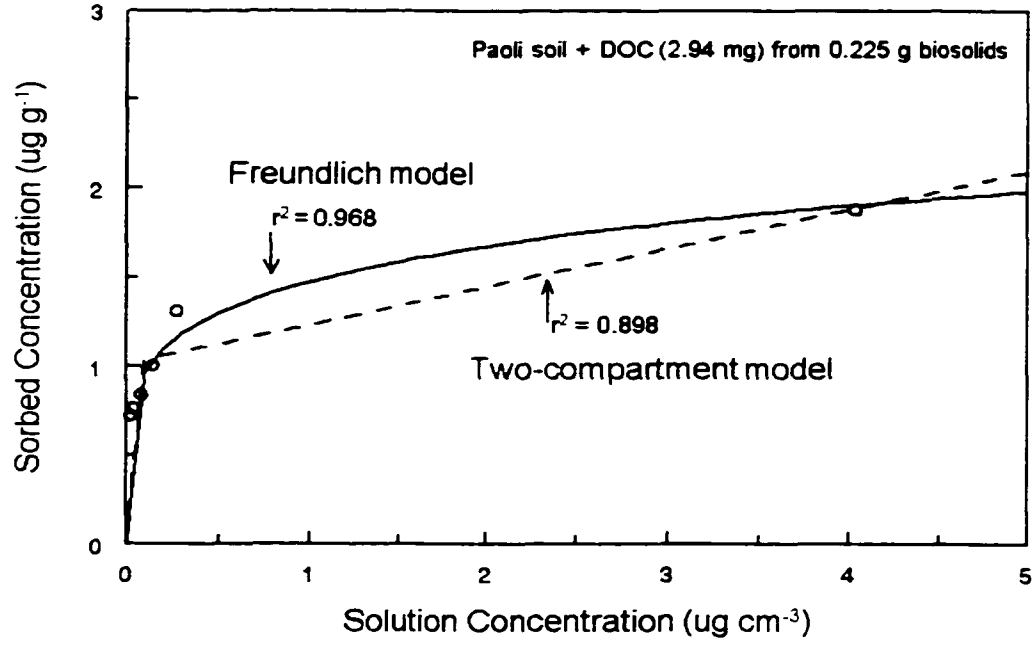


Fig. 4.15. **Desorption of metribuzin from Paoli soil amended with dissolved organic carbon (2.94 mg) from 0.225 g biosolids.**

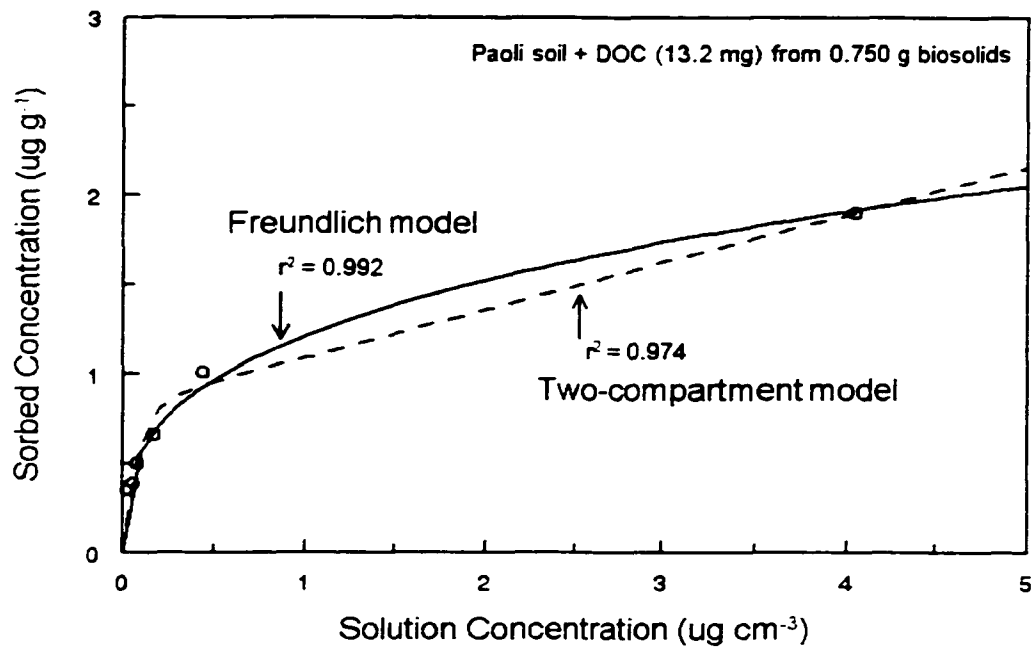


Fig. 4.16. **Desorption of metribuzin from Paoli soil amended with dissolved organic carbon (13.2 mg) from 0.750 g biosolids.**

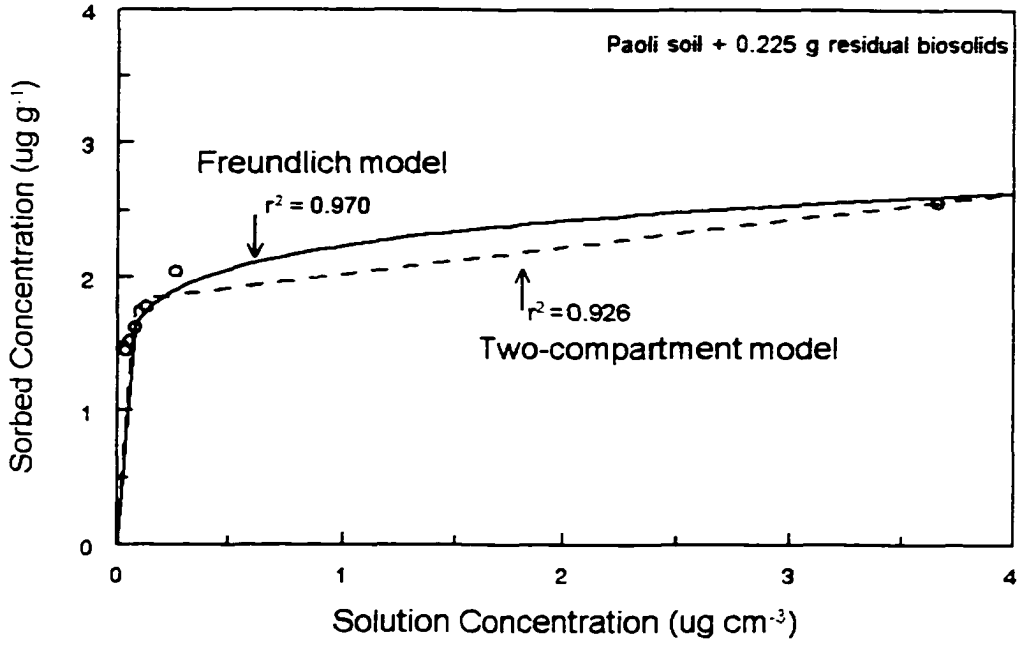


Fig. 4.17. **Desorption of metribuzin from Paoli soil amended with 0.225 g of residual biosolids.**

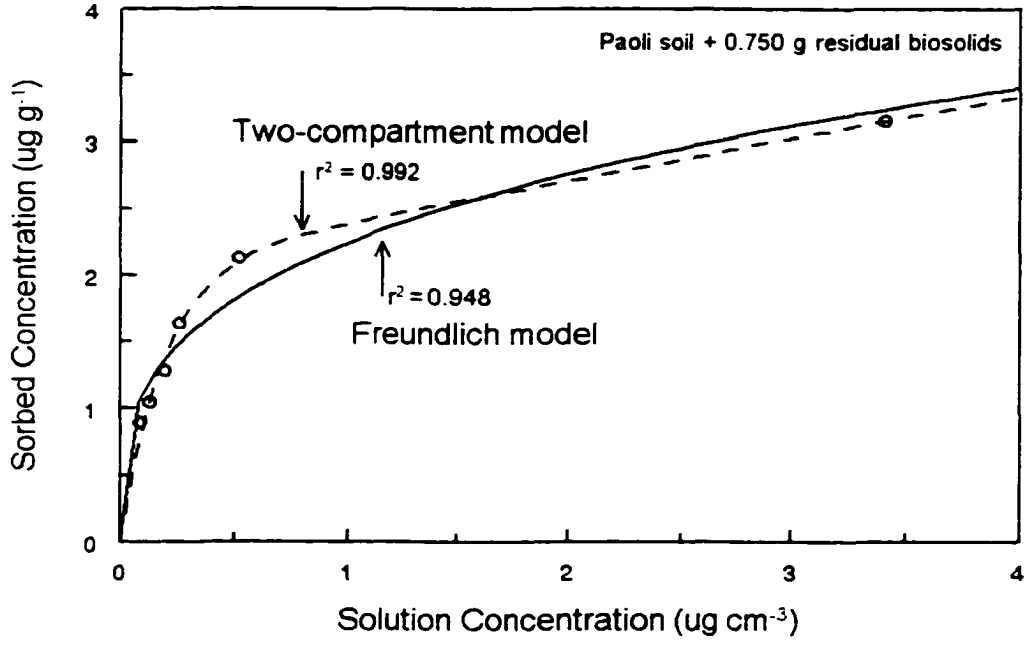


Fig. 4. 18. **Desorption of metribuzin from Paoli soil amended with 0.750 g of residual biosolids.**

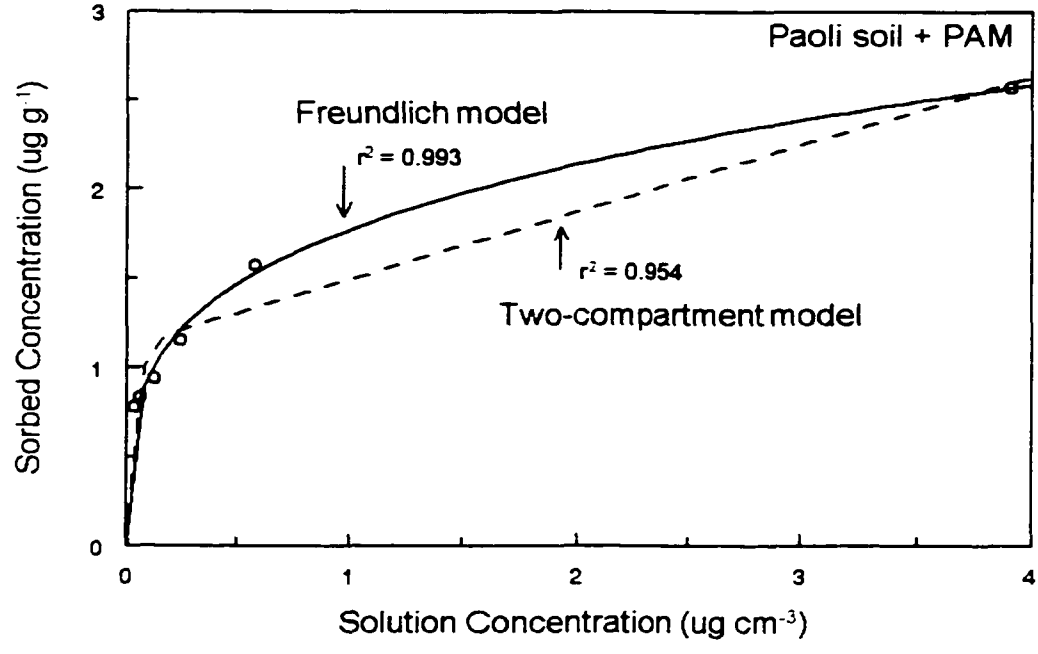


Fig. 4. 19. **Desorption of metribuzin from Paoli soil amended with polyacrylamide.**

Interpretations of Desorption based on the Freundlich and Two-compartment Models

While both the Freundlich and two-compartment models fit the desorption data to a relatively high degree of confidence (Tables 4.5 to 4.6), the Freundlich model is a parameter-fitting algorithm which provides no insight as to sorption and desorption mechanisms. The equation's empirical constant *n* (Equation 4) provides only a general sense to understanding the variability in sorptive site behavior. That is, as *n* approaches 1, the variability in sorptive site behavior decreases. The two-compartment model (Equation 13) was designed to incorporate a linear and inverse exponential function, corresponding to two different desorption compartments (Barriuso et al., 1992). Therefore, the two-compartment model was used to interpret the metribuzin retention mechanisms from desorption measurements.

For the linear compartment (first 24 h of desorption), the retention force was interpreted as being weak, easily releasing metribuzin to the soil solution, with the isotherm slope being relatively steep. The K_1 parameters (Table 4.5 and 4.6) are the slopes of the linear isotherms (Fig. 4.6 and 4.14) and quantify equilibrium desorption (Carroll et al., 1994; Young and Weber, 1995; Pignatello and Xing, 1996; Xing et al., 1996; Xing and Pignatello, 1997; and Graber and Borisover, 1998). They are related to their sorption isotherm characteristics and increase with increases in amounts of added biosolids OC.

