To the Graduate Council:

I am submitting herewith a thesis written by Jennifer S. Dore entitled "The Influence of Tillage and Dissolved Organic Carbon on the Soil Sorption and Desorption of Fluometuron and Norflurazon". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

Michael E. Essington, Major Professor

We have read this thesis
and recommend its acceptance:

Thomas C. Mueller

Accepted for the council:

Associate Vice Chancellor and
Dean of the Graduate School

The Influence of Tillage Practice and Dissolved Organic Carbon on the Soil Sorption and Desorption of Fluometuron and Norflurazon

A Thesis
Presented for the
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Jennifer S. Dore
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DEDICATION

This thesis, and the work there in, is dedicated to the late Mrs. Jeanette Schaal and Mr. Sheldon Dore. Though they did not see the final thesis, their love and confidence is constant support and inspiration throughout all my endeavors.

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An eternal debt of gratitude is owed to my parents, Michael and Judith Dore. Their support and encouragement continues to bring hope and perspective to my life. I shall *mostly* keep my head down, aim left, leave two inches of juice in the container, and never put my papers in a tree. As a thank-you to Mr. Frederick W. Schaal for his words of wisdom, I plan to H.A.L.F.! As a tribute to Mrs. Gladys Dore, I shall paint my lips and fingernails carnation pink. For Al, I'll spare the alum - but never forget you are my L.B.!

I owe Mr. David Suba 30 months of peace without spasms (*fat chance*) Your patience and attentiveness is greatly appreciated. Thus, I shall keep the mud from being too wet, find the little big hammer, and give you a footschul.

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ABSTRACT

Fluometuron (FLMT) and norflurazon (NORF) are preemergence herbicides applied to cotton in the southeastern U.S. Residual levels of both herbicides have been detected in soils long after application, potentially posing risks to subsequent crops and groundwater resources. Herbicide sorption is an important mechanism influencing their fate and behavior. Sorption by soil organic matter (SOM), which is influenced by tillage practice, is the dominant mechanism by which herbicides are removed from the aqueous phase. Dissolved organic carbon (DOC) concentrations greater than 100 mg L^{-1} have been shown to reduce the sorption of some trace organic compounds in soil systems.

The objectives of this study were to 1) determine the effect of tillage, (SOM content) on the sorption and desorption of FLMT and NORF, 2) determine the effect of DOC source (poultry litter, dairy manure, and no-till (NT) surface soil) and concentration on the sorption of FLMT and NORF, and 3) examine the effect of NT DOC on subsoil sorption of FLMT and NORF.

Sorption of FLMT and NORF to NT and conventional tillage (CT) managed surface soil and subsoil [Lexington silty loam (fine-silty, mixed, thermic, Typic Paleudalf)] was characterized using batch sorption isotherms. Herbicide sorption experiments were conducted in the presence and absence of DOC extracted from poultry litter, dairy manure and NT surface soil. Desorption of FLMT and NORF was analyzed in the absence of DOC, with DOC in the desorption solution only, and with DOC in both the sorption and desorpiton systems. Dissolved organic carbon was extracted from poultry litter, dairy manure, and NT surface soil. The DOC extracts were analyzed for

organic carbon content. The E_4/E_6 ratio and gel permeation chromatography were employed to characterize the DOC extracts.

The increased SOM content of NT soil enhanced the sorption of FLMT and NORF. The retention of FLMT and NORF by Lexington silt loam soil decreases in the following order: NT > CT > subsoil. Herbicide sorption conformed to the L-curve and C-curve isotherms, with the C-curve being more representative of sorption by the high-organic carbon, NT surface soil. Sorption of FLMT and NORF was generally reduced with DOC in the sorption equilibration solution, regardless of source or concentration. The greatest reduction in FLMT and NORF sorption occurred in the presence of poultry DOC. Dairy DOC ranked second in decreasing the amount of herbicide sorbed, followed by NT DOC. Spectroscopic E_4/E_6 ratios of the DOC molecules indicate that the poultry, dairy, and NT DOC extracts are composed of predominately low molecular weight compounds. According to gel chromatography, poultry DOC had the greatest distribution of large DOC molecules, while dairy DOC had a significant distribution of both smaller and larger molecules. No-till DOC was composed of a single size distribution of molecules, close in size to FLMT and NORF. The spectroscopic characterization of the DOC molecules coupled with the sorption results suggests that the large DOC molecules were responsible for the reduced sorption of the herbicides.

The concentration of DOC in the sorption systems also influenced the sorption of FLMT and NORF. In general, sorption decreased with increasing DOC concentration. Recent literature suggests that DOC concentrations below 100 mg DOC L^{-1} do not effect

the sorption of the herbicides. However, this study shows that DOC concentrations as low as 75 and to a lesser extent, 37.5 mg L^{-1}, result in reduced herbicide sorption.

The aqueous association of herbicide with DOC can be quantified by the K_{DOC}. Solid SOM is known to be at least twice as effective a sorbent for herbicides compared to soluble DOC. Therefore, SOM should exert a much greater influence on the sorption of FLMT and NORF. The organic carbon normalized distribution coefficients (K_{OC} values) indicate the contribution of SOM to organic compound sorption. Computed K_{DOC} values greatly exceeded the K_{OC} values calculated in this study. Thus, DOC complexation of the herbicides in solution is improbable in these systems. Reduced herbicide retention in the presence of DOC may result from competition between the herbicide and DOC molecules for limited sorption sites is at work in these systems. Conversely, DOC may coat the soil surfaces and present a hydrophobic surface that forces the herbicides to remain in aqueous solution.

Desorption of FLMT and NORF was hysteretic in all soils. Hysteresis was greater with NORF, compared to FLMT. No effect of SOM content on desorption hystersis was evident. Desorption of FLMT and NORF from soil was enhanced with the addition of DOC to the soil systems. Poultry DOC enhanced desorption the greatest followed by dairy and NT DOC, respectively. The addition of DOC at the desorption step appeared to reverse herbicide sorption when compared with the no-DOC isotherm. However, the addition of DOC at the desorption step changed the chemistry of the system. Thus, desorption should revert to a DOC sorption isotherm. Some poultry DOC isotherms showed reversible herbicide sorption. However, in general, desorption was

incomplete with DOC in the desorption solution only. In systems with DOC concentrations greater than 20 mg L^{-1}, desorption reversibility was approached with equilibration time. However, in systems with 10 mg DOC L^{-1}, desorption became more hysteretic with equilibration time. Thus, a threshold concentration of DOC (regardless of source) exists between 20 and 10 mg DOC L^{-1}, influencing the sorption and desorption of the herbicides.

Desorption of FLMT and NORF sorbed in the presence of DOC, occurred at a much faster rate than in the systems where DOC was absent during sorption. Poultry DOC promoted the greatest decrease in sorption and the greatest desorption, followed by dairy and NT DOC. The desorption of FLMT and NORF from SUB soil with 1150 mg poultry DOC L^{-1} in the desorption solution resulted in less herbicide sorption than at the onset of the desorption process, with only 920 mg poultry DOC L^{-1} in the sorption system. Perhaps, the desorption of herbicides in the presence of 1150 mg poultry DOC L^{-1} followed an sorption isotherm consistent with the presence of 1150 mg poultry DOC L^{-1} in the sorption solution. Dairy DOC facilitated the desorption of FLMT and NORF adsorbed in the presence of lesser concentrations of dairy DOC. Similarly, NT DOC resulted in less sorption of FLMT and NORF, and greater desorption of the herbicides.

The greater SOM content of no-till systems results in greater sorption of FLMT and NORF. The addition of DOC to the systems results in reduced sorption of the herbicides. Desorption of FLMT and NORF exhibits hysteresis without added DOC. However, DOC concentrations greater than 10 mg L^{-1} enhance the desorption of FLMT and NORF from soil.

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CHAPTER I

INTRODUCTION

Fluometuron (FLMT) and norflurazon (NORF) are preemergence herbicides applied to cotton in the southeastern U.S. Residual levels of both herbicides have been detected in soils long after application, potentially posing risks to subsequent crops and groundwater resources. Both batch sorption and field studies have shown that soil organic matter (SOM) is positively correlated with the soil retention of these two herbicides. Tillage methods greatly impact soil properties, including SOM content and distribution. No-till (NT) methods conserve surface mulch and native vegetative cover with minimal disturbance of soil structure during planting. Conventional tillage (CT) methods destroy soil structure and incorporate surface mulch into the plow zone. Surface NT soils typically have greater SOM content and greater macroporosity, while CT soils have less SOM and little macroporosity. These two tillage management methods present different soil matrices that may effect the sorption and movement of herbicides.

Sorption of trace organic compounds (such as herbicides) in the soil environment is an important mechanism influencing their fate and behavior. The partitioning of trace organic compounds into SOM is commonly cited as the dominant mechanism by which trace organics are removed from the aqueous phase. Clay minerals are thought to have a limited sorptive capacity for trace organics in soils. Linear sorption isotherms and non-competitive sorption support the partition mechanism for trace organic retention. However, non-linear isotherms are frequently encountered in sorption studies with nonionic organic compounds.

Dissolved organic carbon (DOC) in the soil solution may alter the fate and transport of trace organic compounds. Water solubility enhancement of many nonionic pesticides has been noted in the presence of dissolved humic and fulvic acids. The aggregate-enhancing properties of DOC may coat soil surfaces and alter the sorption capacity of the soil matrix. Competition for soil sorption sites between trace organic compounds and DOC may also effect sorption. Characterization of the relative size and functionality of DOC may elucidate the interactive mechanisms between dissolved trace organic compounds and DOC.

Desorption hysteresis is a commonly observed characteristic of trace organic compound sorption studies. Hysteresis may be an artifact of scientific methodology or a real phenomenon in compound sorption by soils. The biphasic nature of sorption, especially in soils with significant concentrations of SOM, may influence the fate and behavior of trace organic compounds. Slow sorption of pesticides months after application may be due to the slow diffusion of solutes into organic and soil ped matrices. Moreover, the slowly sorbed fraction of pesticides creates a desorption resistant fraction in the soil. Therefore, it is important to examine the kinetics of desorption when considering the fate and transport of trace organic compounds in soil.

Residual levels of FLMT and NORF have been detected in soils months after application, especially in soils with high SOM content like NT managed soils. Due to the potential for subsequent crop damage, and the potential for the contamination of surface and groundwater, it is important to evaluate the sorption and desorption behavior of these herbicides. The objectives of this study were to determine the effect of tillage (SOM

content) on the sorption and desorption of FLMT and NORF. This was accomplished by evaluating herbicide sorption by CT and NT surface soil and CT subsoil in the presence of absence of DOC extracted from poultry litter and dairy manure biosolids. The influence of DOC from NT surface soil on the sorption of FLMT and NORF by subsoil was also examined. Desorption kinetics of both herbicides were examined as a function of DOC source and concentration.

CHAPTER II

LITERATURE REVIEW

Effect of Tillage on Herbicide Fate and Behavior

Tillage practices employed in agricultural cropping systems influence the porosity, structure, organic matter content, and moisture holding capacity of the soil. These physical and chemical characteristics of the soil environment affect the fate and behavior of herbicides and other trace organic compounds.

Conventional tillage practices disrupt native soil structure in the surface 15 to 20 cm of soil (Sopher and Baird, 1982; Isensee et al., 1990). Tillage breaks up soil aggregates, destroys macroporocity, and incorporates organic matter into the plow zone. This disturbance of the soil structure forces soil water and inorganic and organic solutes to move through micropores, promoting greater attenuation of solutes due to increased pore surface area (Luxmoore et al., 1990).

The use of conservation tillage in agriculture has increased over thirty-fold since introduction in the early 1960's (Thorton, 1987; Isenesee et al., 1990). Conservation tillage methods like no-till (NT), utilize native or indigenous vegetative cover to reduce soil erosion and surface water runoff (Felsot et al., 1990). No-till utilizes the native plant population to provide valuable N, P, K, and micronutrients and structural stability to the soil (Bauer and Black, 1994; Lal et al., 1994). Moreover, the surface mulch of dead and decaying vegetation serves as a water conserving mulch, reducing evaporation losses (Unger and McCalla, 1980). No-till management practices leave about 90% of the soil surface untouched as specialized planters cut a slot, insert seed and fertilizer, and then

close over the slot (Plaster, 1992). Increased water infiltration due to enhanced plant root activity and minimal soil disturbance during planting results in the formation of macropores (cracks between aggregates and biological pores) (Thomas et al., 1973; Quisenberry and Phillips, 1976; Hillel, 1982; Edwards et al., 1988; Adreini and Steenius, 1990), which could enhance the mobility of applied pesticides through the soil profile (Tyler and Thomas, 1977 and 1981; Thomas and Phillips, 1979; Jardine et al 1990; Essington et al., 1995).

Research on NT agricultural systems has shown NT management to impart measurable changes in soil physical, chemical, and biologic properties. The beneficial aspects of erosion control and water conservation are offset by the stratification of SOM and nutrients. With NT, the ability to incorporate fertilizers into the root zone is negated. Further, nutrients removed from subsoil by root uptake are ultimately recycled as surface mulch, leading to an acidification of the root zone and the depletion of subsoil nutrients (Dick, 1983). Higher bulk density and lower porosity have also resulted from the mechanical compaction of NT systems (Gantzer and Blake, 1987). Other researchers, however, have reported enhanced porosity and lower bulk density in soils under NT management (Cullet et al., 1987 a and b). Still others have found no effect of NT management on soil porosity and bulk density (Shear and Moschler, 1969; Blevins et al., 1977). Overall, the physical compaction of soils under NT management is a function of individual soil and mechanical properties (Lal et al., 1994).

The maintenance of continual vegetative cover and minimal disturbance of NT management increases the SOM content at the soil surface (Steerman, 1987; Blevins et

al., 1977; Tyler et al., 1983; Phillips and Phillips, 1984; Isensee et al., 1990). Lal et al. (1994) found that NT management increased the SOM content of the surface 0-to-15 cm depth increment about 5% over chisel plow tillage. Isensee et al. (1990) found that soil under conventional tillage corn had about 0.3% less organic carbon in the top 0-to-10 cm increment, compared with NT. The amount of organic carbon (OC) in the surface horizon of NT versus chisel plow managed soils varies with crop and amount of plant residue returned to the soil. No-till soils consistently have higher SOM content in the surface 0-to-15 cm increment than conventional chisel plow managed soils.

Carringer et al. (1975) stated that SOM content is the most important soil property influencing the sorption of acidic, basic, and nonionic organic pesticides. Since then, several researchers have concluded that the retention of organic compounds in soil is highly correlated to the SOM content (Wood et al., 1987; Chiou, 1989; Koskinen and Harper, 1990; Green and Karickoff, 1990). Bouchard and Lavy (1985) found that the variability in the distribution coefficient (K_D) for hexazinone on three horizons of a forest sandy loam was removed by normalizing for the OC content of the soil. Weber et al. (1983) postulate that nonionic solutes will be associated with and tend to accumulate in soil horizons with the highest OC content. These authors found widely varying K_D values for a variety of nonionic organics when adsorbed by materials with little or no OC. Most researchers have concluded that OC is the primary sorbent in systems with significant SOM concentrations. Further, it has been postulsted that the contribution of mineral surfaces to nonionic organic sorption is insignificant (Banwart et al., 1982;

Murphy et al., 1990). Thus, because of the greater SOM content of no-till soils, herbicide mobility may be decreased under NT management compared to that under CT.