The exponential compartment was interpreted, as having a strong retentive force for metribuzin. This compartment required a greater desorption

time and dilution to release metribuzin to the soil solution. The K_2 parameters decreased with increases in biosolids OC. The size of the exponential compartment $(x/m)_n$ varied slightly (Table 4.5 to 4.6) between soils and amendments (1.0 to 2.1 μg g^{-1}) except for the Paoli soil amended with 0.750 g biosolids (7.5 μg g^{-1}). These observations suggest that the size of the exponential compartment is limited to the asymptotic value, $(x/m)_n$ (Barriuso et al., 1992). The size of this compartment appeared to be an intrinsic property of soil, being invariant to organic matter amendments. The mechanisms controlling desorption from the sub-asymptotic compartment exhibit very slow, reversible kinetics and irreversible, chemical transformations. The two-compartment model isotherms could be resolved into two further isotherms (Fig. 4-20 to 4-30) that correspond to the two compartments defined earlier.

The two-compartment linear, and exponential isotherm goodness of fit (r^2) and standard error of fit are listed in Table 4.7. As expected, the two-compartment goodness of fit values provided the best correlation, explaining with a high degree of confidence the isotherms biphasic and multi-mechanistic characteristics. The standard error of fit was low and varied only slightly, suggesting an overall lack of sensitivity to changes in isotherm shape.

The linear compartment goodness of fit values was low for both soils and amendments. This was not surprising as the size of the linear compartments were small (one desorption cycle). The standard error of fit values was high, and

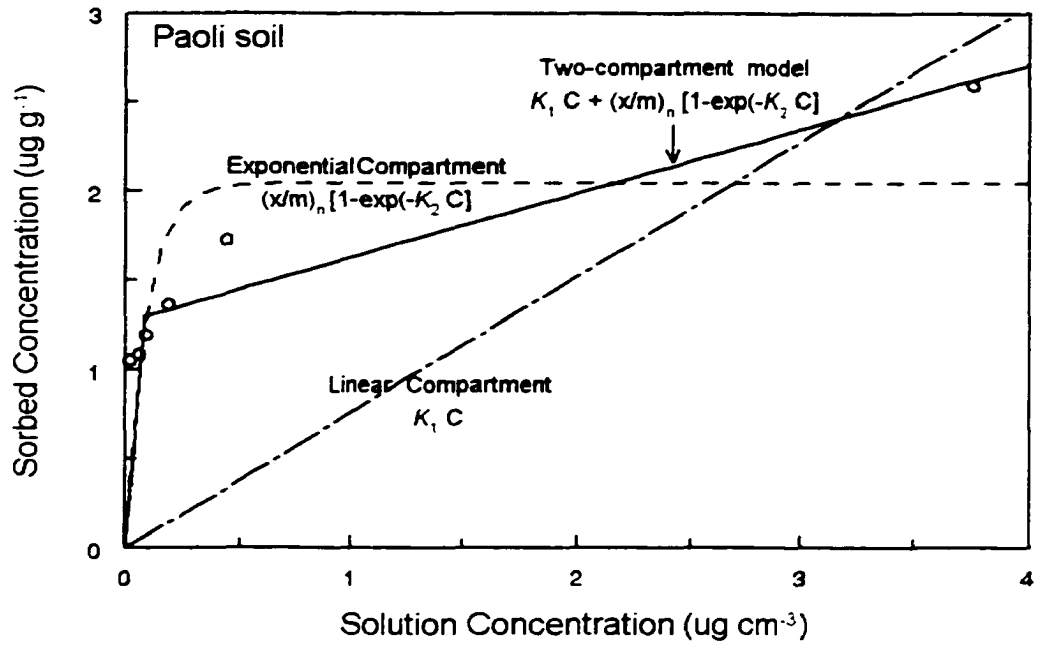


Fig. 4. 20. **The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil.**

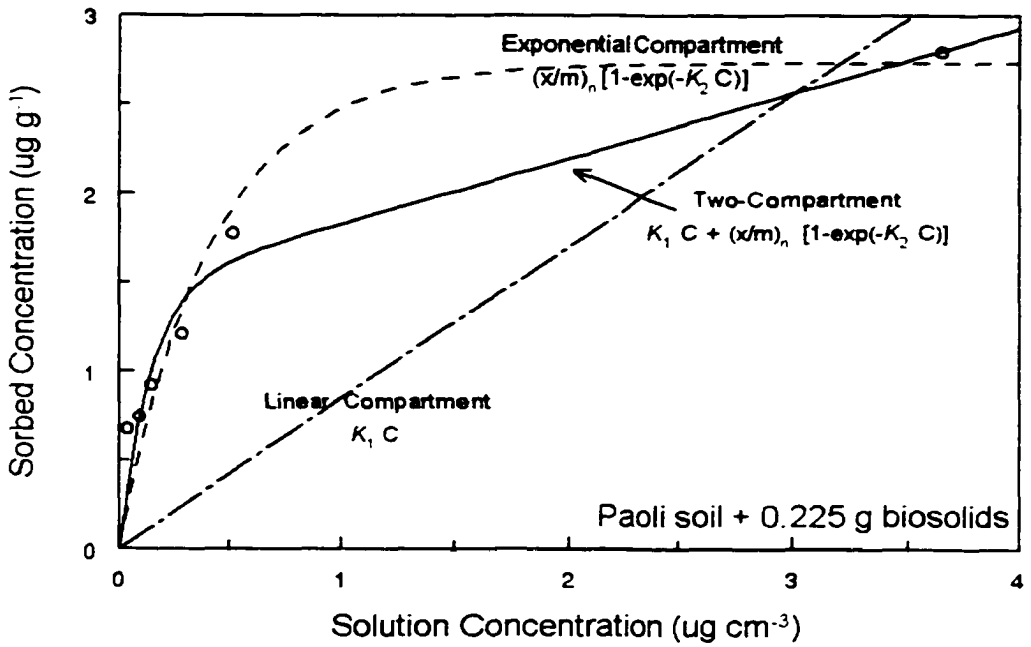


Fig. 4. 21. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with 0.225 g biosolids.

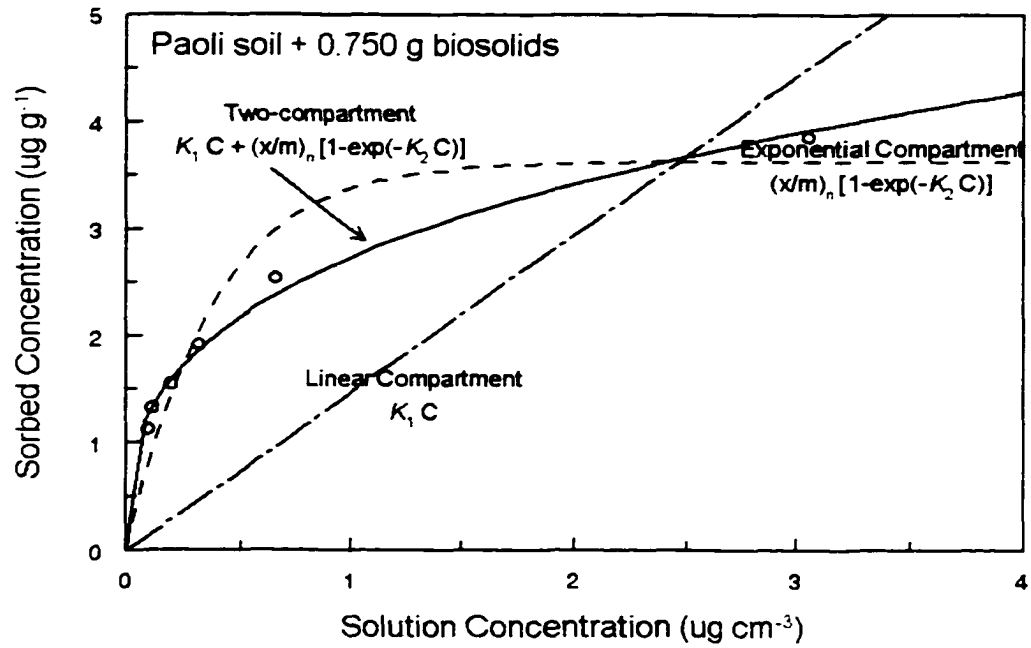


Fig. 4. 22. **The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with 0.750 g biosolids.**

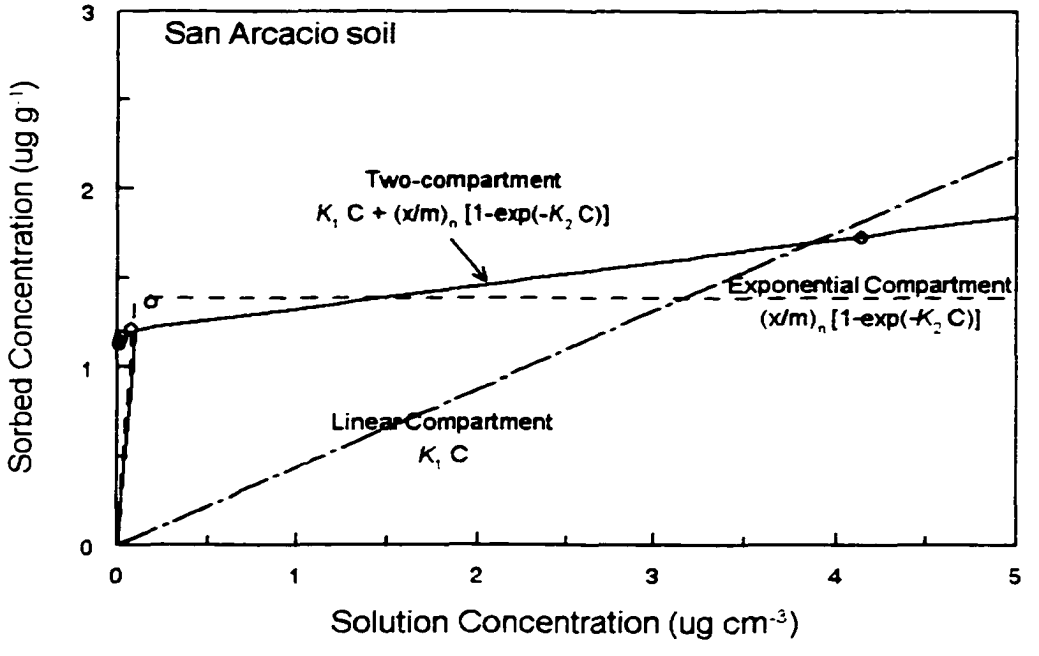


Fig. 4. 23. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for San Arcacio soil.

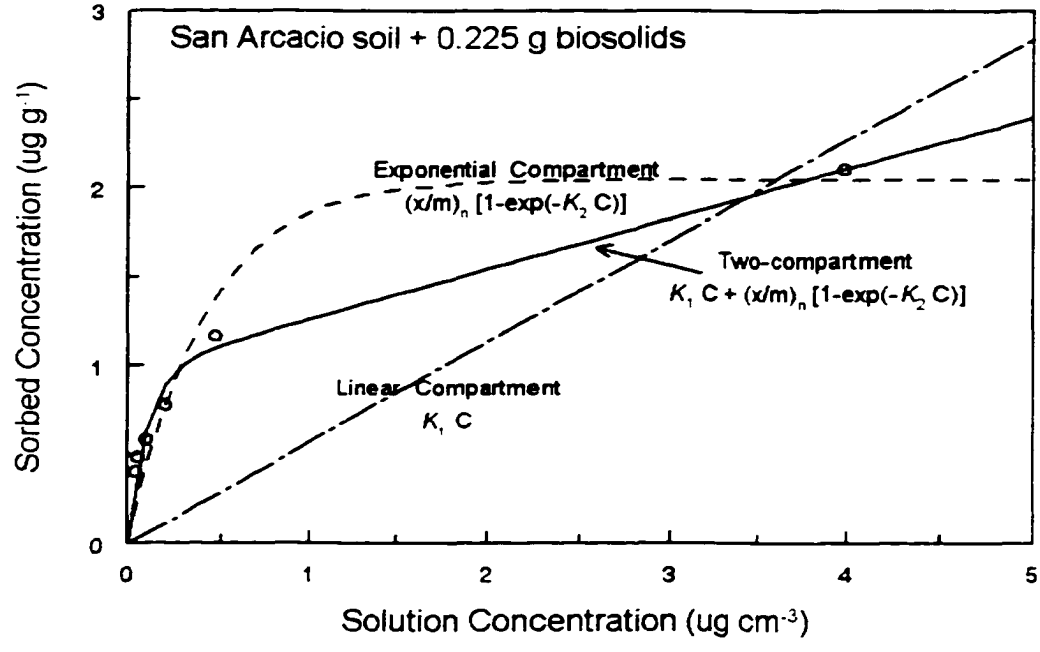


Fig. 4. 24. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for San Arcacio soil amended with 0.225 g biosolids.

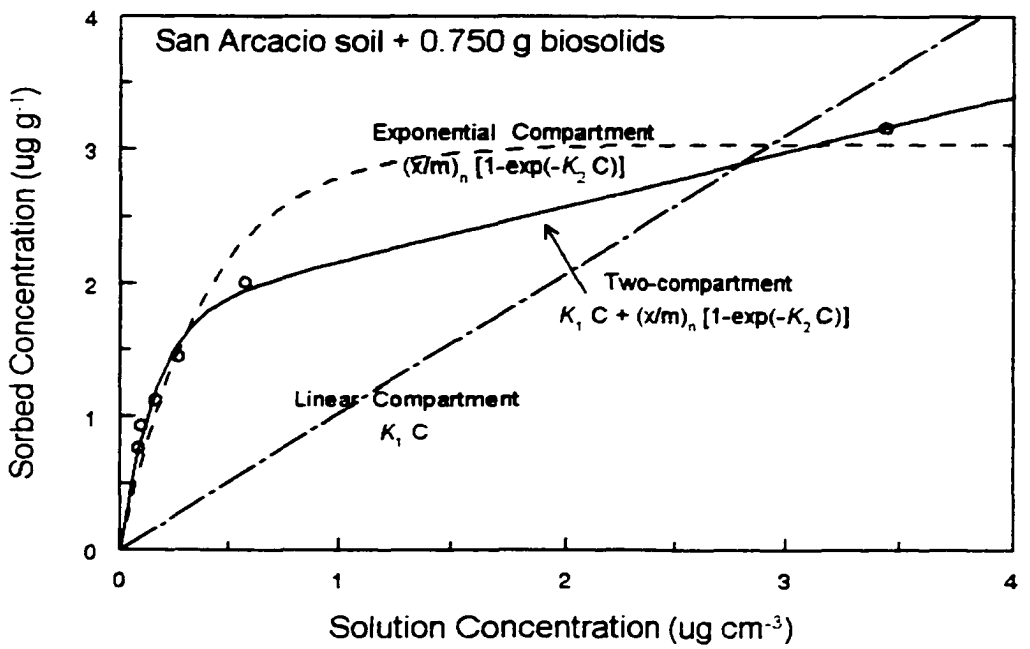


Fig. 4. 25. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for San Arcacio soil amended with 0.750 g biosolids.

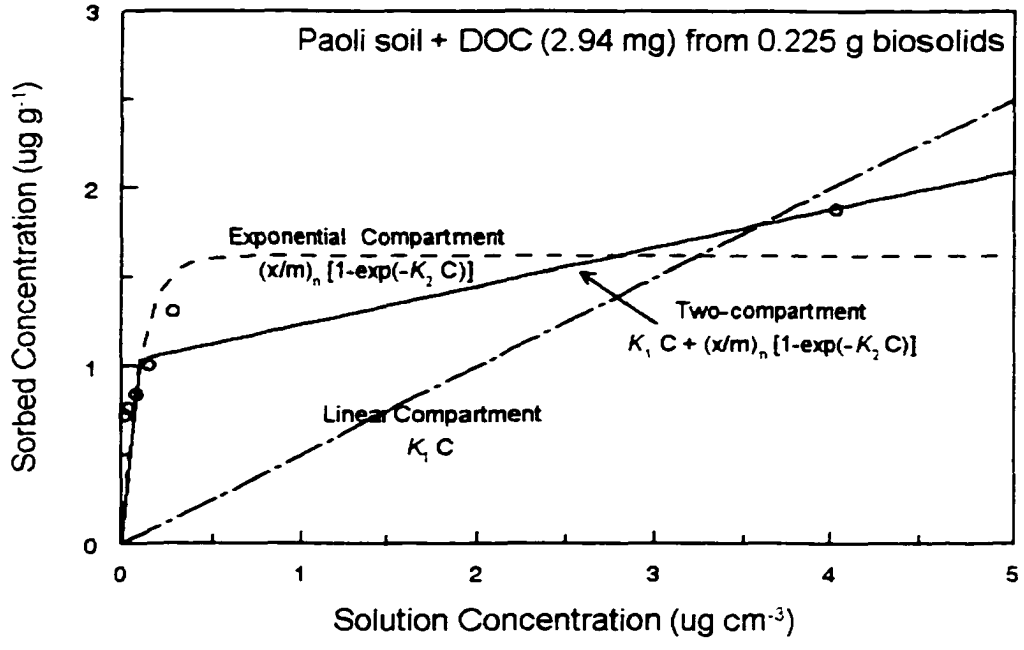


Fig. 4. 26. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with DOC (2.94 mg) from 0.225g biosolids.

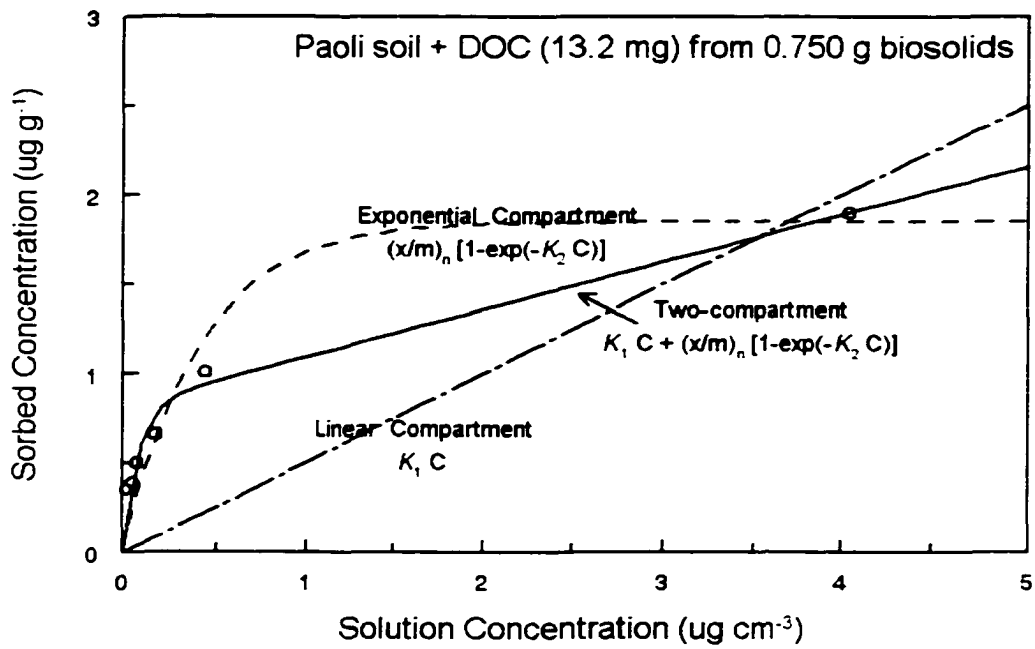


Fig. 4. 27. **The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with DOC (13.2 mg) from 0.750g biosolids.**

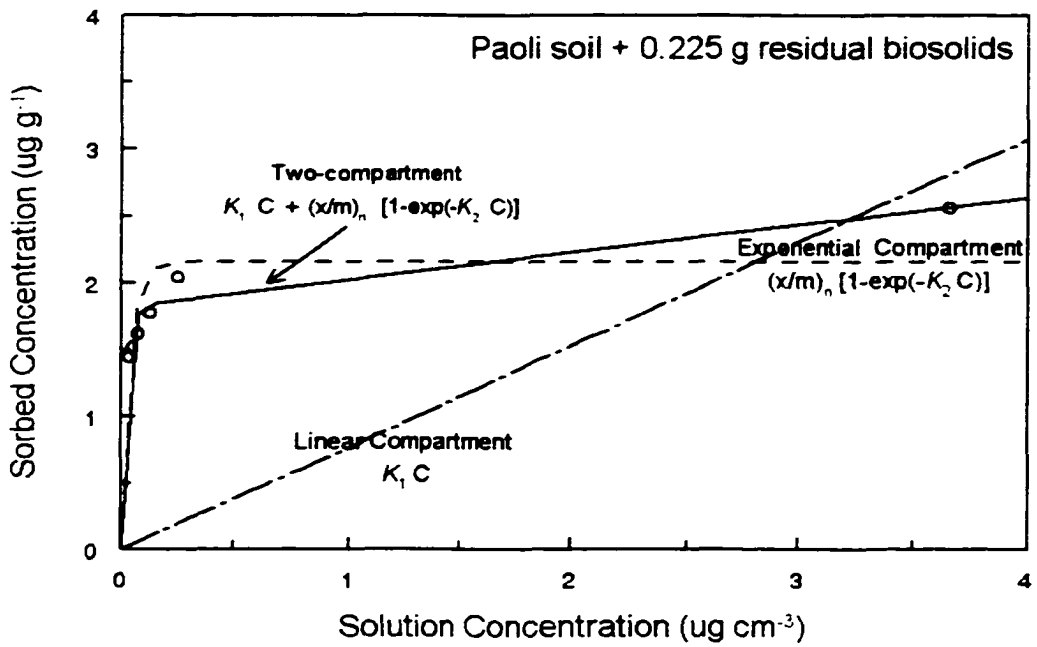


Fig. 4. 28. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with 0.225g residual biosolids.

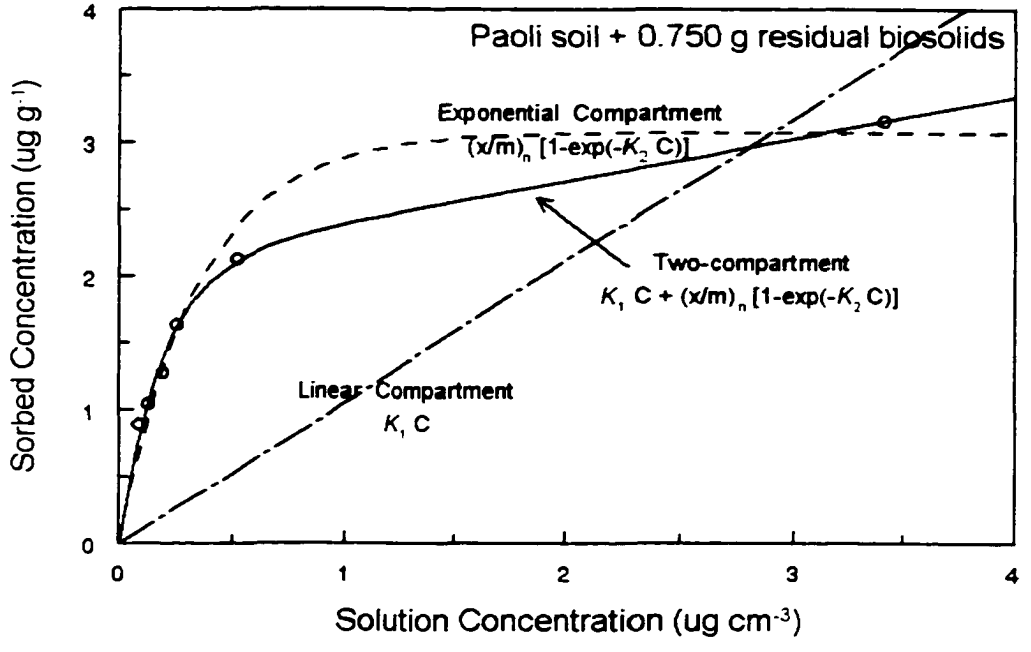


Fig. 4. 29. The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with 0.225g residual biosolids.

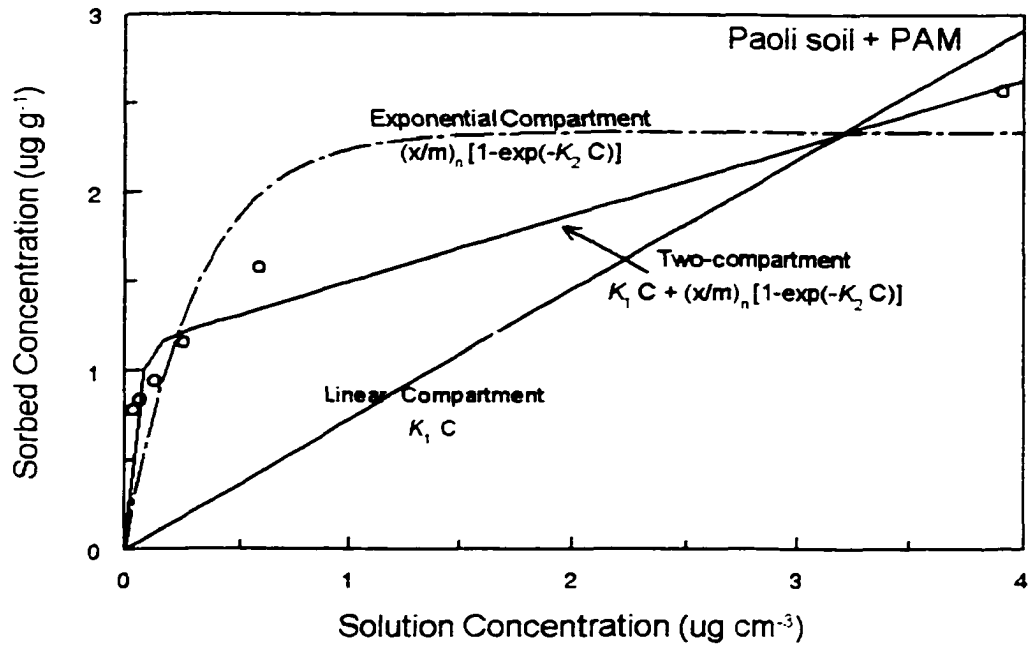


Fig. 4. 30. **The separations of the metribuzin two-compartment desorption isotherm into linear and exponential desorption isotherms for Paoli soil amended with polyacrylamide.**

Table 4. 7. Goodness of fit (r^2) comparison for the metribuzin two-compartment, linear, and exponential desorption isotherms of Paoli and San Arcacio soil and amendments.