Many researchers have sought to quantify the relationship between SOM content and the retention nonionic organics. They concluded that no simple relationship exists between compound sorption and soil OC content. Garbarini and Lion (1986) cite the importance of particle size, surface area, and OC content of the sorbent as parameters that strongly influence organic compound sorption. The source and age of the OC influences the size, functionality, and reactivity of the organic molecules (Chiou et al.,1986; Chiou et al., 1987). Similarly, a difference between commercial and naturally occurring OC has been noted. Commercial humic substances have less carbohydrate and carboxyl-group content, and correspondingly lower hydrophilicity (Chiou et al., 1987). The same trend is noted with aged SOM. Older SOM tends to have larger molecules with less reactive functional groups such as carboxylic, alcoholic, and phenolic groups. (Stevenson, 1994).

The presence of DOC in the equilibrium solution of trace organic compound- soil sorption systems has been reported to enhance the water solubility of some organic chemicals (Chiou et al., 1986, 1987; Lee and Farmer, 1989; McCarthy and Zachara, 1989; Abdul et al., 1990; Chin et al., 1990; Lee et al., 1990). Liu and Amy (1993) concluded that natural DOC facilitated the transport of aromatic hydrocarbons, while solid phase OC retarded the transport of these compounds. Madhun et al. (1986) found that 240 mg L^{-1} of water soluble soil organic matter had a significant binding effect on many hydrophilic and hydrophobic organics. However, Spurlock and Biggar (1990) found no effect of up to 100 mg L^{-1} DOC on the sorption of simazine. Yet, Spurlock and

Biggar (1990) conclude, as have several researchers, that DOC (even at low concentrations) plays a significant role in the binding, solublization, and possible competitive sorption of pesticides in the environment. Lee and Farmer (1989) found a positive correlation between the hydrophobicity of nonionic pesticides and their associations with DOC. Pesticide associated with DOC is rendered less available to participate in sorption reactions, and is mobile in the soil environment (Jardine et al., 1989). Although there is no conclusive scientific evidence to support a specific mechanism of DOC interaction with nonionic organics, hydrogen bonds, van der Waals interactions, ligand exchange, electron-transfer, and free radical formation reactions have been proposed for different DOC-pesticide systems (Senesi and Testini, 1982).

Organic Compound Sorption

Although processes including volatilization, biodegradation, leaching, and plant uptake influence the fate and behavior of herbicides, sorption is the most important physiochemical process effecting the concentration and distribution of nonionic organic compounds in the soil environment (Morrill et al., 1982; O'Connor and Connolly, 1980; Morel and Gschwend, 1987; Kile et al., 1995). Sorption limits the bioavailibility of organic molecules (e.g. microbial breakdown and plant uptake) and minimizes volatilization and leaching from the soil profile (Scow, 1993).

Sorption, Adsorption, and Partitioning

Sorption is a general term describing the reversible association of chemicals with the solid phase and encompasses both adsorption and partitioning mechanisms (Scow, 1993). Organic and mineral matter in soil are known to lend distinct contributions to the sorption of nonionic organic compounds, where SOM functions as a partition medium and the mineral matter acts as an adsorbent (Kile et al., 1995). Sorption processes are driven by enthalpy reactions that bond the solute to the soil particle and entropy related forces that result from the lack of solvation of the solute in solution (Hassett and Banwart, 1989).

Adsorption is a net accumulation of matter at the interface between a solid phase and an aqueous solution phase (Sposito, 1989). Adsorption is also defined as a condensation of vapors or solutes on surfaces or pores of a solid by physical or chemical bonding forces (Chiou, 1989). Molecules that are adsorbed are present on the solid phase as a result of or a combination of van der Waals-London interactions, charge -transfer, ligand exchange, or ion-exchange reactions (Scow, 1993). Adsorption of multiple solutes is competitive, that is, solutes compete for available adsorption sites (Smith et.al., 1988). Adsorption of substituted ureas and other herbicide compounds to mineral surfaces and soils with low SOM content is inversely correlated with herbicide solubility (Bailey et.al, 1968). It has been proposed that adsorption of compounds to mineral surfaces represents an insignificant amount of the total soil uptake because of the strong dipole interaction between water and polar mineral surfaces. Moreover, the adsorption process only

becomes significant for polar solutes when the mineral adsorption sites of a soil are unsaturated with water (Smith et.al., 1988; Kile et.al., 1995).

Partitioning of a solute between the water and the soil organic phase is a mechanism separate from adsorption. Also termed hydrophobic sorption, partitioning is governed by the lack of solvation of the solute in the soil solution and results in a large entropy change from the partitioning of nonpolar organics out of the polar aqueous phase into hydrophobic components in the soil. Moreover, there is a homogeneous distribution of the solute throughout the entire volume of the hydrophobic sorbent (Hassett and Banwart, 1989; Chiou, 1989). Properties of the molecular compounds like polarity, composition, and molecular size determine the relative importance of the partition mechanism in the distribution of the molecule in the soil environment (Smith et al., 1988). The partition process does not exhibit competitive sorption of organic compounds.

The *n*-octanol-water system provides a simple means of quantifying the interaction of an organic solute with SOM. Adding a known concentration of an organic compound to an immiscible mixture of *n*-octonal and water results in the partitioning of the compound between the two phases. The ratio of the concentration of the compound in the *n*-octonal phase to the concentration in the water phase at equilibrium is defined as the octonal-water partition coefficient (K_{OW}) (Chiou et al., 1977 and 1983; Mackay et al., 1980; Yalkowsky and Valvani, 1980; Smith et al., 1988). A second parameter, K_{OC}, can be defined as the distribution coefficient (K_D) divided by the fractional organic carbon (foc) content of a sorbent ($K_{OC} = K_D/foc$; Chiou, 1989). The K_{OW} and K_{OC} are related, as

they both depend on the water solubility of the organic compound. The K_{OC} is only a measure of hydrophobic sorption if the organic is highly hydrophobic and has no reactive functional groups that may exhibit polar properties. Further, K_{OC} can be correlated to the K_{OW} through a regression of the log-log relationship of K_{OW} vs. K_{OC}. The sorption of a nonionic compound by soil may be estimated by the K_{OW} value, with the knowledge that enhanced solute solubility in the polar solvent, used in the K_{OW} determination, results in decreased sorption of the compound in the K_{OW} system (Smith et al., 1988). Thus, the K_{OC} will be greater in soil systems, where there is little organic solute to enhance the solute solubility. Depending on the accuracy of the K_{OW} value, there is a 2 - to - 15 fold error associated with the prediction of K_{OC} using K_{OW} values (Hassett and Banwart, 1989).

Relationships between the organic compound sorption by SOM and the aqueous solubility of the organic compound has been used to estimate compound sorption by a soil (Chiou et al., 1983; Voice and Weber, 1985; Schwarzenbach et al., 1988; Chiou, 1995). Schwarzenbach et al. (1988) stress the importance of Henry's Law constants and acidity constants in determining the fate and behavior of hydrophilic weak-acid organics. For several nitrophenolic compounds, they found that $\log K_{OW} = -0.97 \log Sw - 0.04$ ($\pm$ 12) ($r^2 = 0.98$), where Sw is the molar water solubility of the organic compound. Unflurtuately, these empirical relationships were not able to predict sorption of nitrophenolic compounds in soil systems.

Chiou et al. (1983) found that $\log K_{OM} = 0.904 \log K_{OW} - 0.779$ ($r^2 = 0.989$) for 12 PCB's and benzene derivatives where K_{OM} is defined as the solute partition coefficient

between SOM and water. The partition theory assumes that SOM serves as an organic sorbent for trace organics in solution, and is the dominant sorbent matrices in the soil. Soil organic matter acts as the organic sorbent medium, like the octanol phase in the η-octanol phase in the K_{OW} relationship. Water solubility of the aromatic compounds was the major factor affecting the partition of the organic solutes in both SOM and octanol (K_{OM} and K_{OW}) for all 12 of these organic solutes. To defend the correlation between K_{OM} and K_{OW} regardless of the source and age of the SOM present in the sorbent matrix, Kile et al. (1995) showed that the K_{OM} values for carbon tetrachloride and 1,2-dichlorobenzene were not significantly different for 32 soils. They found that the K_{OM} values for the same compounds were not significantly different with 36 river bed sediments and suspended solids. However, the K_{OM} values for the sediments were approximately 50% higher than the soil K_{OM} values, indicating a compositional difference between SOM and organic matter in river sediments.

Kile et al. (1995) showed large standard deviations between the OC content of soil and sediments. Although not statistically significant in their study, other researchers have found that the age and source of the OC, as well as temperature, microbial population, moisture content, location within soil horizons, and other environmental factors determine the size, functionality, and reactivity of OC (Wood et al., 1987; Chiou, 1989; Koskinen and Harper, 1990; Green and Karickhoff, 1990; Schnitzer, 1971; Stevenson, 1994). Thus, it is essential to characterize SOM to evaluate the mechanisms responsible for the sorption of a trace organic compound by the soil matrix. Further, a K_{OW} is not a parameter that can alone yield sorption estimates. Review of various partition studies has

revealed a 3 - to - 10 fold difference in the sorptive capacity of native SOM (Mingelgrin and Gerstl, 1983; Kile et al., 1995). Rutherford et al. (1992) studied the sorption of carbon tetrachloride and benzene by cellulose, muck, peat, and an extracted peat sample. They found that sorption of the two organic solvents increased as the polarity of the sorbent media decreased (extracted peat > peat > muck > cellulose). They hold that the effect of sorbent polarity on the sorption of hydrophobic organic compounds could allow the estimation of organic compound sorption with knowledge only of the polarity of the sorbent media (SOM). Modern sustainable agricultural methods of applying animal wastes to field soils can significantly influence the character of solid and dissolved OC. Further, the effect of agricultural biosolid wastes on the partition and mobility of pesticides has not been well-established.

Empirical equations relating K_{OC}, K_{OW}, Sw, and K_D do not accurately predict sorption of moderately soluble nonionic organic compounds. An extensive literature review by Spurlock and Biggar (1994, a and b) concludes that sorption of moderately soluble substituted phenylureas is enhanced when the organic carbon content of the sorbent is greater than 0.1 to 0.3%. However, their comparison of phenylurea sorption by soil to that predicted by K_{OW}-K_{OC} relationships showed that sorption was strongly dependent on specific interactions between phenylurea functional groups and the organic phase of the soil. Sorption isotherm non-linearity results from these specific interactions between the solutes and the sorbents.

The partitioning equilibrium is characterized by an absence of interfering or competitive effects between binary solutes (Schellenberg et al., 1984; Smith et al., 1988).

Nonionic solutes partition between water, the particulate organic phase, and hydrophobic -Si-O-Si- bonds of mineral surfaces in bulk soil, much the same as solutes partition between water and *n*-octanol (Hassett et al., 1981; Smith et.al., 1988). Chiou (1986 and 1989) has outlined 3 arguments that support the partitioning mechanism of nonionic moderately water soluble organic compound sorption by soils:

1. Sorption is correlated with SOM content more strongly than with any other factor
2. Water competes more effectively than neutral organics for mineral sorption sites
3. Sorption of similar nonpolar organic compounds by soil is not competitive like sorption on mineral and other surfaces.

The partitioning theory is supported by the small changes in enthalpy measured when compounds sorb to SOM (Hassett and Banwart, 1989). Sorption of nonionic and nonpolar organics is independent of temperature, providing further support for the partition mechanism, rather than an adsorption or precipitation mechanism (Chiou et al., 1977; Hassett et al., 1980). Further, the adsorption of small molecules on exposed surfaces (inorganic and organic) occurs with little or no activation energy (Hayward and Trapnell, 1964; Adamson, 1976; Pignatello, 1990 a and b).

Effect of Soil Organic Matter Content on Trace Organic Compound Sorption

Sorption of nonpolar organic compounds by soil is highly correlated with SOM content, and to a lesser extent, clay type and content (Wood et al., 1987; Chiou, 1989; Hassett et al., 1980; Karickhoff , 1979; McCall et al., 1980; Koskinen and Harper, 1990; Green and Karickhoff, 1990). The organic matter in soil contains a large number of low-polarity, hydrophobic sites that may adsorb low-polarity solutes (O'Connor and

Connolly, 1980; Wauchope and Koskinen, 1983). Sorption of trace organic compounds on soils containing greater than 0.1% organic carbon is dominated by the organic fraction, whereas the pH, and amount and type of clay tends to be more important in the retention of trace organic compounds in matrices with less than 0.1% OC (Pingatello, 1989; Hassett and Banwart, 1989).

Murphy et al. (1990) showed that anthracene (log K_{OW} = 4.45), exhibited the greatest sorption enhancement from mineral sorbed humic substances, compared with dibenzothiophene (log K_{OW} = 4.38) and carbazole (log K_{OW} = 3.29). These findings support the theory that sorption is inversely correlated with the K_{OW} of a compound. The authors note that the K_{OC} of a solute-sorbent system may be influenced by the DOC-mineral or DOC-soil surface associations. Bound DOC and organic mineral coatings have inherently different functionality and influence on the sorption of trace organic compounds in the soil environment. Moreover, the molecular characteristics of the SOM influence the diffusive capabilities of nonionic organics in the SOM structure (Pignatello and Huang, 1991; Schribner, 1992). It is believed that the size, chain branching, functionality, and tightness of the polymeric chains in SOM and DOC would impede aqueous diffusion throughout the organic structure (Hayes and Himes, 1986; Pignatello, 1989). The diffusion related component of equilibrium could render these inner-aggregate regions of SOM unavailable for sorption of trace organics. However, many researchers attribute slow diffusion of trace organics into the structure of SOM to the biphasic nature of sorption reactions.

Moreale and Van Bladel (1979) found that increasing SOM content greatly enhanced the sorption of aniline and p-chloraniline. Moreover, the 8.52 g OC kg^{-1} soil had a 5 - fold slower sorption rate than the 2.49 g OC kg^{-1} soil. The authors attributed the slow sorption to both diffusion of the pesticides through the organic matrix and the electrostatic and electrochemical forces common to solution and adsorption. Bouchard and Lavy (1985) reported that sorption kinetics of hexazinone and metributzin were effected by the humification of the organic matter in the soil sample. Less humified SOM sorbed the most herbicide from a 0.01 M $CaCl_2$ solution (Bouchard and Lavy, 1985; Steinsiek, 1981). Less humified SOM has cellulose and other small unaltered organic constituents that are typically hydrophilic (Stevenson, 1994). Older humic matter is composed of larger molecules having a condensed, complex nature. Thus, water and solute diffusion to and through these humic materials may impede access to sorption sites for organic solutes (Scow, 1993).

The combination of type of clay matrix, age and functionality of organic matter, and the chemistry of the organic solute in the soil solution creates a complex interaction of components that may influence the rate of sorption reactions. Thus, current soil science literature presents no conclusive view of the relevance and importance of the kinetic component of diffusion of aqueous nonionic organic molecules through organic matter and soil colloidal particles.

The effects of solid and sorbed OC on smaller more soluble trace organics is largely unknown. Spurlock and Biggar (1994, a and b) found that specific interactions (H-bonding and or charge transfer mechanisms) occur between substituted phenyl ureas

and surface bound humic substances at low concentrations. But, these effects seem to disappear with increased urea concentrations and a hydrophobic bonding-partitioning mechanism is assumed. It is important to understand the sorption chemistry of soluble trace organics as more soluble herbicides are available, and the degradation of larger hydrophobic molecules results in the formation of small, polar, and water soluble daughter products (Spurlock and Biggar, 1994, a and b).

The partition mechanism of organic compound sorption has been questioned by many authors (Mingelgrin and Gerstl, 1983; Spurlock and Biggar, 1994, a and b). Linearity of isotherms (C-type) is frequently cited to support the partition process. However, nonlinear isotherms (e.g., L-type) are frequently encountered in the literature, especially for non-ionic and moderately water soluble organic molecules (Spurlock and Biggar, 1994, a and b; Minglegrin and Gerstl, 1983; Weber et al., 1983). Chiou (1989) states that soil mineral phases have a limited ability to adsorb nonionic organic compounds from water due to the strong dipole interaction of minerals with water. However, significant sorption of a wide range of nonionic organic compounds by kaolinite, montmorillonite, metal oxides, and other silicate minerals has been reported (Talbert and Fletchall, 1965; Goring and Hamaker, 1972; Moreale and Van Bladel, 1979; Voice et al., 1983; Carringer et al., 1975; Hassett and Banwart, 1989; Zhang et al., 1990; Essington and Tyler 1993; Pusino et al., 1994).

An evaluation of the sorption of nonionic organic compounds by reference clay minerals is made difficult by the presence small concentrations of organic matter (<0.3%) (Lee et al., 1990; Smith and Jaffe, 1992; Pennell et al., 1992; Spurlock and Biggar, 1994 a

and b). It is recognized that mineral-organic matter complexes often enhance the sorption of nonionic organics by soils and soil minerals (Mortland, 1970; Curl and Keolelan, 1984; Jardine et al., 1989; Murphy et al., 1990, 1994). Thus, the mineral fraction of soil contributes a significant influence on the sorption of nonionic organic molecules from aqueous solution through direct sorption of the molecules onto the oxygen rich surfaces of minerals and the mineral-organic matter complexes in the soil environment. The rate of diffusion of aqueous organic compounds through clay structures may impede the kinetics of trace organic compound sorption reactions, causing researchers to overlook the importance of clay and organic matter-clay sorptive matrices. Moreover, the intimate association of organic matter with clay forming microaggregates may either enhance or reduce the aqueous diffusion of solutes clay surfaces (Greenland and Hayes, 1981; Wu and Gschwend, 1986).

One problem associated with herbicide sorption studies lies in the concentration range studied. Many researchers use herbicide-organic chemical concentrations from 50 to several hundred mg L^{-1} (Alva and Singh, 1991; Pusino et al., 1994; Kan et al., 1994; Brown et al., 1994). However, herbicide concentrations found sorbed on solid phases in the soil environment are typically less than 100 $\mu g\ kg^{-1}$ (Donigan and Carsel, 1987; Hall et al., 1989). Many recent studies cite linearity only in the lower portions of isotherms while a Langmuir curvature dominates the higher portions.

Effect of Dissolved Organic Carbon on the Sorption of Trace Organics

Dissolved organic carbon compounds may compete with trace organic compounds for sorption sites. Pignatello (1989) reports that the interaction between synthetic and

natural soluble organic compounds for surface sorption sites is probable but imperfectly understood. The soluble humic and fulvic acid fractions in the soil environment resemble nonionic organic compounds in size and solubility. Thus, competitive interactions between the two could result in the soil environment (Chin et al., 1994). Dissolved organic carbon has been reported to form soluble complexes with herbicides in soil solutions (Lee and Farmer, 1989 and 1990; Lafrance et al., 1994).

The functionality and reactivity of dissolved humic substances is a function of the source, age, climate, moisture content, concentration, and other solution and environmental factors affecting a soil (Schnitzer, 1971; Stevenson, 1994). The humic and fulvic acid fractions of soluble organic matter differ in size, functionality, and reactivity. Moreover, these physiochemical differences exert distinct influences on the sorption of organic compounds by soils (Stevenson, 1994). Empirical methods that differentiate the ratio of humic to fulvic acid in soil extracts may help explain the influence of DOC on the sorptive behavior of trace organic compounds in soils.

Many physical, chemical, and electrostatic interactions can occur between hydrophobic and hydrophilic DOC molecules and organic and inorganic soil components. These reactions underscore the importance of DOC characterization in soil solution systems (Chin et al., 1994; Stevenson, 1994; Huber and Frimmel, 1994). The size and functionality of DOC ultimately determines the chemical reactivity of the molecule with soil components in the aqueous and solid phases. Many experimental methodologies, including acid-base fractionation, IR spectra evaluation, spectrographic, chromatographic, and various nuclear, C, H, and pyrolysis NMR procedures have been employed to

examine the chemical functionality and composition of DOC (Schnitzer, 1971; Goring and Hamaker, 1972; Gieseking, 1975; Chin et al., 1994; Stevenson, 1994). Each method provides unique insight into the complex organic structures. However, each method is accompanied by various experimental artifacts and limitations (Chin et al., 1994; Stevenson, 1994; Schnitzer, 1982).

Spectrometric absorbance ratios (E_4/E_6) and HPLC size exclusion chromatography are two common, relatively simple qualitative DOC characterization techniques. The raiio of the spectrometric absorbance of humic substances at 465 nm and 665 nm yields a characteristic color quotient (E_4/E_6) ratio that indicates the relative concentrations of humic and fulvic acid fractions in a soil solution (Schnitzer, 1982). The E_4/E_6 ratio decreases with increasing molecular weight and condensation of humic molecules (Stevenson, 1994). Soil solutions with E_4/E_6 ratios of less than 5 contain DOC that is dominated by humic acid molecules, while ratios greater than 5 indicate that fulvic acid molecules dominate the soluble OC fraction.

The elemental content of humic substances is effected by pH, parent material, vegetation, and age of the soil and residue. Further, the carbon content of the humic material has been found to increase with increasing the depth in the soil profile (Steelink, 1985). Absorption of visible light wavelengths (400-800 nm) is caused by atomic and electrometric vibration of unbonded electrons in oxygen, sulfur, and conjugated C=C double bonds (Stevenson, 1994). Electrons in η, π, and σ orbitals absorb visible light causing them to move to a higher orbital and an excited electronic state (Holtzclaw et al., 1988). The amount of energy absorbed at the specific wavelengths of 465 and 665 nm

distinguishes between molecules composed of C=N, C=O, C=C, C=S, N=N, and other double bond combinations between O, C, N, and S atoms. The elemental and functional group content of humic and fulvic acids produces the fundamentally characteristic E_4/E_6 spectral ratio. The oxygen to carbon ratio (O/C) for humic acids are about 0.5. Fulvic acid ratios are characteristically higher (around 0.7) due to higher amount of carboxylic functional groups and carbohydrate contents (Visser, 1983). The hydrogen to carbon ratio (H/C) of humic substances is directly correlated to the E_4/E_6 ratio. The E_4/E_6 ratio is inversely proportional to the aromaticity and degree of condensation of the humic material.

The Beer-Lambert law states that the amount of light absorbed by a substance is proportional to the number of light absorbing molecules that the light passes through. Therefore, because fulvic acids are smaller and have fewer double bonds in their molecular structure, the light absorption at both 465 and 665 nm is less than for humic acids. Humic acids have more aromatic, condensed molecular structure and more of the double and conjugated bonds that absorb light; therefore, the absorbance at 465 nm is highest (Stevenson, 1994).

Humic acid molecules are typically larger (molecular weight range: 50,000 - 100,000 Da) and more aromatic and hydrophobic in nature than the smaller fulvic acid molecules. Fulvic acid molecules range in weight from 500 - 2,000 Da, with greater amounts of nitrogen, sulfur, and other reactive functional groups (phenolic, carboxylic and alcoholic) compared to humic acid molecules (Stevenson, 1994). These two

molecular size categories can be separated and quantitatively compared with HPLC size exclusion chromatographic techniques.

Size exclusion techniques rely on the molecular sieving effect, where eluting organic molecules bind to the macromolecule gel complexes in the column and pass through the column at varying rates (Cooper, 1977; Madhun et al., 1986). Small organic molecules bind to large gel molecules which slow the elution of the compound through the column. Large organic molecules bind sparingly with the gel molecules which allows them to elute more quickly than small organic molecules. In this manner, molecules elute in descending size order. The relative comparison of elution time of DOC from various sources with the elution time of known organic compounds can provide a quantitative comparison of size and molecular weight distribution of DOC in biosolid and soil extracts. The retention times of DOC compounds in size exclusion chromatography are a function of extraction procedure, buffer chemistry and concentration, gel column type, and a variety of other methodology artifacts (Hine and Bursill, 1984; Amy et al., 1987; Barth et al., 1994, Chin et al., 1994). Moreover, DOC extracted from natural biosolids and soil horizons is a conglomeration of many sizes with multiple interactive associations with other aqueous components. Thus, size exclusion chromatography is best used as a quantitative comparative tool in assessing the size of DOC molecules in a biosolid or soil extract (Dorsey and Cooper, 1994; Huber and Frimel, 1994).

Solid and Dissolved Organic Carbon Interactions

Dissolved organic carbon is adsorbed on the surface of various clay and other soil components by combinations of physical, chemical, and electrostatic mechanisms.

Physical sorption is the attraction between natural and induced dipole interactions termed van der Waals interactions. The entropy and enthalpy driven dipole interactions create weak bonds (4 to 8 kJ mol^{-1}) between surfaces and polar molecules (Hamaker and Thompson, 1972; Voice et al., 1983). Chemical mechanisms of anion and cation exchange can also bind organic compounds to mineral surfaces. Ligand exchange of surface -OH groups may preferentially bind small hydrophilic DOC molecules to the surfaces of iron oxides goethite, gibbsite and other clay minerals (Tipping, 1981). However, Leenheer (1980) and Jardine et al. (1989) concur that hydrophobic DOC is preferentially sorbed to soil regardless of the soil characteristics. Mineral surfaces prefer sorption of hydrophobic DOC molecules (about 80% sorption of hydrophobics, 20% hydrophillic DOC) related to the destruction of highly structured water surrounding the solvated DOC macromolecules (Hassett et al., 1981; Jardine et al., 1989). Crystalline and amorphous iron oxides and hydroxides accounted for 50 to 70% of DOC sorption, with phyllosilicates contributing the remainder of adsorptive surface (Jardine et al., 1989). Overall, researchers agree that soil constituents have a capacity to bind DOC on soil surfaces. However, specific bonding mechanisms and implications of the bonding are not yet clear (Bailey and White, 1970; Mortland, 1970; Voice et al., 1983; Jardine et al., 1989).

Isotherms for the sorption of DOC on mineral surfaces follow a Langmuir (L-type) curve (Parfitt et al., 1977; Tipping, 1981; Murphy et al., 1990). The mineral surfaces show high affinity for humic substances at low surface coverage and rapidly diminishing affinity with increased surface coverage (Murphy et al., 1990). Humic acids

with more carbon and greater molar volume are preferentially adsorbed over fulvic acids with greater oxygen to carbon ratios.

Competitive ion-exchange studies reveal that DOC is adsorbed by soil by physical anion exchange mechanisms (Jardine et al., 1989; Murphy et al., 1990). Sorption of humic substances by mineral surfaces increases as pH decreases creating more positive sites on the sorbant surface (Parfitt et al., 1977; Kummert and Stumm, 1980; Tipping, 1981; Tipping and Cooke, 1982). Murphy et al. (1990) further characterized the DOC sorption mechanism by stating that the humic carboxyl groups initially form outer-sphere complexes with protonated hydroxyl groups, then a ligand exchange mechanism of water for the humic carboxyl functional groups yields an inner sphere complex.

The functionality (oxygen to carbon ratio) of sorbed and solid OC determine the sorptive capacity of solid-DOC complexes for trace organic compounds. Bouchard and Lavy (1985) found that atrazine and hexazinone could not compete with water molecules for sorption sites on hydrophilic cellulose residues. However, sorbed humic substances enhance sorption of hydrophobic trace organic compounds. Gabarini and Lion (1986) and Murphy et al. (1990) found that the oxygen/carbon ratio was inversely correlated to DOC sorption on soil surfaces. This same trend is also noted for sorption of trace organic chemicals by soil surfaces (Gabarini and Lion, 1986; Murphy et al., 1990). In other words, humic acid is preferentially adsorbed to solid matrices in the soil. The sorbed humic acids represent a hydrophobic bonding site which preferentially sorbs hydrophobic trace organic molecules. Thus, distribution coefficients should increase with an increase

in the K_{OW} of the sorptive trace organic compound (Schwarzenbach and Westall, 1981; Curtis et al., 1986).

Aqueous Dissolved Organic Carbon Interactions

Soluble humic substances can increase the apparent water solubility, bind by means of hydrogen, charge transfer, and van der Waals interactions and hydrolyze, photosensitize, or reduce the bioavailibility of nonpolar trace organic compounds in solution (Landrum et al., 1984). Bulk phase SOM is estimated to be about twice as efficient as soil humic acid in the uptake of sparingly soluble nonionic organic solutes from water (Smith et al., 1988). The polarity and molecular weight of DOC influences the partition of nonionic solutes into DOC structures, and ultimately the sorptive behavior of the compound in the soil environment (Chiou et al., 1986; Smith et al., 1988; Lee and Farmer, 1989). Dissolved organic carbon exhibits greater molecular oxygen contents and thus, increased polarity in comparison to SOM (Garbarini and Lion, 1986). Moreover, the concentrated nature of commercial DOC fulvic and humic acid fractions exhibit enhanced binding capabilities with anthropogenic organics when compared with naturally occurring DOC (Chin and Weber, 1989; Chin et al., 1990). Thus, it is difficult to ascertain the effects of natural DOC on the sorption of trace organic compounds in the soil environment from studies with commercial humic substances.

The association of sparingly soluble organic compounds with various bulk and DOC phases has been used to develop the theory that solubility is inversely correlated with the partitioning of the organic compound into the DOC phase (Chiou et al., 1986). However, the theory has been examined primarily using hydrophobic organic pollutants,

such as DDT and trichloroethylene (Caron et al., 1985; McCarthy, 1983; Chiou et al., 1983, 1986). Lee and Farmer (1989) examined the association of several hydrophilic trace organic compounds with DOC. They found that the hydrophobicity did not govern the association of DOC with nonapropamide, a hydrophilic organic pesticide. Lee et al. (1990) state that many researchers have indicated that the interaction between hydrophilic trace organics and DOC are much more complex. Specific site reactions, such as hydrogen bonding, exchange, and electron donor-acceptor processes may contribute to the interactions of DOC and trace organic compounds. The effect of polarity and solubility of dissolved and bulk organic matter has been postulated from comparative theory but inconclusive, contradictory evidence has been put forth (Lee and Farmer, 1989; Chiou, 1986).

Herbicide-DOC association in solution may be described by a linear distribution coefficient, K_{DOC}. This parameter is defined in a manner similar to K_D, and is the concentration of herbicide partitioned with DOC in the equilibrium solution, (in units of mg kg^{-1} or comparable) divided by the free unbound concentration of the herbicide in solution (in mg L^{-1}). This linear partitioning mechanism implies that the DOC does not have a maximum capacity for binding the herbicide and that there is a constant interaction intensity. The intensity of the herbicide-DOC complexation is a function of the hydrophobic character of the herbicide and DOC in the soil solution.

Studies that evaluate the herbicide-DOC partition and enhanced solubility phenomenon show that non-polar solutes exhibited greater partitioning and solubility enhancement with DOC (Chiou, 1986, 1989; Smith et al., 1988). Chiou (1986)

postulated that a dilute concentration of DOC, as is commonly found in the environment, could produce a significant solubility enhancement on organic compounds having comparable or greater solubility than the concentration of DOC in the aqueous phase.

Recent studies have found no effect of DOC on sorption of moderately water soluble herbicides (Spurlock and Biggar, 1990; Clay et al., 1988). Spurlock and Biggar (1990) found no significant influence of up to 100 mg L^{-1} DOC from a sandy loam soil on simazine (Sw = 3.5 μg L^{-1}) sorption. However, the 30-1900 mg L^{-1} concentrations of simazine used in the experiment were in excess of DOC concentrations examined and were not characteristic of simazine concentrations in a soil environment.