Soil	Amendment	Two-compartment†	Linear Compartment‡	Exponential Compartment§
		r^2		
Paoli	-	0.9181 ± (0.3771)¶	0.6231 ± (2.635)¶	0.6806 ± (1.049)¶
Paoli	0.225 g biosolids	0.9529 ± (0.4268)	0.6986 ± (2.085)	0.9328 ± (0.5712)
Paoli	0.750 g biosolids	0.9889 ± (0.2432)	0.6909 ± (3.004)	0.9204 ± (0.7581)
San Arcacio	-	0.8935 ± (0.1678)	0.5434 ± (2.639)	0.3555 ± (0.4326)
San Arcacio	0.225 g biosolids	0.9867 ± (0.1701)	0.7330 ± (1.381)	0.9394 ± (0.4207)
San Arcacio	0.750 g biosolids	0.9924 ± (0.1767)	0.6978 ± (2.378)	0.9476 ± (0.5248)
Paoli	DOC (2.94 mg) from 0.225 g biosolids	0.8976 ± (0.3269)	0.6096 ± (1.992)	0.7752 ± (0.6682)
Paoli	DOC (13.2 mg) from 0.750 g biosolids	0.9737 ± (0.2260)	0.7438 ± (1.198)	0.9286 ± (0.4307)
Paoli	0.225 g residual biosolids	0.9264 ± (0.2602)	0.5559 ± (3.601)	0.6805 ± (0.6099
Paoli	0.750 g residual biosolids	0.9923 ± (0.1689)	0.6631 ± (2.689)	0.9687 ± (0.3661

† Based on the $x/m = K_1 C + (x/m)_n [1-\exp(-K_2 C)]$.
‡ Based on $x/m = K_1 C$.
§ Based on $x/m = (x/m)_n [1-\exp(-K_2 C)]$.
¶ Standard error of fit in parenthesis.

supported the theory that size of the linear compartment was a sensitive factor in the model.

The exponential compartment goodness of fit was similar to that of the two-compartment results. Results for soil amended with biosolids separates were initially similar to the linear compartment values (low r^2) but approached the whole biosolids r^2 values with increasing OC (Table 4.7). The added effects of increases in organic matter from amendments were quite visible, especially when compared results with the unamended soil. The compartment's K_2 parameter appears to be the most sensitive to changes in soil OC and organic matter amendments.

Sorption-Desorption Hysteresis

To further characterize and describe the effects of soil and biosolids organic matter on sorption and desorption of metribuzin, hysteresis was quantified. Hysteresis as defined by O'Connor et al. (1980) and Cox et al. (1997), is based on the ration of Freundlich desorption and sorption isotherm *n* coefficients:

$$H = \left[\frac{n_{fd}}{n_f}\right] x 100 \qquad (18)$$

The *H* quotient provides an indication of the difference in characteristics of a chemical being sorbed to soil particles and the chemical's release (desorption).

Theoretically, when the Freundlich *n* coefficients of sorption and desorption are the same ($n_{fd} = n_f$), hysteresis is not observed.

Soil and Biosolids

Although the sorption of metribuzin to both soil and soil plus amendments was partially instantaneous and reversible, a measured amount of sorption-desorption hysteresis was apparent. The characteristics of metribuzin sorption-desorption hysteresis are described in Table 4.8 and illustrated in Figures 4.31 to 4.36. Hysteresis decreased as the organic matter content of the amended soils increased. However, a pared two-sample t-test for means ($P<0.10$) showed no statistical differences. The lack of statistical differences could be related to the small number of measurements. Additional data points would help to resolve this issue. No difference in hysteresis was observed between the Paoli soil amendments, while minimal differences were observed for the San Arcacio soil amendments. The two soils amended with 0.750 g biosolids showed a slight increase in hysteresis.

Table 4. 8. Summary of hysteresis (*H*) coefficients and curve areas for desorption of Paoli and San Arcacio soil and amendments.

Soil	Treatment	$H^{\dagger}$	$\varphi^{\ddagger}$
Paoli	Unamended	20 ± (2)[§]	2.84 ± (0.40)[§]
Paoli	Biosolids, 0.225g	32 ± (1)	2.51 ± (0.07)
Paoli	Biosolids, 0.750g	32[¶]	2.95[¶]
San Arcacio	Unamended	9.1 ± (1.1)	2.50 ± (0.04)
San Arcacio	Biosolids, 0.225g	36 ± (3)	1.72 ± (0.13)
San Arcacio	Biosolids, 0.750g	33 ± (3)	2.76 ± (0.26)

§ Standard error of the mean in parentheses.
¶ Value of a single data point.
† $H = [n_{fd}/n_f] \times 100$
‡ Difference in the desorption-sorption integrals.

Effects of Biosolids, Residuals, and Polyacrylamide

Hysteresis for soil amended with DOC from biosolids decreased as a function of increases in DOC concentration (Table 4.9 and Fig. 4.37 to4.38). Hysteresis for soil amended with residual biosolids in which water-soluble organic matter had been extracted (Fig. 4.39 to 4.41) was more difficult to interpret. Hysteresis decreased with increasing biosolids content. This could have been due to residual organic carbon remaining with the mineral fraction of the biosolids after extraction. Hysteresis of soil amended with PAM was greater than unamended soil, less than soil amended with biosolids DOC, and greater than soil amended with residual biosolids (Table 4.9 and Fig 4.31).

Table 4. 9. Summary of hysteresis (H) coefficients and curve areas for desorption of Paoli soil amended with biosolids separates and PAM.

Treatment	$H^{\dagger}$	$\varphi^{\ddagger}$
DOC (2.94 mg) from 0.225 g biosolids	0.19	1.81
DOC (13.2 mg) from 0.750 g biosolids	0.33	1.27
Residual biosolids, 0.225 g	0.12	3.47
Residual biosolids, 0.750 g	0.35	3.36
PAM	0.26	2.41

† $H = [n_{fd}/n_f] \times 100$
‡ Difference in the desorption-sorption integrals.
PAM Polyacrylamide.

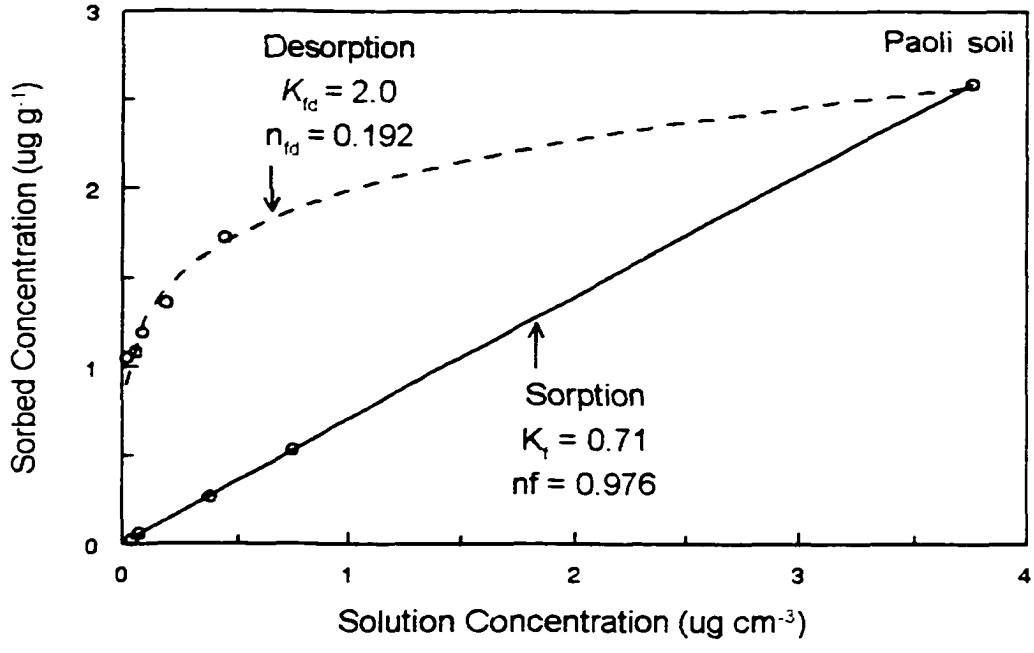


Fig. 4.31. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil.**

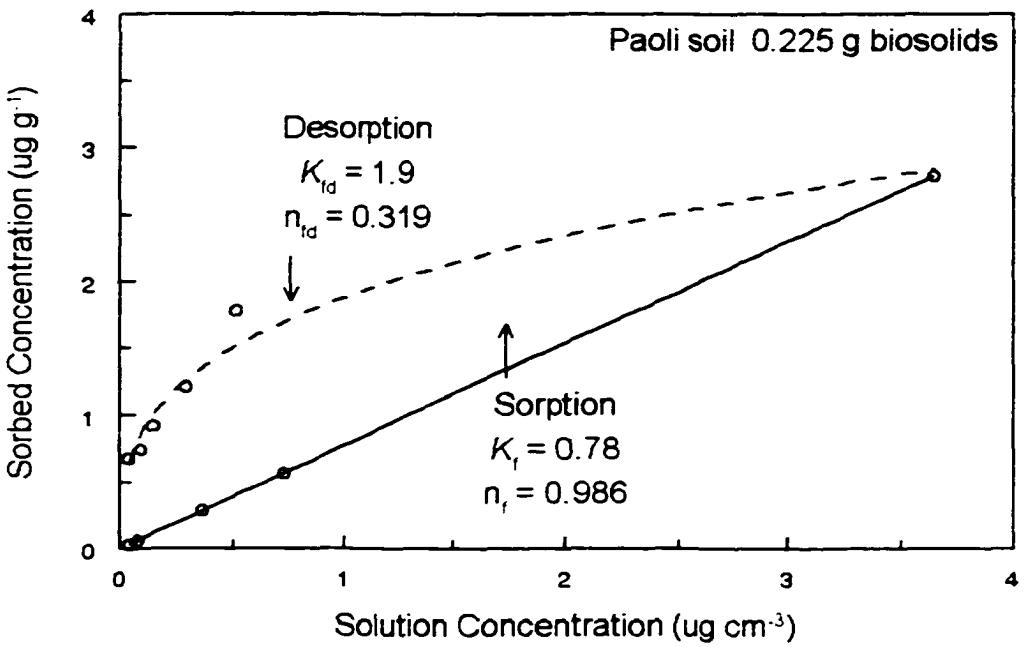


Fig. 4. 32. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil amended with 0.225 g biosolids.**

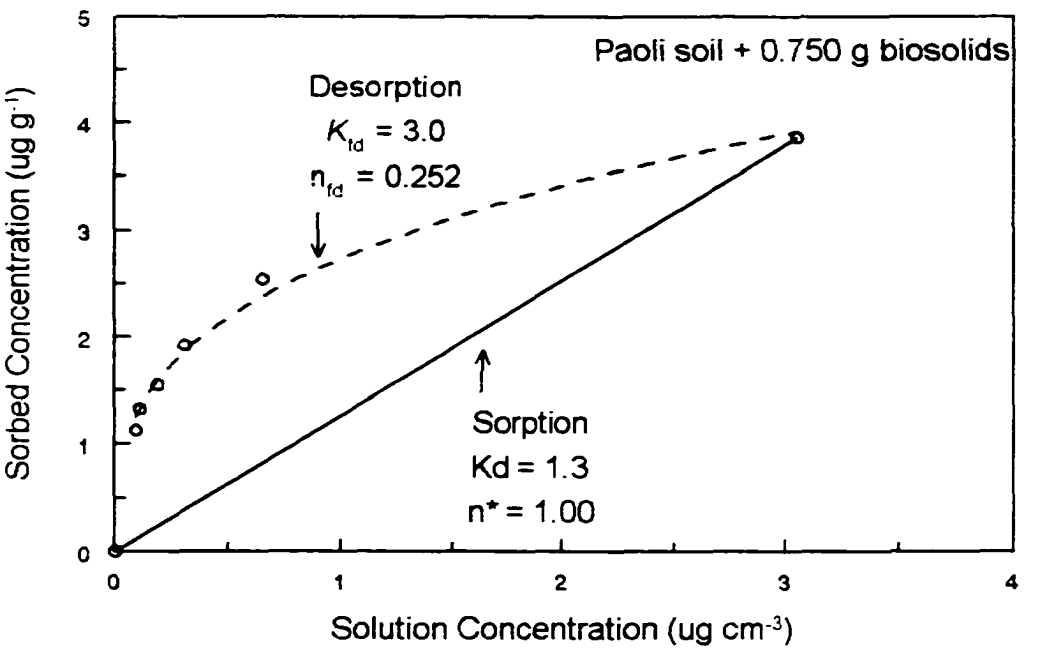


Fig. 4. 33. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil amended with 0.750 g biosolids.**