Wijayaratne and Means (1984) found that DOC from an estuarine environment (<5000 Da) had a capacity to bind atrazine at concentrations below the water solubility of atrazine. Madhun et al. (1986) found that soil solutions containing 240 mg L^{-1} of commercial humic acid significantly influenced the water solubility of bromacil, chlorotoluron, diuron, and simazine. Overall, the effects of smaller more soluble humic substances (<5000 Da) on the solubility and sorption of hydrophilic compounds in the soil environment is largely unknown.

The binding of sparingly soluble organic compounds by DOC has been found to enhance their water solubility (Chiou et al., 1986; Chiou et al., 1988) and potentially alter their fate and transport (Madhun et al., 1986; Lee and Farmer, 1989; McCarthy and Zachara, 1989; Abdul et al., 1990; Chin et al., 1990; Lee et al., 1990). Dissolved soil humic acids provide a sufficiently large intramolecular nonpolar environment for promoting a partition mechanism with nonpolar solutes like DDT, PCB and 1,2,3-

trichlorobenzene (Choiu et al., 1986). Using the same compounds, the authors found that K_{DOC} values from soil derived DOC partition are about 4 and 5-7 times greater than dissolved fulvic and humic acids, respectively. Chiou and Kile (1994) examined 12 compounds of varying solubility to establish that polar interactions (H-bonding and to a lesser extent London dispersive forces) facilitate the binding of trichloroethylene, ethylene glycol monoethyl ether, carbon tetrachloride, benzene, hexane, and other solvents by humic acids. Still other researchers found that the lower aromaticity and higher amount of hydrophilic functional groups of fulvic acid acted as a carrier and extraction media for atrazine and catechol derivatives (Huang et al., 1995). Weak physical bonds, hydrogen and ionic bonds and charge transfer complexes could account for the binding capacity of fulvic acids. Lee and Farmer (1989) found that DDT and lindane exhibited different affinities for Suwannee stream reference fulvic acid and Greenfield sandy loam fulvic acid. Kinetic studies with atrazine indicated that soluble fulvic-bound atrazine was dominant at the beginning of the experiment (Schiavon et al., 1995). However, the fulvic-bound fraction decreased over the 6 month field experiment and atrazine was found in the soluble humic acid and solid organic carbon fractions of the soil. Murphy et al. (1994) found that carbazone and anthrazine display competitive sorptive behavior on peat humic acid coated kaolinite. They hypothesized that hydrophobic adsorption rather than partitioning was the dominant mechanism responsible for the competitive behavior. While a number of studies have examined the influence of DOC on herbicide fate and behavior, no clear mechanism has been proposed (Chiou et al., 1988).

It has been suggested that herbicide molecules can form stable water-soluble associations with DOC (fulvic and humic fractions) and become mobile DOC-herbicide complexes in the soil environment (Ogner and Schnitzer, 1970; Pierce et al., 1974; Madhun et al., 1986; Jardine et al., 1990; Weber, 1994; Huang, 1995). Some researchers have found that the transport of pesticides is relatively unaffected by natural DOC (Lafrance et al., 1994; Spurlock and Biggar, 1990). Lafrance et al. (1994) observed that pentachlorophenol (PCP) transport was unaffected by natural groundwater DOC using environmentally relevant concentrations of 0.1 and 15 mg DOC L^{-1}. Chin et al. (1990) and Chin and Weber (1989) found that DOC collected from the Huron river during spring runoff and commercial Aldrich humic acid had a marked binding effect on α-chlordane and 2,2', 5-PCB and enhanced the sorption of the compounds to Lake Michigan sediments.

Desorption of Trace Organic Compounds from Soil

Research clearly indicates that the bulk of nonionic organic compound sorption is accomplished rapidly in soil systems. However, following this initially rapid sorption stage, organic compound sorption continues at a slow rate for several weeks to months. Scow (1993) states that there tends to be a irreversibly sorbed fraction of organic compound that increases with time in soil systems.

Desorption Hysteresis

In an ideal system, true equilibrium conditions will yield K_D constants and isotherms that are identical when equilibrium is approached from the sorption or desorption direction (Pignatello, 1989). Hysteresis or non-singularity has been reported

in many studies in which desorptive points do not lie on the sorption isotherm and K_D values are greater when equilibrium is approached in the desorption direction (Schriber, 1992; Pignatello, 1989). Several explanations for desorption hysteresis have been proposed (Hamaker and Thompson, 1972; Rao and Davidson, 1980; Pignatello, 1989; van Genuchten and Wierenga, 1974; Davidson and Chang, 1972). These include:

1. Method artifacts
2. Chemical or biologic degradation or transformation of the target compound
3. Failure to establish true equilibrium conditions
4. Portions of the compound are resistant or irreversibly sorbed.

Method artifacts, such as the sorption of nonionic organic compounds to colloidal particles in solution can inflate aqueous concentrations of the target organic and prevent solid sorption from occurring (Gschwend and Wu, 1985; Pignatello, 1989). Gschwend and Wu (1985) examined the sorption of polychlorinated biphenyl isomers to clay and organic matter rich lake sediments. They found that centrifugation for long periods of time did not remove soluble DOC-biphenyl complexes from solution. The DOC had complexed a significant fraction of the trace organic compounds which were not reflected by solvent-HPLC analysis. This resulted in the significant underestimation of the sorptive potential of the sediment, as the analytical methodology did not account for colloidal DOC-organic complexes. Moreover, the effect of colloidal sorption of the organic compounds diminished with decreasing DOC concentrations. Thus, trace organic compounds tend to sorb to the solid phase when DOC concentrations are low. This may lead researchers to conclude hysteresis in typical batch desorption experiments that remove the equilibrium solution and replace it with background electrolyte, effectively

diluting the DOC concentration and forcing sorption of the trace organic compounds (Di Toro and Horzempa, 1982; Wu and Gschwend, 1986). Clay et al. (1988) examined the possibility of DOC consuming organics in solution and reducing sorption by removing the DOC from a clay loam before sorbing atrazine and cyanazine. The researchers noted significant hysteresis in the desorption of these herbicides. Thus, even in the absence of DOC-organic complexation, desorption hysteresis and the formation of a resistant fraction of sorbed organic compounds seems evident.

Chemical or microbiologic decomposition of the trace organic compound during the sorption equilibration period results in the loss of the organic from the system, and consequently, an overestimation of sorption. Because the organic compound is removed from the system by degradation, the amount released from the sorbed state during desorption will appear to support hysteresis. Most batch systems employ a biocide and monitor the chemical degradation of the compound to avoid such problems. However, some soil column flow-through and field sorption experiments often do not employ biologic control of organic chemical degradation. In these experiments, estimation of the contribution of degradation to the removal of the organic compounds from solution must be taken into account.

Failure to reach equilibrium conditions in the sorption or desorption direction can also skew experimental results. Typical batch isotherms for nonionic organic compounds in soils are produced by equilibrating a known amount of compound with a soil slurry for 3 to 72 hours (Wauchope and Koskinen, 1983; Pusino et al., 1994). An apparent temporary equilibrium condition at constant aqueous phase concentration is produced and

assumed to represent the uptake of the organic compound by the given sorbent. However, desorption hysteresis will be evident if sorption equilibrium has not been attained (Wauchope and Koskinen, 1983). Thus, the kinetic component of solid-solution exchange and sorption reactions must be known and included in the experimental design to ensure equilibrium conditions and complete sorption of the trace organic compounds.

In batch sorption experiments, the processes of diffusion through solution to surfaces and diffusion through small pores in sorbent matrices are generally avoided by the constant mixing of the soil-solution slurry. Thus, diffusive limitations inherent under field soil conditions are avoided. Experiments that compare agitated soil slurries with non-agitated slurries report more and faster sorption with increased available surface area, the agitated systems (Wu and Gschwend, 1986). Studies that use flow through or field condition sorption methods compound the effects of tillage, stratified organic matter, and microbial degradation components. These factors are important in consideration of sorption kinetics. However, the interaction of the components does not allow for the comparison and evaluation of sorbent-solute effects.

Desorption Kinetics

The same bi-phasic kinetics associate with sorption reactions has also been noted for desorption reactions (Leenheer and Ahlrichs, 1971; Kahn, 1973; Farrell and Reinhard, 1994). Theoretically, sorption is best represented as a two-phase process with an initial fast stage followed by a longer slow phase controlled by mass transfer of the solute to internal sorption sites (Cameron and Klute, 1977; Karickhoff, 1979; McCall and Agin, 1985; Scow, 1993). Carbaryl, parathion, 2,4-D, and picloram exhibited biphasic sorption

kinetics with soil and SOM sorbents (Leenher and Ahlrichs, 1971; Kahn, 1973). Diffusion kinetics were used to determine that the rapid initial sorption of the organic compound was attributed to surface sorption while secondary phase sorption was limited by diffusion into the sorbent particles.

Karickhoff (1979) and Karickhoff and Morris (1985) showed that about half of the sorption of pyrene, phenanthrene, and other hydrophobic compounds to river sediments was achieved in about 4 minutes while the remaining sorption took weeks to equilibrate. The same study showed that the hexane-extractable, labile portion of sorbed organic decreased incrementally from about 0.94 mg kg^{-1} at 4 min to 0.36 mg kg^{-1} after about 5.5 days. A study by Pignatello and Huang (1991) compared the field sorption of atrazine and metolachlor using batch sorption methods. They found that the Freundlich sorption isotherm coefficients for a 24 hour batch equilibration time period was 2.3 to 42 times less than those determined for atrazine and metolachlor from 2 to 4 years. The herbicide residues were much more strongly sorbed to the soil component with a very low labile residue concentration. Thus, the biphasic nature of sorption influences the nature of the sorbed particles and the apparently irreversible nature of the sorptive bond between solute and sorbent with increasing equilibration time.

Other recent researchers have reported sorption related nonequilibrium with the slow diffusion and partition of organic compounds through SOM in the sorbent matrix (Ball and Roberts, 1991; Brusseau and Rao, 1989; Scow, 1993). Brasseau and Rao (1989) and Scow (1993) distinguish between transport and sorption related nonequilibrium, stating that sorption is instantaneous but diffusion of the compound

throughout the sorbent matrix is the rate limiting step. Wu and Gschwend (1986) evaluated the sorption kinetics of organic compounds in soils by assuming compound diffusion into spherical porous particles (a theoretical representation of OM or soil particles). Their theory holds that internal diffusion of the organic compounds to regions inside the particles is retarded by immediate sorption on the walls of the matrix pores. Depending on the size and functionality of the organic compound, diffusion within particles may be restricted. Their theory was supported in the literature and with experiments that showed hydrophobic particles to exhibit slower sorption kinetics and restricted movement of chlorinated hydrocarbons and pesticides within the particles.

The kinetics of sorption reactions are often reflected in the sorption partition coefficients, where slower sorption kinetics are indicated by a higher partition coefficient (Van Genuchten and Wierenga, 1976; Karickhoff and Morris, 1985; Wu and Gschwend, 1986). Water solubility is often positively correlated with the sorptive kinetics of compounds (Wu and Gschwend, 1986). Large hydrophobic molecules are often entrained in soil pore spaces and have low diffusivity and dispersion within soil colloids and pore spaces. Whereas smaller, more hydrophillic molecules have greater physical access to surface sorption sites in the soil matrix. Thus, smaller, more hydrophilic organic compounds exhibit faster sorption kinetics while hydrophobic compounds show slower sorption kinetics. The diffusion of nonionic organic compounds through SOM provides another dimension to the study of sorption-desorption kinetics.

With increased sorption equilibration time there is an increase in the amount of irreversibly sorbed organic compound, even with weakly sorbed nonpolar organic

compounds (Pignatello, 1989; McCall and Agin, 1985; Curtis et al., 1986). Curtis et al. (1986) found that sorption of several low molecular weight halogenated compounds, including carbon tetrachloride and tetrachloroethene, was 50% complete in the first 2 hours of equilibration. However, equilibrium was not achieved for several days.

In review of the literature, it is apparent that past researchers have focused on hydrophobic organic compounds and used concentrations much greater than are typically found in agricultural soils (Spurlock and Biggar, 1990). Moreover, most studies assume equilibration of the sorption process in 2 to 72 hours. These short sorption times neglect the diffusive transport of solutes through bulk solution to surfaces and transport within soil solids and associated colloidal particles. Although slow sorption kinetics have been reported for most types of organic compounds, there is currently no way to estimate the consequences to herbicide fate and behavior because the mechanisms and interactive contributing factors to these processes are not fully understood (Pignatello et al., 1993).

In many sorption studies, including weakly sorbed nonpolar organic compounds, there appears to be an irreversibly sorbed fraction of organic that increases in size with time (Pignatello, 1990; McCall and Agin, 1985; Scow, 1993). Gschwend and Wu (1985) used an equilibration period of 48 hours when studying the sorption of polychlorinated biphenyl isomers to clay and OM-rich lake sediments. A similar study by Wu and Gschwend (1986) found the sorption of polychlorinated hydrocarbons to be incomplete, even after several weeks. Other authors have noted that organics sorbed by DOC and suspended colloids tend to move to SOM or soil particulate sorbed states with time (Karickhoff, 1979; Karickhoff and Morris, 1985). Unfortunately, many studies in the

literature have used relatively short sorption equilibration times ranging from less than 2 to 48 hours (Gschwend and Wu, 1985; Clay et al., 1988; Pignatello and Huang, 1991; Scribner, 1992).

Theoretically, in order for a chemical reaction to be reversible, the reaction must proceed through states of equilibrium (Sposito, 1984). Infinitesimal changes in soil solution chemistry must occur to maintain equilibrium. Thus, removal of all the equilibrating solution and replacing it with background electrolyte with no trace organic compound would not satisfy the theoretical requirement for reversibility, resulting in non-equilibrium conditions and apparent hysteresis. At best, such procedures, when implemented, determine extractability rather than desorbability.

Current Theories on Desorption Hysteresis

Desorption hysteresis has been attributed to a change in equilibrium solution chemistry during the desorption step (McGlamery and Slife, 1966; Weber, 1977; Clay et al., 1988). Rao and Davidson (1980) reviewed many sorption experiments and concluded that nonsingularity of sorption isotherms could be real and significant under environmentally relevant conditions for some compounds. However, a careful examination of the experimental methodologies is required to assess the contributions of experimental artifacts to organic compound desorption hysteresis (Pignatello, 1989). The physiochemical explanation of hysteresis is the focus of many recent studies. However, scientists are still hypothesizing on the contributions of experimental artifacts, such as continued sorption, diffusion, and physical and chemical alteration of sorbent on the

apparent hysteretic behavior of organic compounds in soils (Kan et al., 1994; Brusseau and Rao, 1989; Wu and Gschwend, 1986).

It is essential to consider the importance of environmentally relevant conditions and time frames when exploring sorption and desorption reactions. Karickhoff and Brown (1978) found that significant concentrations of paraquat and diaquat were bound to surface and interlayer regions of clay minerals. Moreover, a dilute $BaCl_2$ solution used to model the salt content of soil solutions, removed little (<5%) of the sorbed herbicides. However, a study by Weber and Weed (1968) found that dilute solutions of paraquat could displace clay-sorbed diaquat, and the reverse. These conditions mirror the field environment during rainfall events, where a slow, continual release of trace organic compounds results in competitive sorption.