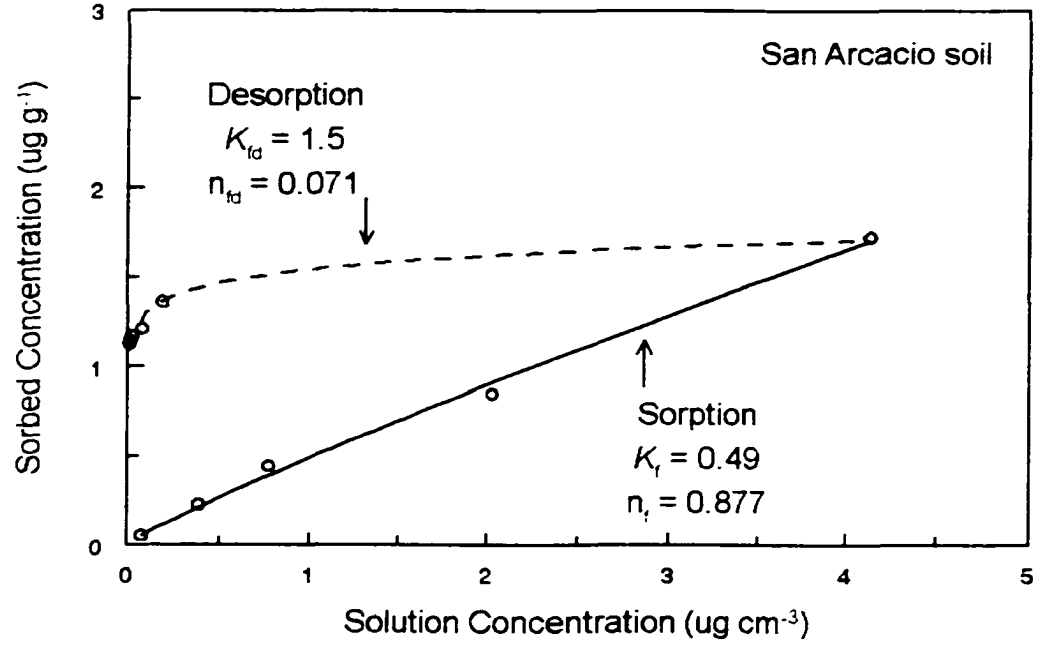


Fig. 4. 34. **Hysteretic characteristics of metribuzin sorption and desorption for San Arcacio soil.**

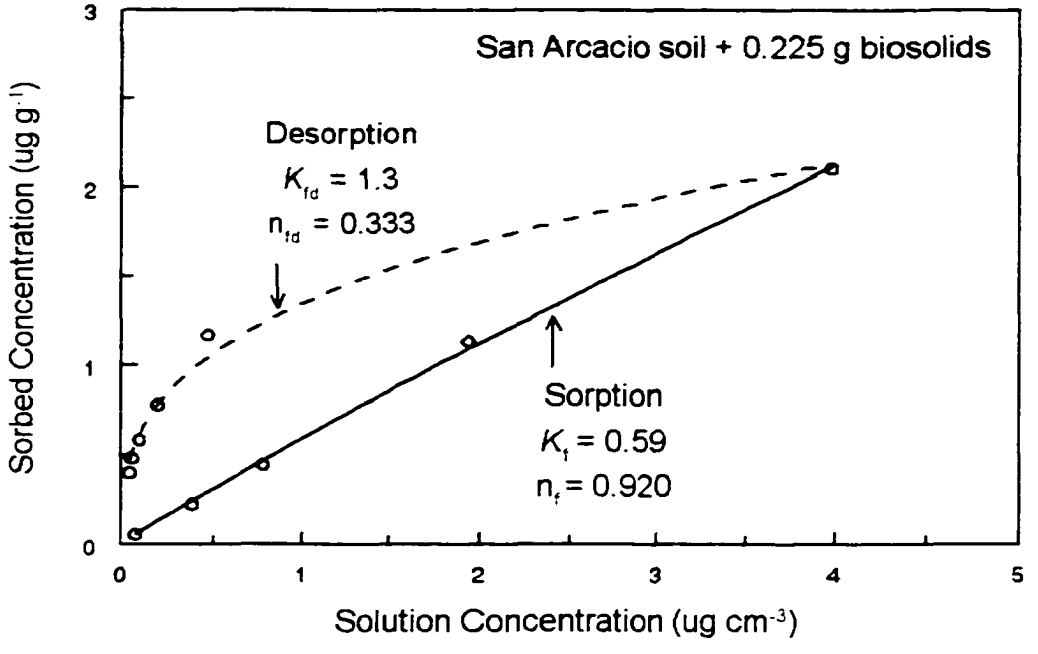


Fig. 4.35. **Hysteretic characteristics of metribuzin sorption and desorption for San Arcacio soil amended with 0.225 g biosolids.**

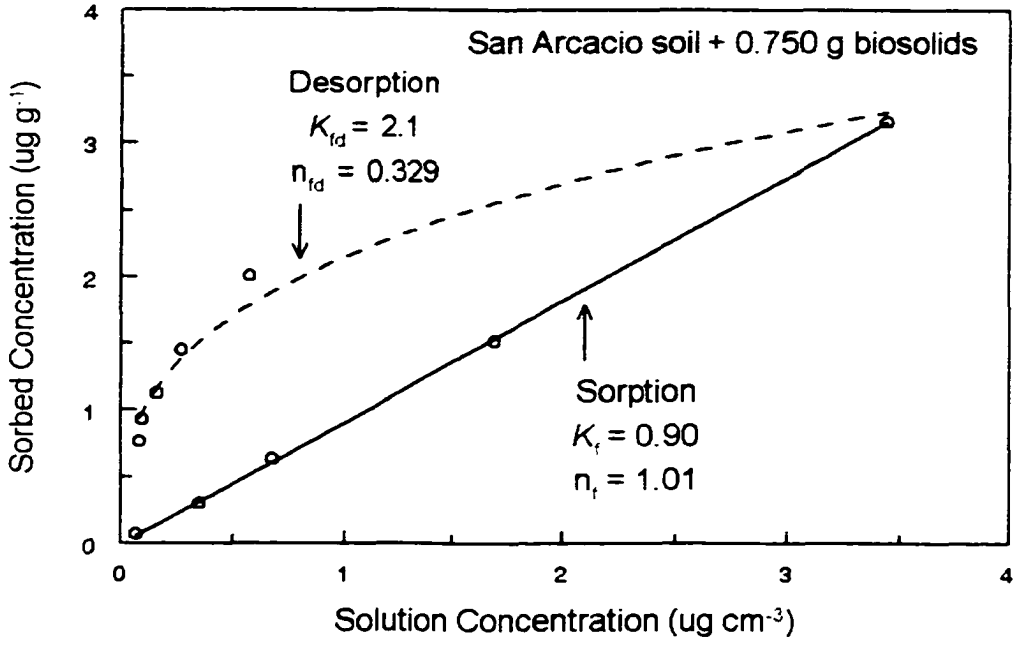


Fig. 4.36. **Hysteretic characteristics of metribuzin sorption and desorption for San Arcacio soil amended with 0.750 g biosolids.**

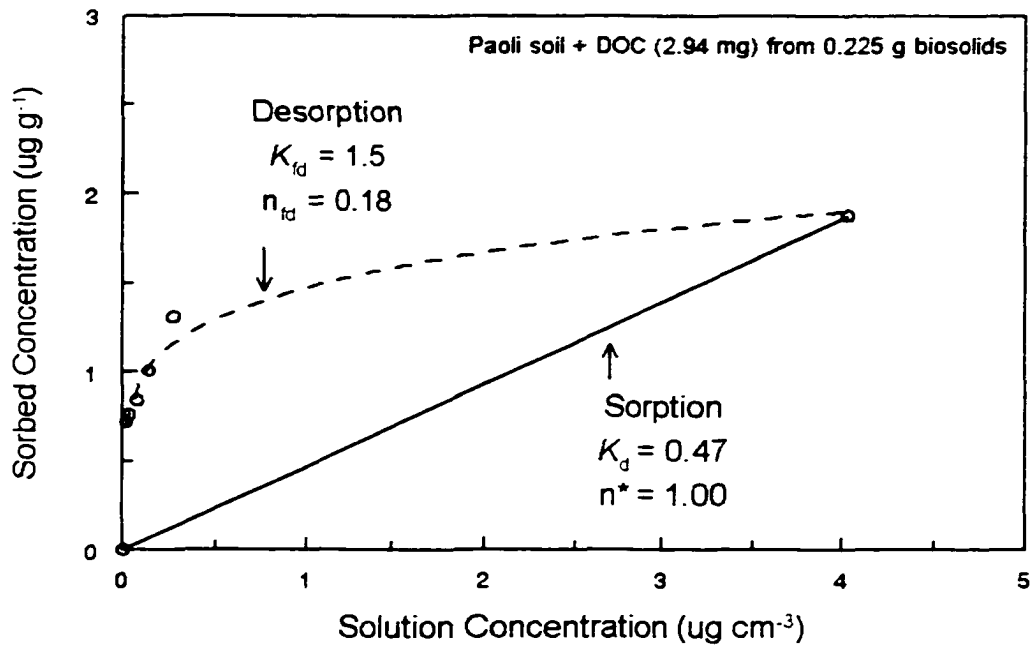


Fig. 4.37. Hysteretic characteristics of metribuzin sorption and desorption forPaoli soil amended with dissolved organic carbon (2.94 mg) from 0.225 g biosolids.

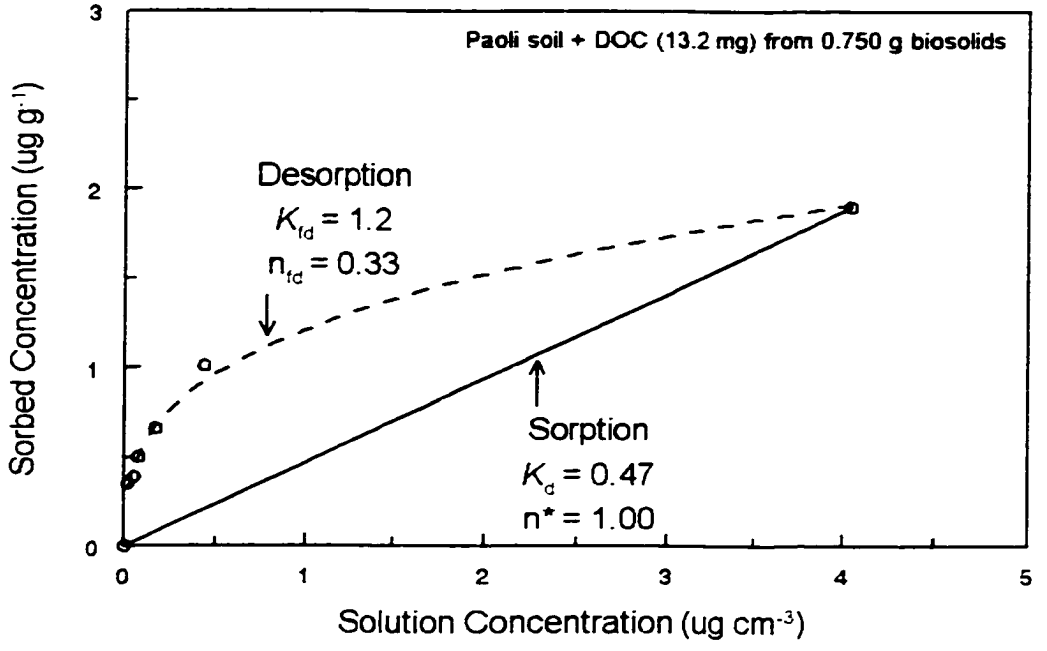


Fig. 4.38. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil amended with dissolved organic carbon (13.2 mg) from 0.750 g biosolids.**

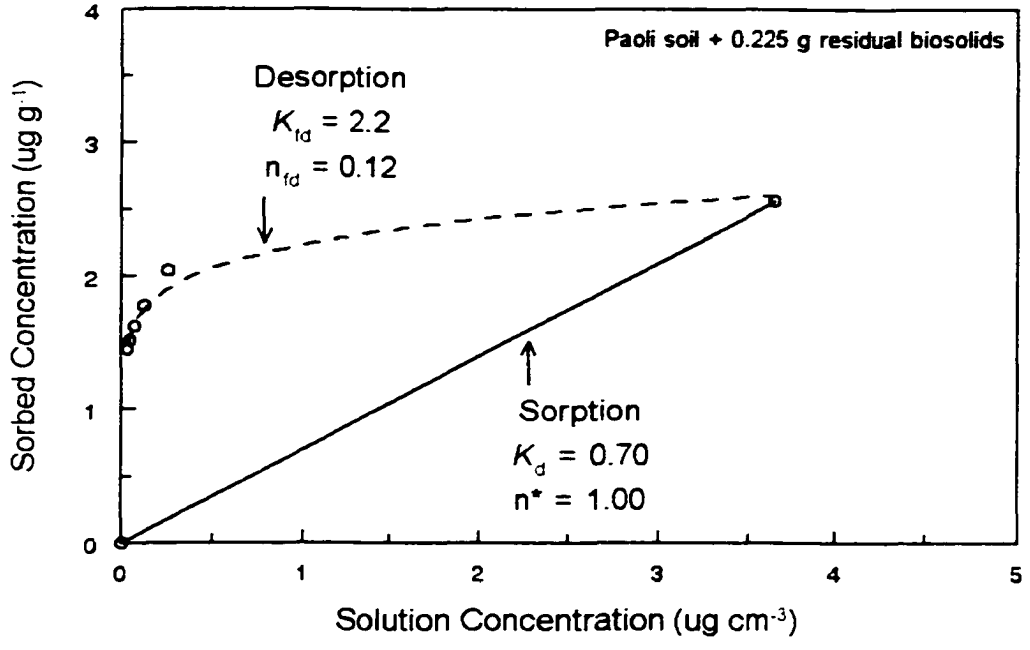


Fig. 4.39. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil amended with 0.225 g of residual biosolids.**