Pignatello et al. (1993) compared one and two component desorption models to determine the kinetics and fractions of sorbed atrazine and metolachlor. Approximately 50 % of the aged herbicide was eluted from the soil in a 3.5 month desorption period, when the soil was eluted with 0.01M $CaCl_2$. Most of the desorption occurred within the first 3 weeks of elution, the initial fast phase of the biphasic desorption process. Despite the good fit of the models to the experimental data in this study, the authors reported that herbicide behavior is specific to each soil system. Farrell and Reinhard (1994) found that trichloroethylene also displayed biphasic desorption. In their study, the slow phase of desorption took more than 2 years to remove trichloroethylene from the sorbed state. Further, they found that the slowly desorbed fraction of trace organic compound increases with decreasing organic sorbate concentration. Soil properties like internal porosity, SOM

content, internal surface area, pore size, and particle size showed no correlation with the fraction of slowly released trichloroethylene.

Fluometuron and Norflurazon

Physiochemical Characteristics

Fluometuron, N, N-dimethyl-N'-[3-(trifluoromethyl)phenyl] urea (FLMT), is a pre- and post-emergence herbicide used to control annual grasses and broadleaf weeds in cotton (Herbicide Handbook, 1994). This substituted urea herbicide is applied to approximately 35% of the cotton hectarage in the U.S.(Weaver, 1993). Fluometuron has a water solubility of 110 mg L^{-1} , an octanol-water partition coefficient (K_{OW}) of 242, an organic carbon-normalized distribution coefficient (K_{OC}) of approximately 140 (Herbicide Handbook, 1994; Savage and Wauchope, 1974; Essington and Tyler, 1992). Norflurazon, 4-chloro-5(methylamino)-2-3-(trifluoromethyl)phenyl-3-(2H)-pyridazinone (NORF), is a preemergence herbicide used to control grasses, sedges, and rushes in cotton (Weaver, 1993). This nonionic pyridazinone is applied to approximately 16% of cotton hectarage in the U.S. The solubility of NORF in water is 28 mg L^{-1}, while K_{OC} values reportedly range between 248 and 700 (Herbicide Handbook, 1994; Alva and Singh, 1990; Wauchope, 1992).

Behavior in Field Soils

Research indicates that FLMT and NORF persist beyond the growing season in soils under cotton cultivation (Rogers et al., 1985). In order to assess the potential damage to subsequent crops and groundwater the behavior of FLMT and NORF in field and laboratory soil studies needs to be assessed. Thus, it is important to determine the

nature of the sorption-desorption relationship and leaching potential of herbicides and the various components of soil matrices to determine the fate of applied herbicides.

Essington et al. (1995) found that FLMT depth distribution was related to rainfall timing and SOM content. Long-term no-till soil had greater organic carbon content in the surface 0 to 2 cm (17.7g OC kg^{-1}), compared with CT surface soil (10.2 g OC kg^{-1}). They found that 10.7% and 6.4% of the applied FLMT remained in the surface 0-8 cm NT and CT soils one year after application, respectively. They also found that about 79% of the applied herbicide that was lost to leaching was lost in the first month after application, with rainfall timing having the greatest influence on herbicide leaching. Brown et al. (1994) also reported that increased SOM content resulted in the increased sorption of FLMT in NT surface soil, relative to CT managed soil. Fluometuron sorption was also positively correlated to CEC and inversely correlated to soil depth.

Liu (1974) found less than 5.5% of total applied FLMT was leached below a depth of 20 cm in clay soils. They concluded that these losses of FLMT would not pose any threat to groundwater resources. La Fleur et al. (1973) found that about 3.3% of applied FLMT was leached to shallow groundwater from a silty field soil. Baldwin et al. (1975) also found low runoff losses of FLMT from conventional till cotton fields. They found that the first 4 liters of surface runoff collected had higher concentrations of FLMT than the remaining 42 liters collected during the rainfall simulation. Fluometuron retained by sediment was much greater in concentration than that found in the aqueous phase. Fluometuron sorbed by the sediment particles did not desorb. Moreover, the

researchers reported that FLMT in runoff follows the desorption isotherm of FLMT (which exhibits considerable hysteresis) rather than the sorption isotherm.

Fluometuron was found to be moderately persistent in the 10 to 20 and 40 to 50 cm depth increments of silt loam soils (Bouchard et al., 1982). The half-life in soils incubated with 0.3 and 0.6 mg FLMT kg^{-1} at room temperature was 9.4 weeks. Rogers et al. (1985) reported significant phytotoxic levels of FLMT under cotton cultivation. They found that leaching of FLMT did not result in the removal of FLMT from the soil profile. However, leaching did account for the movement of FLMT to deeper levels in the soil profile.

The modeling experiments of Nicholls et al. (1982) found that commonly employed Addiscott and Liestra models could not predict FLMT movement through clay loam field soils. Both models overestimated the desorption potential of FLMT from the profile under conditions of high water flow. Cargill and Davidson (1969) noted that another common mathematical model overestimated the desorption and movement of FLMT through a soil profile. They stated that during desorption the sorbed and solution FLMT do not come into equilibrium.

Natural soil heterogeneity tends to influence the movement of soil water, and many researchers have noted the difficulty of determining the amount, rate and equilibrium status of soil water in soil profiles. Without equilibrium conditions, it is impossible to determine the sorption-desorption behavior of herbicide residues in the soil profile.

Due to the relatively low water solubility of NORF, minimal leaching of the herbicide and sorption by SOM and clay cause NORF residues to persist in surface horizon of soil (Singh et al., 1985). Alva and Singh (1990) found that when 5 μg NORF was applied per gram of sandy soil, 0.3 μg of herbicide was not sorbed and potentially leachable to lower depths in the soil profile. However, in the silty loam soils typical of southern cotton cultivation, leaching does not contribute significantly to NORF dissipation in the field. Schroder and Banks (1986) found that Bradford clay loam (2.83 g kg^{-1} SOM) previously treated with 0.6 kg ha^{-1} NORF retained 0.5 mg kg^{-1} of the herbicide. Retreatment of the soil with 0.6 kg ha^{-1} NORF 297 days after the initial treatment resulted in the retention of 0.27 mg kg^{-1} NORF.

Southwick et al. (1993) reported low leaching losses of NORF from field soils. Moreover, they note the importance of rainfall event timing regarding the amount of NORF lost to leaching. They found that when no significant rainfall occurred for the first 171 days after NORF application, only 0.07% was lost after this time as runoff. However, when a runoff event occurred 22 days after NORF application 2.3% of the applied herbicide was lost as runoff. The overall loss of NORF to runoff in field situations is low.

Schroder and Banks (1986) found that NORF leaching was inversely related to SOM content. Hubbs and Lavy (1990) report that NORF sorption was positively correlated with SOM and montmorillonite clay content. They observed a wick effect (upward movement) of herbicide residues that corresponded to soil water movement.

However, the significant sorption of NORF in field soils reduces the mobile fraction of the herbicide.

It has been reported that both FLMT and NORF are metabolized in the soil environment (Mueller et al., 1992). Microbial degradation of anthropogenic organic solutes may result in the mineralization of significant proportions of applied herbicide in the soil environment.

The field behavior of FLMT and NORF suggests significant leaching losses and overall persistence of the herbicides in the soil profile. The sorption-desorption dynamics of sorbed herbicides are of prime importance in the fate and transport of these sorbed herbicide residues.

Sorption - Desorption Behavior

The sorption of FLMT in a Beluah silt loam was found to be greatest in the surface 0 - 7.5 cm (K_D = 0.599) (Mueller et al., 1992). A biphasic sorption pattern was observed as FLMT sorption initially followed a first order kinetic model and later exhibited a slower liner phase during the 96 hour sorption equilibration period. Fluometuron sorption was weakly though significantly correlated with SOM content (r^2 = 0.556)(α = 0.01). Fluometuron sorption by a soil containing 1.3 g kg^{-1} SOM conformed to the Freundlich model and was not influenced by moisture content (K_F = 0.9 and n = 1.08) (Savage and Wauchope, 1974). However, an increasing shift to the adsorbed state with each of 5 desorption steps was noted. The researchers also compared the sorption of FLMT in 8 silt loam soils typical of southern cotton production. They found that SOM content (ranging from 0.3 to 3.6 g kg^{-1}) was the most influential factor effecting FLMT

sorption by these soils. Bouchard et al. (1982) also found that SOM content was the most influential property correlated with FLMT sorption. They reported greater sorption of FLMT in the 10 to 20 cm soil (K_F = 1.56) than in the 40 to 50 cm depth (K_F = 0.70) where SOM content as about one half that of the 10 to 20 cm depth increment.

FLMT desorption from a Beluah silt loam was analyzed by equilibrating a 1 mg L^{-1} herbicide solution with soil for 24 hours, centrifuging, and adding background $CaCl_2$ to the existing soil solution (Mueller et al., 1992). The researchers found that about 52 to 63% of sorbed FLMT was desorbed in 24 hours with the $CaCl_2$ addition. Desorption was not significantly correlated with any soil factor.

Reddy et al. (1992) found that the sorption of NORF was correlated with organic carbon content, pH, and cation exchange capacity in sandy soils with low organic matter contents (0.94 - 0.67 g kg^{-1}). Noflurazon sorption ranged from 49 to 61% of applied concentrations which ranged from 2.03 - 3.86 mg herbicide kg^{-1} soil (K_D = 0.63 to 2.2). The K_{OC} values reported in this study ranged from 116 to 229 L kg^{-1} with an average K_{OC} of 157 L kg^{-1}. These K_{OC} values are significantly lower than those previously reported for NORF. Alva and Singh (1990) studied the sorption of NORF in two sandy soil profiles to a depth of 120 cm. They found that the varying OC content of the horizons in these two profiles was significantly correlated with the sorption of NORF (r^2 = 0.84 to 0.94).

The successive extraction of NORF from sandy soils was performed by Reddy et al. (1992). They replaced the entire supernatant solution with 0.5 M $CaCl_2$ or water. About 35 to 54% of sorbed NORF was extracted by water and 27 to 50% by $CaCl_2$. The

researchers found an inverse relationship between the amount sorbed and amount extracted from the soils. The amount extracted was also inversely correlated to SOM content. However, the overall low SOM content of these soils suggests the importance of other sorption mechanisms other than partitioning of trace organic into SOM (Reddy et al., 1992).

Objectives

The influence of tillage on the sorption of trace organic compounds is primarily attributed to the differences in the SOM content of the surface soils. The influence of DOC on the sorption of FLMT and NORF has not been examined. The formation of DOC-herbicide complexes in solution would consume herbicide from solution and effectively reduce the amount of sorbed herbicide. The competition of DOC with the herbicides for sorption sites on the solid matrix may also occur. However, little information on DOC competition with these herbicides is available

The desorption of FLMT and NORF in the presence of DOC has not been examined. Dissolved organic carbon residues are inherent in all soil systems, especially in those subjected to biosolid and manure fertilization. Thus, the influence of DOC on the sorption and desorption of FLMT and NORF is an important factor in the fate and behavior of these herbicides in the soil environment.

The objective of this study is to examine the influence of tillage practice and DOC source and concentration on the sorption and desorption of FLMT and NORF on a loessal derived West Tennessee soil. The specific research objectives are:

1. To determine the effect of tillage management practice, specifically, no-till and conventional chisel plow tillage, on the sorption of FLMT and NORF by surface soil.

2. To examine the effect of DOC, derived from NT surface soil, on the sorption of FLMT and NORF by subsoil.

3. To determine the effect of DOC source (poultry litter and dairy manure) and concentration on the sorption of FLMT and NORF by NT and CT surface soil, and subsoil.

4. To examine the effect of tillage on the desorption of FLMT and NORF from NT and CT surface soil, and subsoil.

5. To determine the effect of DOC, extracted from NT surface soil, on the desorption of FLMT and NORF from subsoil.

6. To determine the effect of DOC source (poultry litter and dairy manure) and concentration on the desorption of FLMT and NORF from NT and CT surface soil and subsoil.

7. To examine the kinetics of FLMT and NORF desorption from NT, CT surface soil, and subsoil in the presence and in the absence of DOC.

CHAPTER III

MATERIALS AND METHODS

Soil Characterization

Soil samples were collected in the late spring of 1992 from continuous no-till (NT) and chisel plow tillage (CT) corn (Zea mays L.) plots located at the West Tennessee Experiment Station in Jackson, TN. The Lexington silt loam (fine-silty, mixed, thermic, Typic Paleudalf) had no history of fluometuron (FLMT) or norflurazon (NORF) use in the 15 years prior to sample collection. However, this soil is representative of cotton producing soils in the region, and therefore is representative of soils subjected to FLMT and NORF applications.

Soil samples were obtained from the 0 to 8 cm and the 30 to 40 cm depth increments from several locations within each plot. The samples were composited, air dried, passed through a 2 mm sieve, and stored at room temperature. Selected chemical and physical characteristics of the soil samples are presented in Table 3.1.

Dissolved Organic Carbon Extraction and Characterization

Dissolved organic carbon (DOC) extracts were obtained from NT surface soil, poultry litter, and dairy manure. Poultry litter and dairy manure were obtained from The University of Tennessee Poultry and Dairy Units of the Knoxville Research Station. The biosolids were air dried at room temperature and stored at 4°C. Dissolved organic carbon was extracted from NT soil and biosolids with 0.01 M $CaCl_2$ using a solid-to-solution ratio of 1:2 and a 24 hour extraction period. The suspensions were centrifuged at 4800 x

Table 3.1. Selected chemical and physical characteristics of the Lexington silt loam soil samples (<2 mm in diameter) used in this study.

Sample†	Depth	Sand	Silt	Clay	pH‡	Total Carbon§	CEC¶	Surface Area#
	cm	-----	%	-----		g kg^{-1}	cmol kg^{-1}	m^2 kg^{-1}
NT	0 - 8	11	76	13	5.1	24.5	11.8	61200
CT	0 - 8	19	71	10	5.2	14.2	9.0	56700
SUB	30 - 40	8	75	16	5.3	3.7	7.7	94800

† No-till (NT) and chisel plow (CT) surface soils, chisel plow subsoil (SUB).

‡ 1:1 soil to 0.01 M $CaCl_2$ solution extract

§ Combustion.

¶ Hammer and Lewis (1987)

Carter et al. (1986).

g for 4 hours to separate the solid and solution phases. The supernatant was clarified further by filtration through a 0.45 μm membrane filter. All DOC extracts were stabilized with $HgCl_2$ (250 mg L^{-1}) and stored at 4°C in amber glass bottles (Wolf et al., 1994). The total carbon content of the extracts was determined within 5 days of extraction by coulometric titration using a Dohrman Carbon analyzer.

Spectrometric absorbance ratios (E_4/E_6) and HPLC gel filtration chromatography were employed to elucidate the physiochemical characteristics of the soil and biosolid DOC suspensions used in this study. The spectrometric absorbance of humic substances at 465 nm (E_4) and 665 nm (E_6) yields a characteristic value that represents the relative concentrations of humic and fulvic acid fractions of the DOC (Schnitzer, 1982). The E_4/E_6 ratio decreases with increasing molecular weight and structural density of the humic molecules (Stevenson, 1994). Humic acid molecules are typically larger (molecular weight range: 50,000 - 100,000 Da) and more aromatic (greater hydrophobic character) compared with the smaller fulvic acid molecules (molecular weight range: 500 - 2,000 Da). Fulvic acid contains greater amounts of nitrogen, sulfur, and other reactive functional groups (e.g., carboxyl, alcoholic, phenolic) (Stevenson, 1994). E_4/E_6 ratios less than 5 are indicative of a greater portion of humic acid molecules, while ratios greater than 5 indicate that the DOC is dominated by fulvic acid molecules. A Milton Roy Spectronic 401 spectrophotometer was used to measure the absorbance of the DOC suspensions at 465 nm and 665 nm. The absorbance values and E_4/E_6 ratios of soil and biosolid extracts containing 150 mg DOC L^{-1} are reported in Table 3.2.

Table 3.2. E_4/E_6 ratios of biosolid and NT soil extracts containing 150 mg DOC L^{-1}.