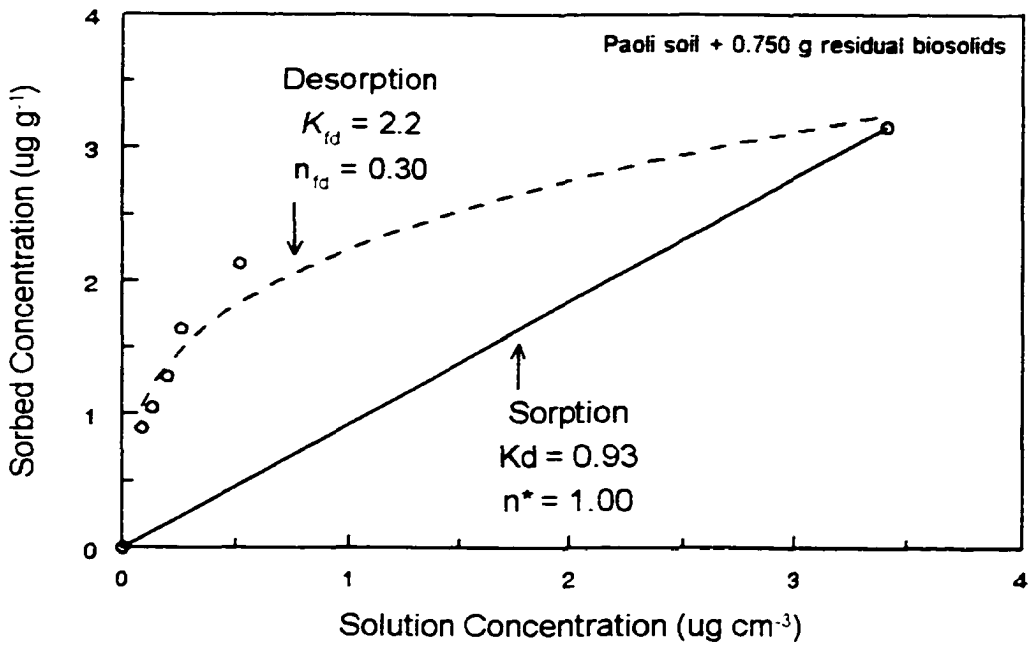


Fig. 4.40. **Hysteretic characteristics of metribuzin sorption and desorption for Paoli soil amended with 0.750 g of residual biosolids.**

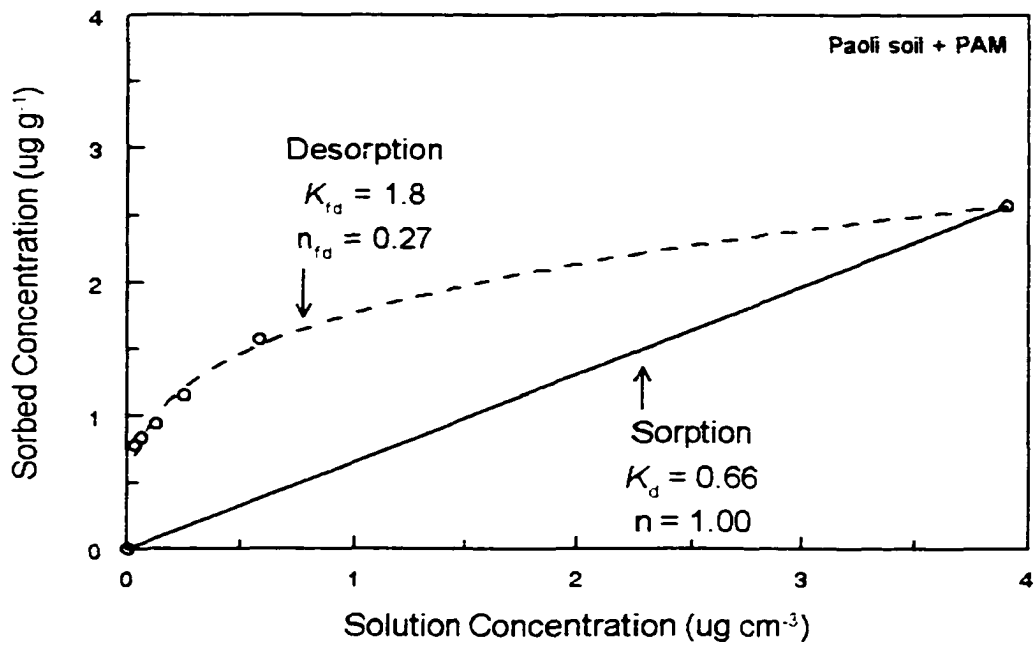


Fig. 4.41. **Hysteretic characteristics of metribuzin sorption-desorption for Paoli soil amended with polyacrylamide.**

Decreased hysteresis as a function of increases in organic matter content is in direct conflict with the findings of Peck et al. (1980). These workers reported that hysteresis became more pronounced as the organic matter content of the adsorbent increased. The differences in findings may be explained by considering the sorptive characteristics of organic matter. As discussed earlier, it was determined that sites that sorbed and released metribuzin in an instantaneous manner dominated the organic matter of biosolids. This domination resulted in an increase in the Freundlich empirical constant *n*, which is a description of the overall heterogeneity of sorptive sites. Consequently, the decrease in heterogeneity of sorptive sites decreased hysteresis.

The similarities in hysteresis within soil amendments were surprising because of the differences in the sorption and desorption *K* coefficients (Tables 4.1, 4.3, 4.4, and 4.6). Freundlich sorption and desorption coefficients are not independent from each other (Hornsby and Davidson, 1973; van Genuchten et al., 1974). The beginning point of desorption is a measured concentration point on the sorption isotherm. Hysteresis is influenced by the starting sorbed concentration point of desorption (van Genuchten et al., 1974). The starting sorbed concentration points of desorption (C_s) along with the soil's propensity for sorption and desorption (*K*) should be included in algorithms quantifying hysteresis.

In order to test this lack of difference in quantification of hysteresis (*H*) with these soils and amendments, I expanded the definition of hysteresis to include the differences in area between desorption isotherms and their corresponding

sorption isotherms. Therefore, I quantified hysteresis based on the difference in *n* coefficients for sorption and desorption, along with propensity for sorption and desorption, and the common sorption-desorption starting point value.

To incorporate this expanded definition of hysteresis, a series of equations were developed which define defines the hysteresis parameter φ as,

$$\varphi = \left[\frac{IAd - IAs}{IAs} \right] x\ 100 \tag{19}$$

Where IA_d and IA_s are calculated from the integrated area under the desorption and sorption isotherms, respectively.

$$IA_d = \int_0^C K_f^d\, C^{nfd}\, dc \tag{20}$$

$$IA_s = \int_0^C k_f^s\, C^{nf}\, dc \tag{21}$$

Substitution of the respective integrals into eq. X and rearranging yields a generalized hysteresis expression:

$$\varphi = \left[\frac{(K_{fd})(n_f+1)}{(K_f)(n_{fd}+1)}\, C^{n_{fd}-n_f} - 1 \right] x\ 100 \tag{22}$$

where K_f, K_{fd}, n_f, and n_{fd} are the corresponding Freundlich parameters for sorption and desorption, respectively, and C is the assumed starting equilibrium solution concentration.

Normalizing eq.(19) to the area under the adsorption isotherm and applying this expression to the same data set as for quantification by H, revealed a difference in magnitude of hysteresis within soil amendments. This more robust approach to hysteresis may be useful in modeling transport of pesticides by better predicting breakthrough curves in column leaching studies.

Artifacts of Hysteresis

Rao and Davidson (1980) have identified three postulated sources or artifacts of hysteresis effects:

(i) artifacts created by the particular methodology; (ii) failure to establish complete equilibrium during the adsorption period; and (iii) chemical and/or microbial transformations of the sorbate during the experiment.

In this study it was assumed that microbial transformations were not a factor in hysteresis as a microbial inhibitor ($HgCl_2$) was present. Additionally, abiotic degradation was not expected as the half-life for metribuzin was reported to be 90 days (Spectrum Laboratories, 1999).

Likewise, the failure to establish complete equilibrium during sorption did not appear to be a factor in the hysteresis for the Paoli soil unamended and both biosolids amendments and for the San Arcacio soil unamended and the 0.750 g biosolids amendment. Each sorption isotherm appeared to be linear ($n \approx 1$),

would result from sorption equilibrium. While non-linearity was exhibited by San Arcacio soil with and without 0.225 g biosolids, their n_f coefficients (0.877 and 0.920, respectively) were not appreciably different from unity. It should be noted that Bowman and Sans (1985) see the failure to establish complete equilibrium during sorption is only a problem when predicting desorption based on sorption isotherms.

Hysteresis from artifacts created by repeated centrifugation after each desorption cycle has received attention. Rao et al. (1980) found a correlation of hysteresis with centrifugation and re-suspension. Bowman and Sans (1984) and Selim and Xue (1995) applied a dilution method during desorption and reported considerably less hysteresis that with the centrifugation method. However, Horzempa and DiToro (1983) using a variation of the dilution method, reported that centrifugation did not appear responsible for hysteretic effects.

As a side note to evaluating hysteresis, one should bear in mind that batch isotherms only represent an approximation to hysteresis. Therefore, caution should be exercised when modeling hysteresis from other than column leaching and field studies.

Multiple Reaction Modeling of Sorption-Desorption Domains

To further describe the sorptive compartments of organic matter from biosolids, desorption results were evaluated using the multi-reaction models of Selim and Xue (1995). These models evaluate the multiple interactions of one chemical species in the soil environment. The models are empirical in nature

and assumes that a fraction of the total sites reacts instantaneously with the solute, whereas the remaining fraction of sites reacts slowly with solute in the soil solution (Selim et al., 1976, Jardine et al., 1985b). The models assume nonlinear equilibrium (Freundlich) and first-order kinetics and accounts for reversible as well as irreversible type reactions as described below:

$$S_e = K_f C^n \tag{23}$$

$$\frac{\partial S_1}{\partial t} = K_1 \frac{\theta}{\rho} C^n - K_2 S_1 - K_3 S_1 \tag{24}$$

$$\frac{\partial S_2}{\partial t} = K_3 S_1 \tag{25}$$

$$\frac{\partial S_{irr}}{\partial t} = K_{irr} \frac{\theta}{\rho} C \tag{26}$$

where C is solute concentration in soil solution (μg cm^{-3}), p is soil bulk density (g cm^{-3}), θ is soil water content (cm^3 cm^{-3}) and t is reaction time (h). The parameter K_f is the Freundlich distribution coefficient (cm g^{-1}) and K_1, K_2, K_3, and K_{irr} are associated reaction rate coefficients (μg h^{-1}). The term S_e is the amount retained (reversibly) by equilibrium type-sites (μg g^{-1} soil), S_1 is the amount retained reversibly by kinetic sites (μg g^{-1} soil), and n and m are empirical parameters (dimensionless). In addition, S_2 is the amount irreversibly transferred from S_1, and S_{irr} represents the amount associated with irreversible sites (μg g^{-1} soil).

The schematic diagram of the multi-reaction model (Fig. 4.42) represents the four model variation reactions for which metribuzin retention mechanisms were modeled. In this model, solute is considered to be present in the soil solution phase (C) and in four phases representing solute retained by the soil matrix as S_e, S_1, S_2, and S_{irr}. The models further assume that S_e, S_1, and S_2 and are in direct contact with the solution phase and that concurrent type reactions are occurring.

Each model variation was tested using a single data set. The Freundlich empirical values of K_f, K_{fd} n_f, *and* n_{fd} were used as inputs to the model. The root square mean (rms) and r^2 statistics were used for estimating goodness-of-fit of each model variation. The results are listed in Table 4.10 for Paoli soil and Table 4.11 for San Arcacio soil for an initial metribuzin solution concentration (C_0) of 5 μg cm^{-3}. Observed and fitted data points for the best goodness-of-fit model variations are shown in Fig. 4.43 to 4.48.

The time-dependent desorption was well described by the model indicating initial fast desorption (equilibrium) followed by slow desorption for which kinetic reactions dominate. As indicated from calculated rate coefficients for the Paoli soil, Model Variation 3 with the concurrent reversible reaction (K_f, K_1, and K_2) and the consecutive irreversible reaction K_{irr} provided the lowest rms and highest r^2.

When Paoli soil was amended with increasing amounts of biosolids, the K_{irr} rate coefficients were significantly decreased when compared to the rate coefficients of K_1 and K_2. For the highest addition of biosolids (0.750 g), Model

Variation 2 gave the best fit where irreversible sorption sites (S_{irr}) are not a compartmental factor. The S_{irr} compartment may be rate limited by concentration, restricted sites (Locke, 1992), and time.

Model Variation 4 with the consecutive irreversible reaction compartment S_2 had a decreasing rate coefficient (K_3) with increasing biosolids amendment. This compartment is where irreversible transformation and degradation is accounted for (Selim and Xue,1995). Transformation is defined as pesticide incorporation into humus. As these experiments were conducted over a relatively short period of time (144 h), transformation of metribuzin was expected to be minimal. Biotic degradation processes should have been minimal due to the presence of a microbial inhibitor ($HgCl_2$). Additional desorption time experiments are required to test the time-dependence theory for irreversible sorption (S_{irr} and K_{irr}) and transformation (S_2 and K_3).

The San Arcacio desorption data overall were better fitted to Model Variation 1 for which reactions are instantaneous (K_f) and have irreversible sorption sites (S_{irr} and K_{irr}). The irreversible compartment (S_{irr}) for the amended soil showed a rate coefficient of less than 0.00001 h^{-1} and thus was deemed non-existent. The unamended soil results fit slightly better to Model Variation 2. Here reversible sorption sites (K_1 and K_2) are present. Upon biosolids amendment, these sorption sites became undetectable.

Table 4. 10. Comparison of goodness of fit of variations of the multi-reaction model for describing metribuzin sorption desorption kinetics for Paoli soil and amendments.

Model variation	r^2	rms	K_f	K_{irr}	K_1	K_2	K_3
			$cm^3\ g^{-1}$	$\mu g\ h^{-1}$			
			Paoli unamended				
1	0.9999	0.0163	0.2426 ± (0.0128)	0.0028 ± (0.0002)	-	-	-
2	0.9999	0.0141	0.2382 ± (0.0145)	-	0.0044 ± (0.0008)	0.0041 ± (0.0025)	-
3	0.9999	0.0068	0.2231 ± (0.0188)	0.0023 ± (0.0006)	0.0022 ± (0.0011)	0.0262 ± (0.0313)	-
4	0.9999	0.0146	0.2334 ± (0.0333)	-	0.0026 ± (0.0017)	0.0132 ± (0.0481)	0.0022± (0.0023)
			Paoli with 0.225 g biosolids				
1	0.9997	0.0277	0.3188 ± (0.0230)	0.0017 ± (0.0006)	-	-	-
2	0.9999	0.0130	0.2923 ± (0.0185)	-	0.0038 ± (0.0010)	0.0107 ± (0.0050)	-
3	0.9999	0.0082	0.2660 ± (0.0395)	0.0010 ± (0.0004)	0.0050 ± (0.0037)	0.0349 ± (0.0292)	-
4	0.9999	0.0104	0.2725 ± (0.0443)	-	0.0046 ± (0.0040)	0.0295 ± (0.0313)	0.0011 ± (0.0006)
			Paoli with 0.750 g biosolid				
1	0.9999	0.0114	0.4734 ± (0.0093)	0.0054 ± (0.0003)	-	-	-
2	0.9999	0.0101	0.4524 ± (0.0140)	-	0.0045 ± (0.0004)	0.0003 ± (0.8357)	-
3	0.9996	0.0613	0.4551 ± (0.1541)	0.0068 ± (0.3259)	0.0001 ± (0.2412)	0.0052 ± (14.04)	-
4	0.9931	0.2396	0.4642 ± (0.3798)	-	0.0010 ± (0.9470)	0.0003 ± (0.1628)	0.0001 ± (0.9276)

Table 4. 11. Comparison of goodness of fit of variations of the multi-reaction model for describing metribuzin sorption desorption kinetics for San Arcacio soil and amendments.

Model variation	r^2	rms	K_f	K_{irr}	K_1	K_2	K_3
			$cm^3\ g^{-1}$		$\mu g\ h^{-1}$		
			San Arcacio unamended				
1	0.9997	0.0252	0.1482 ± (0.0189)	0.0024 ± (0.0005)	-	-	-
2	0.9999	0.0151	0.0025 ± (0.2624)	-	0.0054 ± (0.4548)	0.0780 ± (3.611)	-
3	0.9979	0.1004	0.0005 ± (5.708)	0.0040 ± (0.0081)	0.2306 ± (0.7781)	0.1229 ± (1.270)	-
4	0.9766	0.2806	0.0048 ± (1.363)	-	0.0200 ± (0.0865)	0.4567 ± (1.652)	0.0000± (0.0104)
			San Arcacio with 0.225 g biosolids				
1	0.9991	0.0495	0.2339 ± (0.0332)	0.0000 ± (0.0059)	-	-	-
2	0.9481	0.4018	0.0214 ± (5.228)	-	0.0017 ± (0.4401)	0.0766 ± (10.01)	-
3	0.9993	0.0504	0.2504 ± (0.1183)	0.0000 ± (0.0172)	0.0003 ± (0.1687)	0.0030 ± (0.0722)	-
4	0.9295	0.5056	0.2547 ± (0.9224)	-	0.0016 ± (2.080)	0.0004 ± (0.2366)	0.0001 ± (2.063)
			San Arcacio with 0.750 g biosolid				
1	0.9993	0.0405	0.4257 ± (0.0373)	0.0004 ± (0.0405)	-	-	-
2	0.9193	0.4502	0.0196 ± (4.259)	-	0.0061 ± (0.3068)	0.0623 ± (2.043)	-
3	0.9984	0.0683	0.4466 ± (0.0686)	0.0000 ± (0.1348)	0.0003 ± (0.1253)	0.0000 ± (0.0600)	-
4	0.9305	0.4519	0.1428 ± (0.4519)	-	0.0010 ± (0.0892)	0.0272 ± (2.980)	0.0000 ± (0.0478)

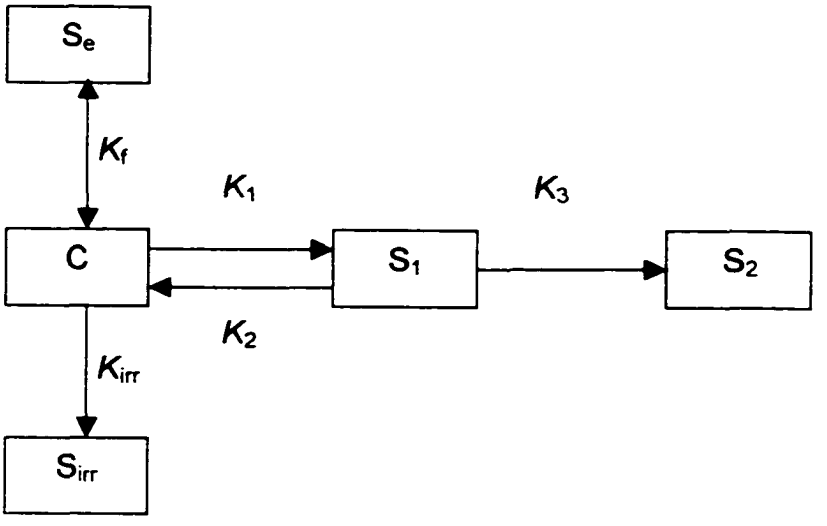


Fig. 4.42. Schematic diagram of nonlinear multi-reaction kinetic model.

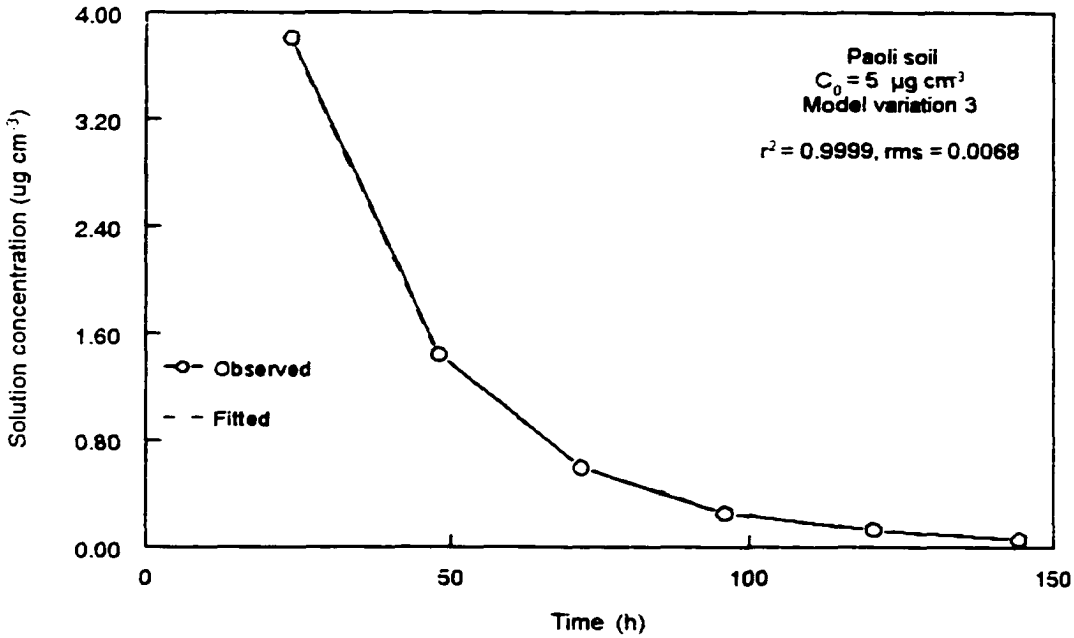


Fig. 4.43. Changes in metribuzin concentrations with time during desorption for Paoli soil. Solid and dashed curves are observed and fitted results, respectively, for Model Variation 3 of the nonlinear multi-reaction model.

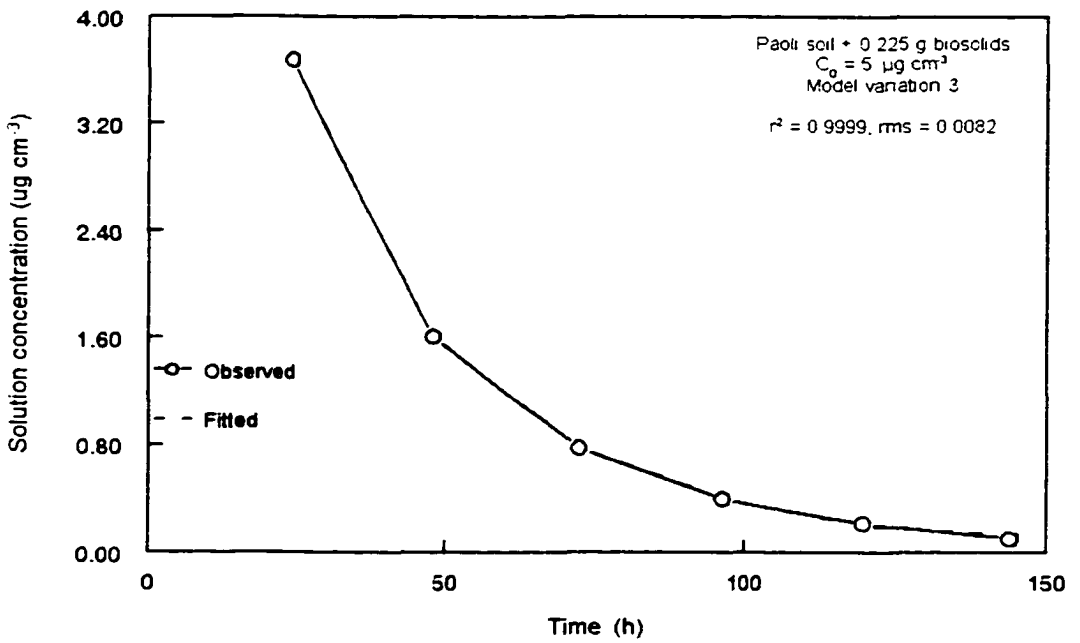


Fig. 4.44. Changes in metribuzin concentration with time during desorption for Paoli soil amended with 0.225 g biosolids. Solid and dashed curves are observed and fitted results, respectively, for Model Variation 3 of the nonlinear multi-reaction model.