DOC source	Absorbance at 465 nm	Absorbance at 665 nm	E_4/E_6 ratio
No-till surface soil	0.029	0.002	14.5
Poultry litter	0.398	0.069	5.8
Dairy manure	1.121	0.184	6.1

The E_4/E_6 ratios indicate that the soil and biosolid DOC sources are primarily composed of fulvic acid type molecules (E_4/E_6 >5). The dairy manure biosolid extract has the greatest amount of color-producing groups or chromaphores. This is indicated by the high absorbance of both 465 and 665 nm wavelengths. However, the dairy biosolid is dominated by fulvic acid molecules, as indicated by the high absorbance at 465 nm. Similarly, DOC in the poultry litter biosolid extract is composed primarily of fulvic acid molecules (Chen et al., 1977; Stevenson, 1994). The DOC derived from NT surface soil is also dominated by fulvic acid type molecules. The dramatic difference in the E_4 and E_6 absorbance indicates that the DOC in the soil extract is almost entirely composed of fulvic acid molecules.

Size exclusion chromatography implements a molecular sieving effect where the functionality of the DOC compounds and the solvent media determine the bonding strength and retention time within a gel packed column. Small organic molecules bind to the large, stationary gel molecules, slowing the elution of the compounds through the column. Large organic molecules bind sparingly with the gel molecules and thus, elute more quickly than small organic molecules. In this manner, molecules elute in decreasing size order and a relative comparison of the size distribution of organic molecules in the solution can be achieved.

Characterization of the molecular size distribution of the soil and biosolid DOC extracts was performed with HPLC size-exclusion chromatography with ultraviolet detection at 240 nm (Madhun et.al., 1986). A DIONEX (Sunnyvale, CA) DX300 Gradient Chromatography System with a Linear Instruments (Reno, NV) UVIS-206

Multiple Wavelength Detector, autosampler, and DIONEX AI-450 Chromatography Software was used for the characterization. All samples were prepared in 5 ml quantities in DIONEX polypropylene sample vials. The HPLC system includes a 200 μL injection loop and a Supelco Progel - TSK G3000PWXL 30 cm x 7.8 mm i.d. (6 μm particle size) analytical column with an in-line 4 cm x 6 mm i.d. Progel guard column. Each sample was eluted with HPLC grade water at a flow rate of 0.55 ml min^{-1}. The HPLC system was flushed with water for 17 minutes between injections.

The chromatogram peaks that eluted between 0.5 and 15 minutes were used to characterize the three DOC sources at concentrations of 150 mg DOC L^{-1} (Figure 3.1). A standard solution containing 300 μg L^{-1} NORF (232 g mol^{-1}) and 300 μg L^{-1} FLMT (303 g mol^{-1}) was analyzed with each set of the DOC extracts to determine the herbicide (small molecule) elution time.

The poultry litter and dairy manure extracts are primarily composed of molecules that are larger than the herbicides of this study. Most of the poultry litter molecules eluted between 5 and 8 minutes of injection into the gel column. This first large concentration represents the humic acid fraction of the extract which was confirmed in the E_4/E_6 ratio. The small residual fraction of the poultry extract that eluted from 8 to 10 minutes represents the fulvic acid molecules in the solution. The dairy manure extract appears to have three distinct size categories of molecules. The initial wide bimodal peak extending from 5 to 7 minutes on the chromatogram represents humic molecules. The third sharp peak at 8.5 minutes represents a concentration of dairy molecules of fulvic

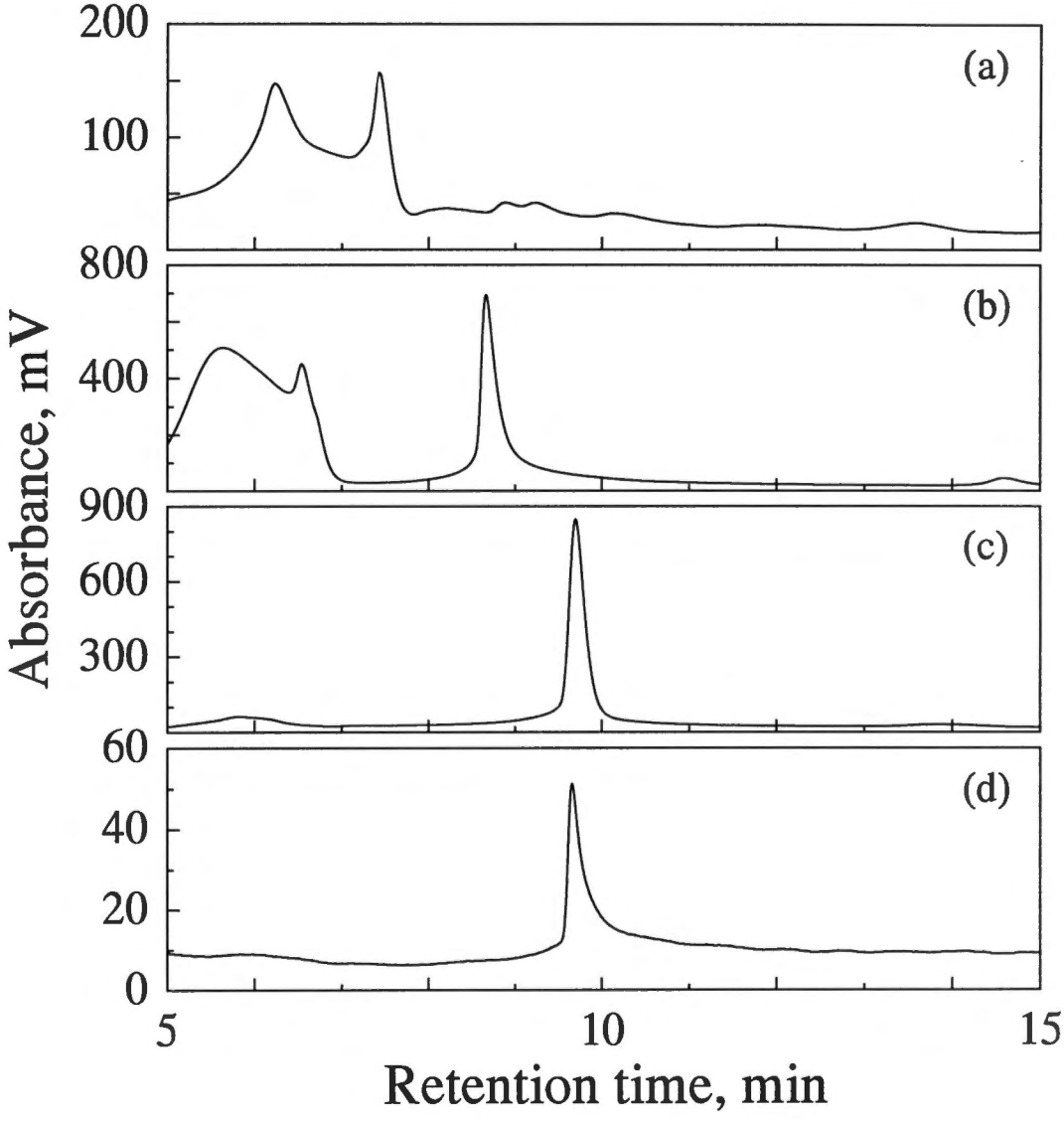


Figure 3.1 Gel-chromatographic size separation of (a) poultry litter, (b) dairy manure, (c) no-till soil extracts containing 150 mg DOC L^{-1}, and (d) a 300 μg FLMT L^{-1} plus 300 μg NORF L^{-1} solution.

size. This is apparent from the single sharp peak at 9.5 minutes. A similar peak at 9.5 minutes represents the elution of FLMT and NORF.

The E_4/E_6 ratio and gel chromatograms of the DOC extracts are consistent. Both the analyses indicate that the NT DOC extract has the largest concentration of fulvic acid size molecules, close in size to FLMT and NORF. The poultry litter extract has the greatest range of different size molecules, mostly humic in nature. The dairy DOC has a significant concentration of both humic and fulvic molecules.

Herbicide Analysis

A stock herbicide solution was prepared by dissolving analytical standard FLMT (98.9%) and NORF (98%) obtained from Chem Service (West Chester, PA) in a small volume of HPLC-grade methanol and brought to volume with 10 mM $CaCl_2$. The final stock solution contained 2000 $\mu g\ L^{-1}$ of each herbicide. The stock solution was stabilized with 250 mg L^{-1} $HgCl_2$ and stored at 4°C in an amber glass bottle.

Herbicide concentrations were determined using a DIONEX DX300 Gradient Chromatography System (Sunnyvale, CA). The analytes were detected with a Linear Instruments UVIS-206 Multiple Wavelength Detector tuned to 240 nm (Reno, NV). The HPLC system was controlled by DIONEX AI-450 Chromatography Software. All samples were prepared in 5 ml quantities in DIONEX polypropylene sample vials and injected into the system by the DIONEX autosampler. The HPLC system includes a 200 µL injection loop and a Supelco LC-C_{18} 25 cm x 4.6 mm i.d. (5 µm particle size) analytical column with an in-line 5 cm x 4.6 mm i.d. pellicular C_{18} guard column. Each sample was eluted using an initial acetonitrile-water ratio of 45:55 which was linearly

increased to 60:40 over 12 minutes at a flow rate of 1 ml min^{-1}. The HPLC system was then flushed with acetonitrile-water (90:10) for 7 minutes and re-equilibrated at initial conditions for 10 minutes prior to the injection of the next sample. The analytical method resulted in retention times of approximately 8 minutes for FLMT and 9 minutes for NORF. The analytical technique is described in detail by Essington et al. (1995).

It has been suggested that the degradation product of NORF, desmethylnorfluazon (DMN), may coelute with FLMT (Mueller and Moorman, 1991; Willian and Mueller, 1994). To determine if coelution could occur, solutions containing various combinations of FLMT, NORF, DMN, and the FLMT degradation products, desmethyl fluometuron (DMFN) and 3-(trifluromethyl)phenyl urea (TFMPU) were analyzed. The degradation products were obtained from Chem Services. The solutions were prepared in methanol and 10m M $CaCl_2$ to obtain herbicide and degradation product concentrations of 25 to 150 $\mu g\ L^{-1}$. The chromatograms displayed in Figure 3.3 clearly illustrate that the degradation products do not coelute with the parent compounds.

As a further assessment of potential herbicide degradation during the study, a stock solution containing approximately 300 $\mu g\ L^{-1}$ of each herbicide was prepared as a sample blank and stored in an amber glass bottle at 4°C for the 2 year duration of the study. This sample was periodically analyzed for the herbicides. No degradation products were detected nor did the original concentration of the herbicide change throughout the two-year duration of the study.

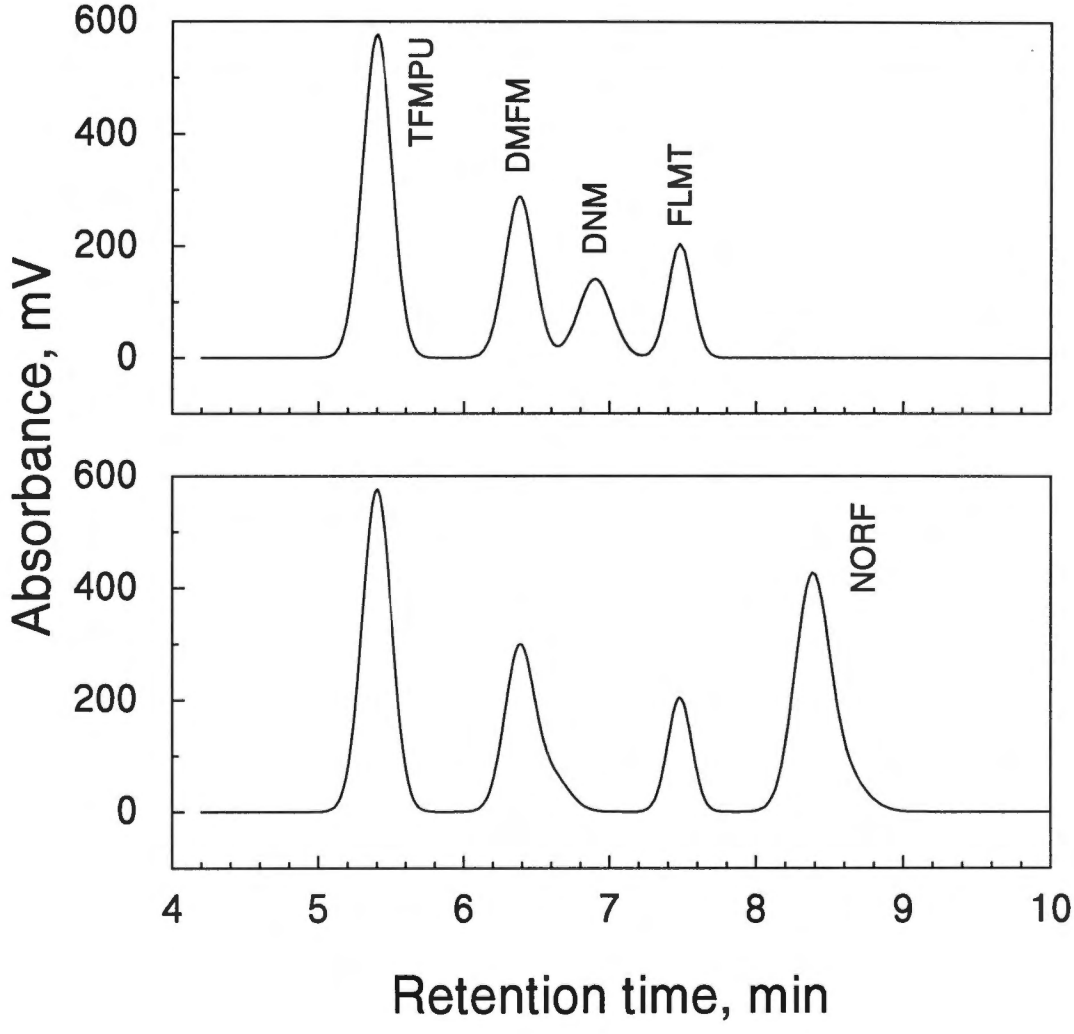


Figure 3.2 HPLC chromatograms illustrating the retention times for fluometuron (FLMT), norflurazon (NORF), desmethyl fluometuron (DMFN), 3-(trifluromethyl) phenyl urea (TFMPU), and desmethyl norflurazon (DMN) using the analytical procedure described by Essington et al. (1995).

Experimental quality assurance/quality control (QA/QC) employed for all analyses consisted of instrument calibration every 10 samples and one or two spiked or diluted samples embedded within each calibration set. The QA/QC sample was accepted if it was within 5% of the projected sample concentration. If the QA/QC sample failed, the instrument was recalibrated and the samples within the 8 to 12 sample calibration sequence were reanalyzed and accepted with an appropriate QA/QC sample result. All samples, QA/QC samples, and standards were diluted into the working range of the standard curve (150μg L^{-1} for both herbicides).

Sorption Isotherms

Herbicide sorption studies were performed using a batch equilibration technique. Ten gram soil samples were placed into 50 ml Teflon® centrifuge tubes that were previously washed and rinsed in methanol. Other clean centrifuge tubes were marked and set aside to be used as blanks to determine the actual herbicide concentrations in the solutions added to the soil. Triplicate tubes and blanks received 0.5, 1.0, 1.5, 3.0, or 5.0 ml of the 2000 μg L^{-1} herbicide stock solution described previously. The solution volume in each tube was brought to 20 ml with 10 mM $CaCl_2$. This resulted in initial herbicide concentrations of approximately 50, 100, 150, 300, and 500 μg L^{-1} for both FLMT and NORF. Biocide was added such that the solution contained 250 mg L^{-1} $HgCl_2$ to prevent any microbial degradation of the herbicides or DOC solutions in the sorption systems. The samples and blanks were vortexed and placed on a reciprocating shaker for a 72-hour equilibration period. Preliminary evaluations found that NORF and FLMT sorption equilibrium was attained within this 72-hr period.