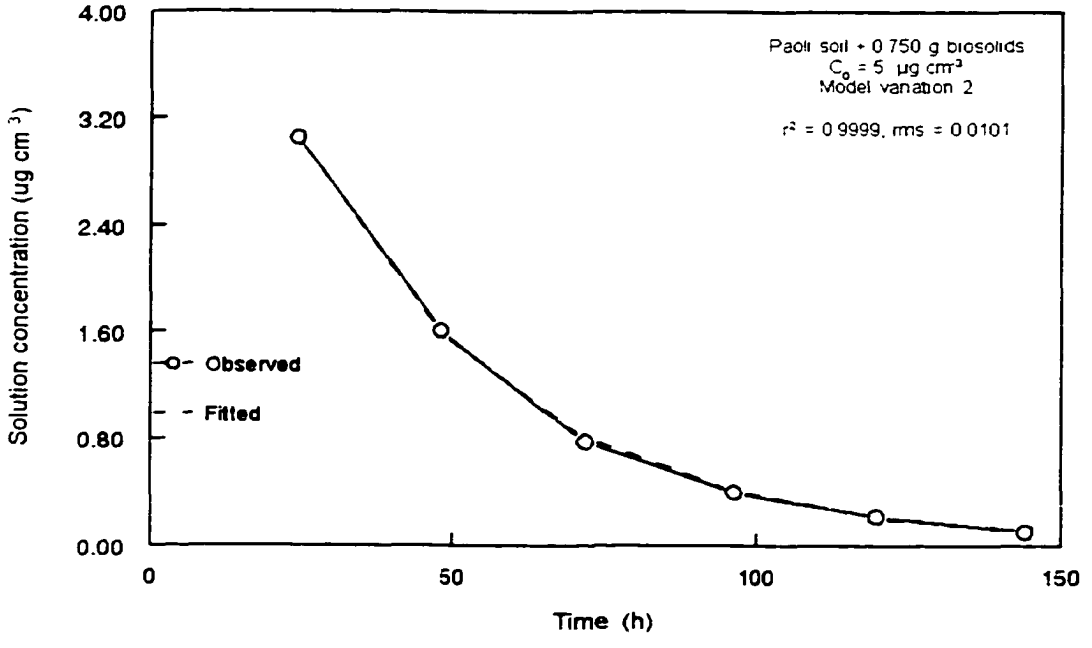


Fig. 4.45. Changes in metribuzin concentration with time during desorption for Paoli soil amended with 0.750 g biosolids. Solid and dashed curves are observed and fitted results, respectively, for Model Variation 1 of the nonlinear multi-reaction model.

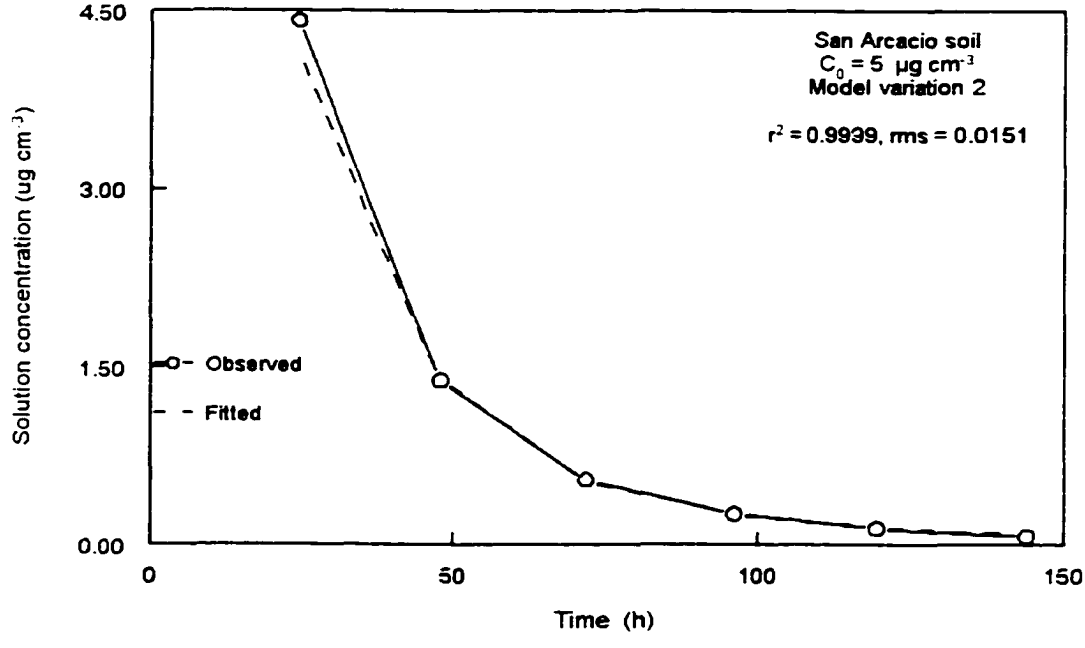


Fig. 4.46. Changes in metribuzin concentration with time during desorption for San Arcacio soil Solid and dashed curves are observed and fitted results, respectively, for Model Variation 2 of the nonlinear multi-reaction model.

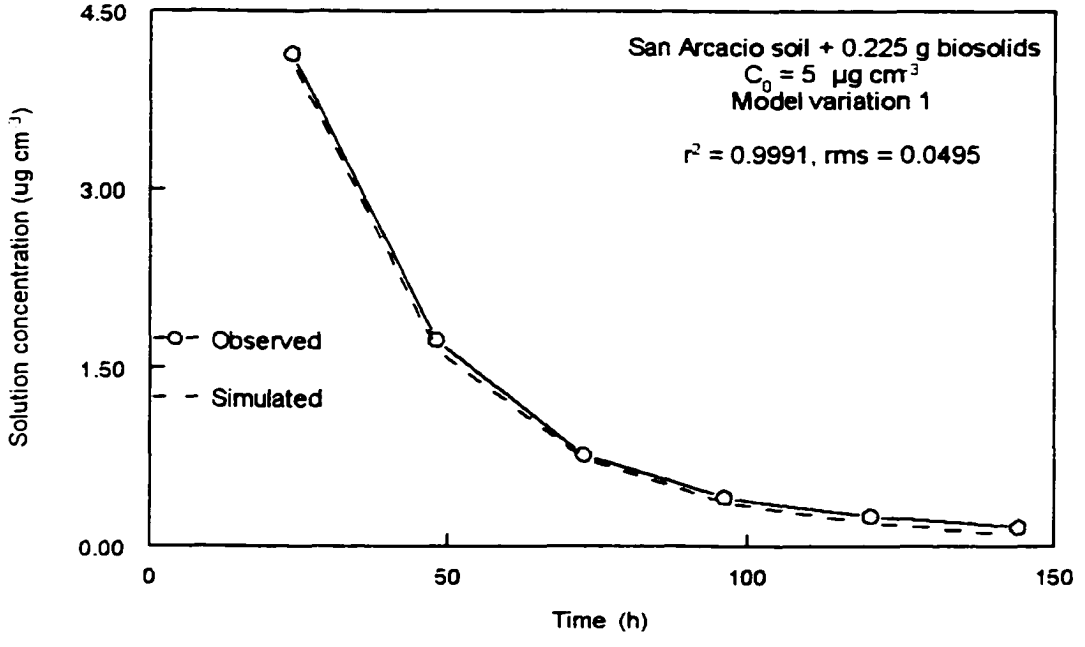


Fig. 4.47. Changes in metribuzin concentration with. time during desorption for San Arcacio soil amended with 0.225 g biosolids. Solid and dashed curves are observed and fitted results, respectively, for Model Variation 1 of the nonlinear multi-reaction model.

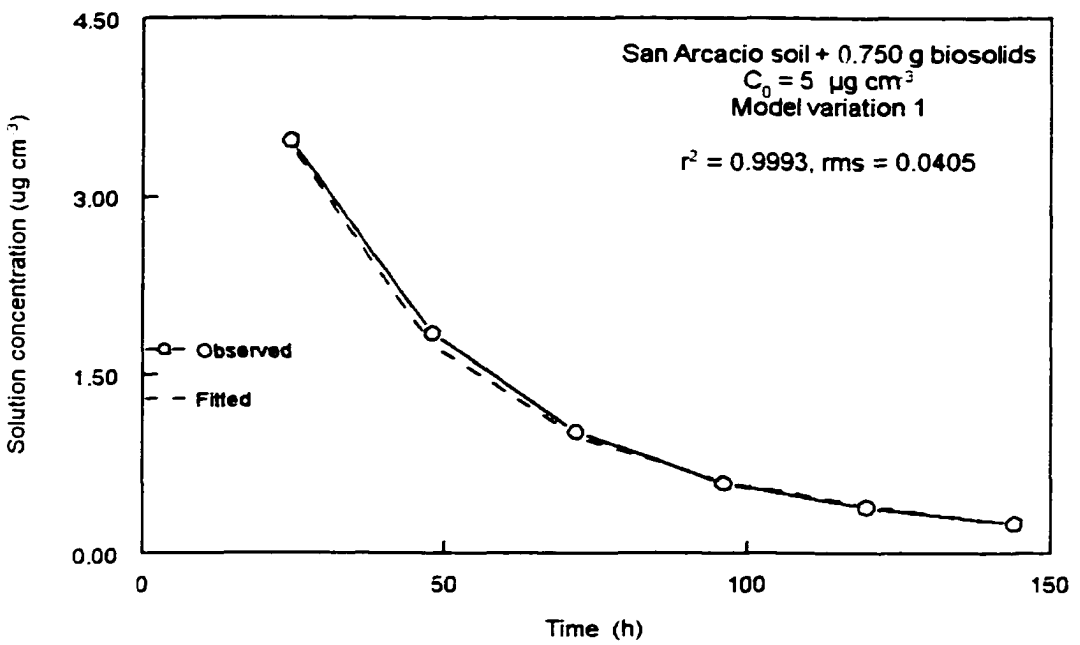


Fig. 4.48. Changes in metribuzin concentration with. time during desorption for San Arcacio soil amended with 0.750 g biosolids. Solid and dashed curves are observed and fitted results, respectively, for Model Variation 1 of the nonlinear multi-reaction model.

CHAPTER 5

GENERAL DISCUSSION AND CONCLUSIONS

Metribuzin Sorption

The shape of the sorption isotherm characteristics for metribuzin was related to the type of organic matter present in the soil and biosolids. Sorption of metribuzin increased as did sorption linearity with increasing biosolids amendments. The dual-mode glassy/rubbery model for soil organic matter could be used to explained the increase in linearity. If a rubbery domain dominated the biosolids organic matter, this would decrease the overall heterogeneity of sorptive sites. Non-linear sorption isotherms characteristic of a glassy domain are time-dependent. These factors indicate that in addition to the quantity of organic matter present in soil, characteristics of the organic matter (i.e. rubbery and glassy domains) and their sorptive rates (instantaneous or slow sorption) are important factors in determining the degree of association between soil and metribuzin.

Metribuzin Desorption

Desorption isotherm characteristics for metribuzin can be explained using the glassy/ rubbery model. An initial linear, fast-release compartment

characteristic of a rubbery domain, followed by an exponential slow-release compartment characteristic of a glassy domain describes the isotherms.

Overall, the Freundlich model better described the shape of the desorption isotherms. The goodness-of-fit for the two-compartment model increased with increased biosolids treatment. Thus, application of the two-compartment model may be suited for soils of higher organic matter content.

Increased rates of metribuzin desorption and total percentage desorption for Paoli soil unamended and amended and the amended San Arcacio soil are consistent with desorption being controlled by a linear, fast-release compartment, as expected with the glassy/rubbery model.

Two-compartment Model Summary

Characterization of desorption isotherms with the Barriuso et al. (1992) two-compartment model provided a means for interpretation of metribuzin retention phenomena. The model distinguished two sorption compartments that were consistent with the predictions of the glassy/rubbery model of Pignatello et al. (1996, 1997). The first compartment, having a linear fast release function, followed by second exponential compartment, which exhibited kinetic sorption sites and a strong retention of metribuzin. The changes in desorption characteristics of these two compartments were directly related to the quantity and description or organic matter from the biosolids amendments.

The second compartment was further identified with a sub-asymptotic compartment, which resisted change from organic matter amendments. The size

characteristics of this compartment were finite and considered to be an intrinsic property of soil.

Sorption-Desoprtion Hysteresis

Hysteresis decreased as a function of increases in biosolids-organic matter amendments and was in contrast to the reports of Peck et al. (1980). The apparent conflict could be explained by characteristics of the biosolids organic matter. The biosolids amendments increased the number of rubbery, instantaneous sorption-desorption sites.

The hysteresis model of O'Connor et al. (1980) was inadequate in quantifying differences in hysteresis associated with soil amendments. Therefore, a model was developed to include differences in sorptive site heterogeneity coefficients for sorption and desorption, along with propensity for sorption and desorption, and a common sorption-desorption concentration starting point value. This more robust model was capable of delineating differences in biosolids amendment hysteresis.

Desorption Kinetics

The multi-reaction kinetic models described desorption as two-compartmental. Desorption from the first compartment was linear and instantaneous as expected by a rubbery domain of organic matter; release from the second compartment was exponential and slow, characteristic of a glassy domain. The model further described the slow release compartment as

dominated by reversible kinetic reactions with minimal irreversible sorption and transformation of metribuzin.

Chemical Movement in Soils Receiving Biosolids Amendments

This study shows that amending soil with organic material containing sorptive sites dominated by a linear domain may in fact enhance chemical transport of metribuzin to groundwater. These results support the theory that the characteristics of organic matter (e.g. stationary and dissolved state, and instantaneous and slow sorptive behavior) are responsible for not only the sorptive capacity of the soil but also how and when a soil will release its sorbate. That is, sorption, desorption, and hysteresis are a function of the quantity and sorptive characteristics of organic matter.

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