Following the equilibration period the tubes were centrifuged at 4800 x g for 15 minutes to separate the soil from the solution phase. The solution was decanted from the centrifuge tubes and stored in 30 ml plastic vials at 4°C until analyzed. All samples were analyzed within 14 days of centrifugation. Three additional Teflon centrifuge tubes with soil received only background electrolyte solution. These samples were used to examine the retention time and intensity of coeluting peaks resulting from soil components. No coeluting peaks were observed in the NT, CT, or SUB soil-blanks.

The influence of DOC source on sorption of FLMT and NORF was determined by adding biosolid extracts from poultry litter and dairy manure in 10 ml quantities to one set each of CT, NT, and SUB soil systems resulting in concentrations of approximately 920 and 460 mg DOC L^{-1}. The influence of DOC concentration on sorption of FLMT and NORF was determined by analyzing all three soils with poultry litter biosolid extract concentrations approximately one half of the first DOC concentration (205 and 102 mg DOC L^{-1} solution). The influence of NT DOC on the sorption of FLMT and NORF by subsoil was also evaluated. Since the NT DOC was inherently a part of the NT soil and not relevant to CT soil sorption, it was only added to the subsoil system resulting in concentrations of approximately 75 and 37.5 mg DOC L^{-1}.

All supernatant and blank solutions were analyzed with the HPLC system described previously. The equilibrium concentration of herbicide in solution, Ceq (μg L^{-1}), was compared with initial herbicide concentration to compute sorbed herbicide

quantities. The concentration of herbicide adsorbed on the soil, q ($\mu g\ kg^{-1}$), was calculated according to the following formula:

$$q = (B - Ceq) * 0.02L / 0.01\ kg\ soil$$

where B is the concentration of herbicide in the sorption blank (in $\mu g\ L^{-1}$) and Ceq is the concentration of herbicide in the equilibrated solution (in $\mu g\ L^{-1}$).

The sorption data were characterized using the Langmuir and Freundlich sorption isotherm models. The form of the Langmuir equation used in the linear regression analysis was:

$$K_D = bK_L - K_Lq$$

where K_D is defined as q/Ceq , b is the x intercept of the linear relationship of K_D vs. q (classically termed the sorption maxima), and $-K_L$ is the slope of the linear relationship of K_D vs. q.

The Freundlich equation takes the form:

$$\log q = \log K_F + N \log Ceq$$

where K_F is the Freundlich sorption constant, and N is a parameter constrained to lie between 0 and 1.

Both 95% and 90% confidence intervals about each isotherm were calculated. An LSD separation of the 95% confidence intervals about the slope, intercept, and both slope and intercept were conducted to determine the significant difference between the isotherms (α= 0.05). The isotherms were depicted graphically with the appropriate regression forms for visual analysis. The LSD between isotherm slope, intercept and both parameters was reported in tabular form.

The K_F and N parameters are obtained by applying the Freundlich sorption model to experimental data. Freundlich K_F values represent the amount of herbicide retained at an equilibrium solution concentration of 1 $\mu g\ L^{-1}$ (Sposito, 1989). Because sorption at this concentration was not measured, it is more accurate to compare sorption between systems at concentrations measured in the experiment. Sorption distribution constants (K_D values) offer an alternative method of quantifying herbicide retention.

Sorption distribution constants were calculated for both FLMT and NORF for all sorption isotherms. These values were calculated according to the equation:

$$K_D = q/Ceq$$

Where q = the concentration of herbicide sorbed at equilibrium, and Ceq = the solution concentration of the herbicide at equilibrium. The K_D values were computed at a Ceq of 100 $\mu g\ L^{-1}$ and using the q computed from the Freundlich isotherm equation.

Sorption distribution coefficients may be adjusted to remove the apparent sorbent effect of the organic carbon content of the sorbent. The organic carbon normalized sorption distribution coefficient is calculated according to the following equation:

$$K_{OC} = K_D / foc$$

Where foc is the fractional organic carbon content of the sorbent. The K_{OC} values allow for the comparison of sorption between sorbents with the effect of the organic carbon removed.

By defining the K_{DOC} parameter, it is possible to utilize sorption data to estimate the influence of DOC on the sorption of trace organic compounds in soil systems

(Essington et al., 1995). The K_{DOC} parameter is a measure of the hydrophobic partition of an organic solute into DOC in solution (Chiou et al., 1986). The dissolved organic carbon sorption distribution coefficient, K_{DOC}, relays the difference between the sorption isotherm of a compound without added DOC and the sorption isotherm with DOC in the equilibration solution. The K_{DOC} is a linear distribution coefficient, implying that DOC has a constant interaction intensity denoted by the K_{DOC} parameter. Several assumptions are necessary to employ the K_{DOC} parameter in soil systems:

1) DOC competes with the soil solid for the herbicide by direct solute interaction either by adsorption or partition mechanisms

2) Sorption of the DOC - herbicide complex is not significant

3) Herbicides in soil solution interact with DOC and this interaction can be quantitatively describe by a linear partitioning (Essington et al., 1993).

The calculation of K_{DOC} is described in detail by Lee and Farmer (1989) and Essington et al. (1993). The partitioning of a herbicide between free and DOC - bound species in the soil solution is defined by:

$$K_{DOC} = m_{DOC} / C_F$$

where K_{DOC} is the distribution coefficient, m_{DOC} in the concentration of a herbicide partitioned with DOC in the equilibrium solution, and C_F is the free unbound concentration of the herbicide. The mass balance expression is :

$$C_T = C_{DOC} + C_F$$

where C_T is the total concentration of a herbicide in solution and C_{DOC} is the concentration of herbicide associated with DOC. In the presence of DOC:

$$C_F = C_T / (1 + K_{DOC} [DOC]).$$

Sorption of herbicide by soil is described with the general sorption model:

$$q = A\ Ceq^N$$

where q is the concentration of herbicide sorbed, Ceq is the equilibrium herbicide solution concentration, A represents the distribution coefficient if N = 1 or the Freundlich constant if $0 < N < 1$. Knowing the concentration of DOC introduced into the system, the following equation may be employed to calculate K_{DOC}:

$$q = A\ (C_T/(1 + [DOC]K_{DOC}))^N$$

Where q and C_T are the adsorbed and equilibrium solution concentration of herbicide, A is the distribution coefficient of the 0 mg L^{-1} DOC system, and N is the slope parameter determined from nonlinear regression. An isotherm may be predicted for the specific DOC system determined above by using the equation:

$$A' = A/l(1 + [DOC]\ K_{DOC})^N$$

where A, DOC, N, and K_{DOC} were determined in the previous equation and A' is the new nonlinear regression parameter for the DOC isotherm (Lee et al., 1989 and 1990). The DOC system isotherm equation takes the form:

$$q = A'\ Ceq^N$$

where q is the concentration of herbicide adsorbed in the DOC system, Ceq is the equilibrium solution concentration of herbicide in the DOC system, and A' and N are substituted from previous computations. The K_{DOC} and predicted DOC isotherm may be used to estimate the effect of DOC - herbicide complexation in an aqueous sorption system.

Desorption Kinetics of Fluometuron and Norflurazon

All desorption experiments were initiated from the 300 μg herbicide L^{-1} sorption points. Triplicate 300 μg herbicide L^{-1} sorption systems were prepared as described above for each of the 1, 3, 7, 14, and 28 day herbicide desorption periods. These samples were treated identically to the other sorption samples. However, after centrifugation, a 5 ml aliquot of the equilibrating solution was removed and subjected to the HPLC analysis (as described previously). This 5 ml of solution was replaced with a 5 ml volume of either background electrolyte or a DOC extract. The samples were then vortexed and placed back on the reciprocating shaker for the prescribed desorption period. Triplicate samples were then removed, centrifuged and the supernatant removed, stored at 4°C, and analyzed within 14 days for the herbicides.

The influence of DOC on the desorption of FLMT and NORF was examined as a function of DOC source and concentration. Fluometuron and NORF were sorbed by all three soils in the presence of poultry and dairy DOC at concentrations of 920 and 460 mg DOC L^{-1}. After the 72-hr equilibration period (described previously), the tubes were centrifuged and 5 ml of the solution was removed for analysis. The 5 ml of solution was replaced with DOC solution, resulting DOC concentrations of 1150 and 575 mg DOC L^{-1}. The tubes were re-equilibrated on a reciprocating shaker for 1, 3, 7, 14, or 28 days.

The influence of DOC concentration on the desorption of FLMT and NORF was determined by creating a desorption system with the dilute poultry DOC sorption system described previously. The herbicides were sorbed in the presence of 205 and 102 mg DOC L^{-1} and equilibrated for desorption with 255 and 130 mg DOC L^{-1}.

To determine the effect of DOC in the sorption system on the desorption of the herbicides, FLMT and NORF were equilibrated with all three soils for 72 hours without added DOC. Then, poultry and dairy DOC was added in 5 ml portions as the replacement solution for the desorption step. The DOC concentration in the desorption systems was 460 and 230 mg DOC L^{-1}.

Additional desorption systems were analyzed with the subsoil sorbent to determine the effect of dilute DOC concentrations that are more characteristic of this soil depth. FLMT and NORF were sorbed without DOC addition to the soil. Then NT, poultry, and dairy DOC were added as the 5 ml replacement solution for the desorption step resulting in concentrations of 20 and 10 mg DOC L^{-1}.

Desorption data (Ceq vs. q) for the 1, 3, 7, 14, and 28 day periods were determined and plotted on the corresponding sorption isotherms. The Ceq value of the desorption step was taken as the HPLC measured value. The concentration of herbicide adsorbed following the desorption equilibration (q_2) was calculated according to the following formula:

$$q_2 = (\{[B*0.02\ L - C*0.005\ L] / 0.02\ L\} - Ceq) * 0.02\ L / 0.01L$$

where B is the concentration of herbicides in the original sorption blank, C is the equilibrium concentration of herbicide at the completion of the 72 hour sorption period, and Ceq is the equilibrium concentration of herbicide following desorption.

The kinetic component of desorption was examined by comparing desorption 1, 3, 7, 14, and 28 days after the initiation of the desorption process. Duplicate desorption points at each of the five time intervals were determined. A 90% confidence interval

about each of the five desorption points was computed. The confidence interval about the average desorption point for each of the 5 desorption periods was plotted with the 90% confidence interval about the sorption isotherm.

Significant difference between the desorption point and the sorption isotherm is indicated by difference between the 90% confidence intervals about the point and isotherm ($\alpha = 0.05$). The 95% level of significance between the 90% confidence intervals about the points and isotherm is derived from the t-test. The following equation is used to test if two values are equal with a t-test:

$$t = (x_1 - x_2)/(2 * MSE/n)^{1/2}$$

Where x_1 and x_2 are the points being compared, MSE = the mean square error of one of the points, and n is the number of observations. The equation reduces to: $(2)^{1/2} * Se * t_{\alpha,dfe} = x_1 - x_2$. Where Se is the standard error of the observations, and dfe is the degrees of freedom for error. This equation calculates the minimum difference between values that will be significant, or the least significant difference from the mean separation point of view. However, if two confidence intervals are used to execute this test, a $(1 - \alpha)$ 100% confidence interval is $[x_1 + t_{\alpha, dfe} * Se$ and $x_1 - t_{\alpha, dfe} * Se]$ for both the point and the isotherm. This results in $[x_1 - x_2 = 2 * t_{\alpha,dfe} * Se]$, when only $[x_1 - x_2 = (2)^{1/2} * t_{\alpha,dfe} * Se]$ is necessary to yield a 95% confidence between the point and isotherm. Therefore, a less conservative t_α is needed to make $[2 * t_{\alpha,dfe} * Se]$ for the confidence intervals equal to $[(2)^{1/2} * t_{\alpha,dfe} * Se]$. For infinite degrees of freedom, $t_{0.05} = 1.96$. If a t_α value of 0.16 is used then $[(2)^{1/2} * t_{\alpha,dfe} * Se] = (2)^{1/2} * t_{0.16} = (2)^{1/2} * 1.38 = 1.96$. If dfe are equal to 10, $t_{0.05} = 2.228$. And, if $t_\alpha = 0.015$ is used then, $(2)^{1/2} * t_{0.15} = (2) * 1.57 = 2.28$. Thus, an

85% confidence interval about the point and line should produce a 95% confidence between the point and line. For ease of calculation, and a more conservative approach, a 90% confidence interval about both point and line were calculated.

Desorption was considered non-hysteretic if the 90% confidence interval about the desorption point lay within the corresponding 90% confidence interval of the sorption isotherm. Conversely, hysteresis was evident if the desorption point confidence interval did not overlap with the appropriate confidence interval of the sorption isotherm.

CHAPTER IV

RESULTS AND DISCUSSION

Sorption of Fluometuron and Norflurazon

Sorption of FLMT and NORF to Lexington silt loam soil was analyzed by developing sorption isotherms. Norflurazon was adsorbed to a greater extent than FLMT by all three Lexington silt loam soil samples (Figure 4.1). Water solubility has been cited as the primary factor determining the partitioning of trace organic compounds between solid and solution phases (Choiu et al. 1983; Miller and Waslk, 1985; Schwarzenbach et al. 1987). Sorption of trace organic compounds in soils is inversely correlated with the water solubility of the organic compound (Chiou et al., 1983; Voice and Weber, 1985, Chiou, 1995). Sorption increases with decreasing aqueous solubility. Conversely, organic compounds with high solubilities tend to be weakly retained by soils. The lower water solubility of NORF (28 mg L^{-1}), relative to FLMT (110 mg L^{-1}), suggests that NORF may be retained to a greater degree than FLMT. Comparison of the sorption coefficients of both herbicides in all three soils quantitatively illustrates the greater sorption of NORF over FLMT (Tables 4.1 and 4.2). Mean log K_F values for NORF (mean NORF K_F = 1.08) are more than 10 times greater than the log K_F constants for FLMT (average FLMT K_F = 0.103) (Tables 4.1 and 4.2). Similarly, average K_D values computed at Ceq = 100 μg L^{-1} FLMT or NORF show that sorption of NORF is approximately five times greater than sorption of FLMT by these soils (Tables 4.1 and 4.2).

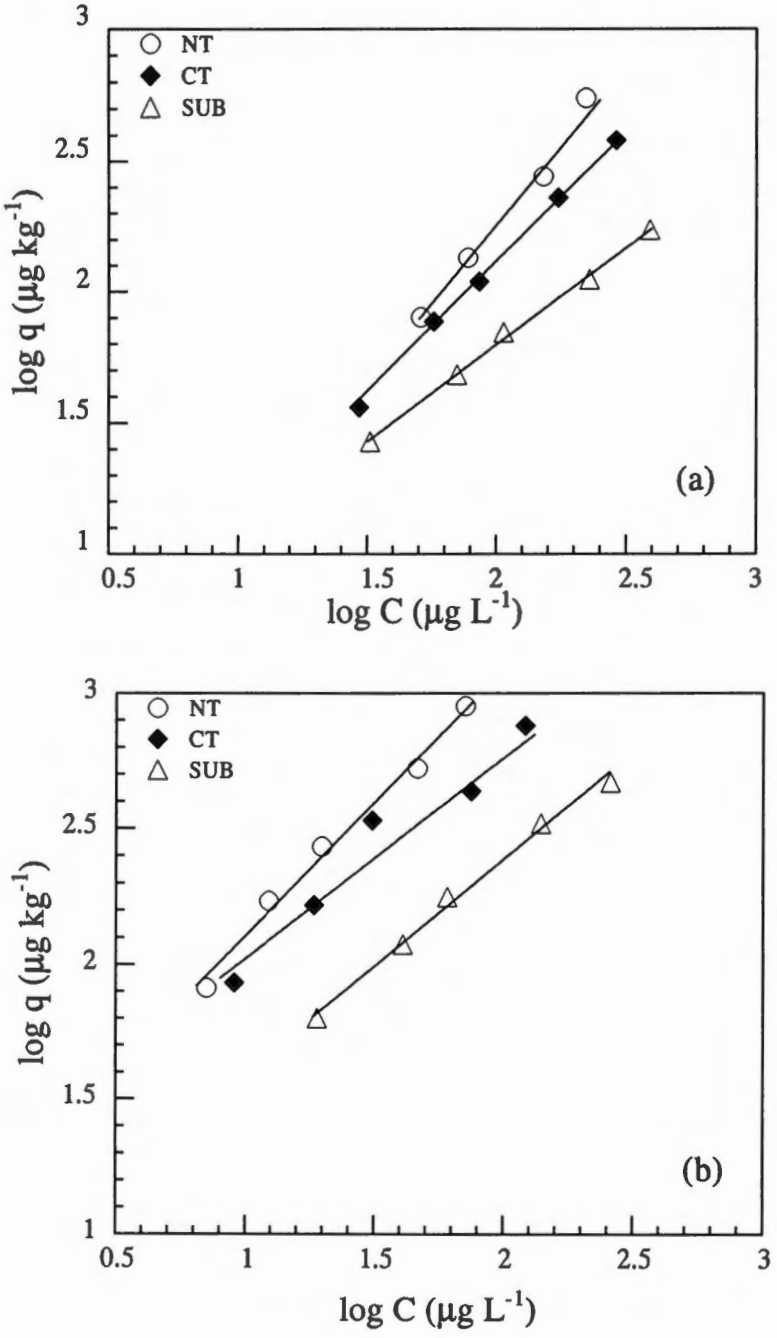


Figure 4.1. Freundlich isotherms showing the sorption of (a) fluometuron and (b) norflurazon by conventional tillage (CT) and no-till (NT) surface soil and subsoil (SUB).

Table 4.1. Freundlich isotherm parameters, distribution coefficients (K_D) and K_D values normalized for the organic carbon content of the sorbent (K_{OC}), for the sorption of fluometuron by Lexington silt loam soil.

Soil†	log K_F‡	N‡	Sorption Model§	r^2¶	K_D#	foc††	K_{OC}‡‡
NT	-0.38	1.30	a	0.9679**	1.66	0.0245	67.8
CT	0.14	0.99	b	0.9004**	1.32	0.0142	93.0
SUB	0.282	0.76	c	0.9013**	0.63	0.0037	170.3

† CT: conventional tillage surface soil; NT: no-till surface soil; SUB: conventional tillage subsoil

‡ K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

§ Sorption models identified by the same letter are not significantly different at the 0.05 level.

¶ *, ** indicate significance at the 0.05 and 0.01 levels.

Distribution coefficients derived from the equation: $K_D = q/C$, C = 100 μg L^{-1} and q computed from the Freundlich model.

†† Fractional organic carbon content of the sorbent where: foc = % organic carbon / 100.

‡‡ Organic carbon normalized distribution coefficient derived from the equation: $K_{OC} = K_D$ / foc.

Table 4.2. Freundlich isotherm parameters, distribution coefficients (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}), for the sorption of norflurazon by Lexington silt loam soil.

Soil†	log K_F‡	N‡	Sorption Model§	r^2¶	K_D#	foc††	K_{OC}‡‡
NT	1.17	0.94	a	0.9710**	11.2	0.0245	458
CT	1.28	0.74	b	0.9344**	5.75	0.0142	405
SUB	0.79	0.80	c	0.9885**	2.45	0.0037	663

† CT: conventional tillage surface soil; NT: no-till surface soil; SUB: conventional tillage subsoil

‡ K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide.

§ Sorption models identified by the same letter are not significantly different at the 0.05 level.

¶ *, ** indicate significance of the model at the 0.05 and 0.01 levels.

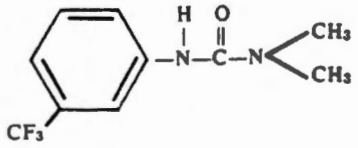
Distribution coefficients derived from the equation: $K_D = q/C$, C = 100 μg L^{-1}, and q computed from the Freundlich model

†† Fractional organic carbon content of the sorbent where: foc = % organic carbon / 100

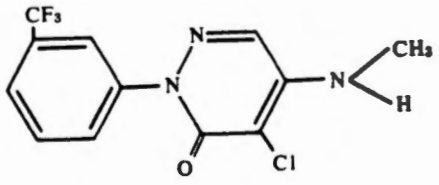
‡‡ Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D$ / foc

Differences in the sorption of the two herbicides may be attributed to physiochemical differences between the two compounds. Sorption is influenced by the size, shape, and functionality of the organic molecule (Weber, 1994). Figure 4.2 displays the molecular configurations of FLMT and NORF. Both molecules have an aromatic ring. The alternating double and single bonds of these ring structures resonate and evenly disperse electrons around the ring structure (Holtzclaw, 1991). The aromatic rings have no acidic or basic character that could easily protonate or deprotonate to bind with soil. Functional groups attached to the central aromatic rings provide specific regions of electrical charge with acidic and basic properties (Manahan, 1994). Fluometuron has two areas of charge deficit. The N - H and C = O groups represent regions of the FLMT molecule where electron concentrations and deficits cause electrical instability. These two sites could bind with soil or solution components. The NORF molecule has many regions of charge deficit and surplus. The O and CL atoms attached to the nitrogen ring represent areas of electron surplus which yield a net negative charge on this region of the NORF molecule. The three nitrogen atoms in the NORF molecule also represent three separate and different regions of electrical charge that could promote binding of the herbicide to sorbents and solutes.

The water solubility and octanol water partition coefficients of the two herbicides can be correlated to the sorption behavior of the two compounds. Fluometuron is more soluble in water than NORF (110 mg L^{-1} vs. 28 mg L^{-1}) and, FLMT is more hydrophilic than NORF (K_{OW} = 140 mg L^{-1} vs. 248 to 700 mg L^{-1}) (Herbicide Handbook, 1994). Thus, FLMT molecules are more electrically stable in water and less stable in organic



fluometuron (a)



norflurazon (b)

Figure 4.2. Molecular structure of (a) fluometuron and (b) norflurazon.

matrices than NORF molecules. In the soil environment, FLMT is more likely to stay in aqueous solution than partition into SOM. Conversely, NORF is more likely to partition into SOM and less likely to remain in solution.

Influence of Tillage on the Sorption of Fluometuron and Norflurazon

The influence of tillage on the sorption of FLMT and NORF was examined by analyzing herbicide sorption by no-till (NT) and chisel plow tilled (CT) surface soils and subsoil (SUB). These soils are representative of those under cotton production in West Tennessee. The influence of tillage management practice extends below the surface plow zone. Conventional tillage mixes soil and incorporates surface residues into the soil profile. Moreover, macropores and plant root channels are also destroyed. The increased SOM content of NT surface soil can contribute DOC to soil solutions and form clay-organic matter complexes in both surface and subsoil horizons (Greenland and Hayes, 1981; Wu and Gschwend, 1986). Enhanced macroporosity and plant root activity influences the soil water distribution and movement in no-till systems. The reduction in surface water runoff and soil erosion coupled with decreased evaporation of soil water from NT managed systems also imparts physical and chemical characteristics to NT soils that differ from CT systems (Unger and McCalla, 1980; Felsot et al., 1990). Many researchers agree that SOM content is the most important soil property influencing the sorption of trace organic compounds in soil (Wood et al., 1987; Chiou, 1989; Koskinen and Harper, 1990). Thus, it is expected that the SOM content is the major influence in FLMT and NORF sorption in these soil systems. The SOM content of the NT soil was

24.5 g kg^{-1}, while the CT surface soil contained 14.2 g kg^{-1} and the subsoil had 3.7 g kg^{-1} SOM.

Fluometuron sorption was greatest to the NT surface soil, which, correspondingly has the highest SOM content (Figure 4.1). The isotherms primarily conform to the Freundlich and partition models. Although the NT isotherm slope is greater than 1, which exceeds the $N < 1$ constraint of the Freundlich model, the Freundlich model best fit all the isotherm data and was used to describe all isotherms. The CT soil sorbed less FLMT than the NT soil. Further, the SUB soil retained the least amount of FLMT. All three FLMT isotherms are significantly different from each other (α=0.05). Fluometuron retention was directly related to the SOM content of the three soils (NT > CT > SUB).

The NT isotherm has a log K_F value of -0.15, which is significantly lower than the log K_F values of 0.14 for CT and 0.32 for SUB soil (Table 4.1). These values appear to be inconsistent with the sorption behavior observed in Figure 4.1. Freundlich K_F values represent the amount of herbicide retained at an equilibrium solution concentration of unity (Sposito, 1989). The K_F is obtained by applying the Freundlich sorption model to experimental data. The slope of the FLMT isotherms (N) with NT, CT, and SUB soils are 1.20, 0.98 and 0.74, respectively (Table 4.1). The SOM content of the three soils is correlated to the slope of the sorption isotherms. With this isotherm slope trend, it follows that the greater the SOM content of the soil, the greater slope of the sorption isotherm. A direct comparison of the K_F values for FLMT sorption by the three soils suggests that retention is least in the NT soil. However, the NT isotherm clearly shows significantly greater FLMT sorption throughout the concentration range examined. An

alternative method of quantifying herbicide retention is the comparison of distribution coefficients (K_D values). The sorption of FLMT by NT surface soil resulted in a K_D = 1.66 (Ceq = 100 $\mu g\ L^{-1}$). Conventional tillage surface soil had a K_D of 1.32 while SUB soil had a K_D = 0.63. The K_D values reflect the graphical representation of FLMT sorption, which shows FLMT sorption to follow the pattern: NT > CT > SUB (Figure 4.1).

The variation in K_D as a function of FLMT concentration at equilibrium illustrates the influence of soil type on sorption throughout a range of concentrations (Figure 4.3). The K_D values increase with increasing FLMT concentration in the NT system. The K_D values for FLMT do not vary with Ceq in the CT systems and decrease with increasing Ceq in the SUB systems. It is theorized that SOM is the primary sorbent of trace organic compounds in the soil environment, resulting in partition behavior. Fluometuron sorption by the NT and CT surface soils, containing the higher SOM contents, generally exhibit partitioning behavior. Whereas, FLMT sorption by SUB soil exhibits Langmuir behavior.

Many authors point out that variation in K_D with herbicide concentration is often overlooked in current studies (O'Connor and Connolly, 1980; Voice and Weber, 1985). It is commonly assumed that herbicide sorption conforms to the c-curve isotherm. Thus, a single K_D value is determined and assumed valid over a wide range of herbicide concentrations in a soil system (Wauchope and Myers, 1985; Seybold, et al., 1994). Bowman and Sans (1985 a and b) found that concentration did not influence the distribution coefficients of 4 insecticides. However, the authors used insecticide

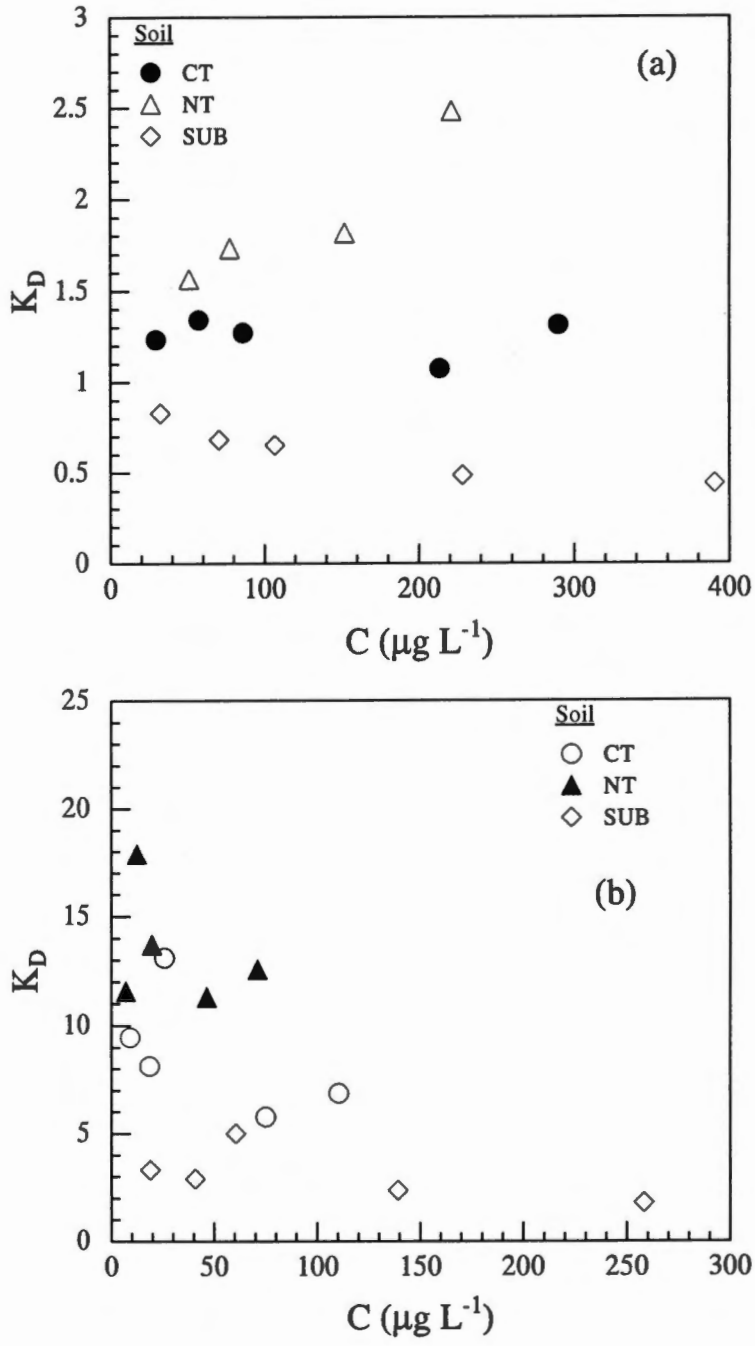


Figure 4.3. The variation of sorption distribution coefficients (K_D) as a function of equilibrium (a) fluometuron and (b) norflurazon concentration in the conventional tillage (CT), no-till (NT), and subsoil (SUB) systems

concentrations from 600 mg L^{-1} to over 30,000 mg L^{-1}. These concentration ranges greatly exceed concentrations likely to be present in the soil environment, and the computed K_D values may not reflect insecticide behavior in environmentally relevant systems.

Another way to compare the influence of tillage on the sorption of FLMT is to normalize the distribution coefficients using the organic carbon content of the soil. The resulting K_{OC} values are a measure of herbicide retention by the SOM in the soil samples. The K_{OC} for FLMT sorption by CT is 93; by NT soil, 68; and by SUB, 170 (Table 4.1). Accounting for the SOM content of the soil reduced the variability in the sorption coefficient for the two high SOM surface soils. However, the greater SUB K_{OC}, coupled with the computed N-value of 0.74, indicate that FLMT retention is not as strongly associated with SOM, compared to sorption in the CT and NT systems. The K_{OC} values for the NT and CT systems suggests that the difference in FLMT sorption between these two systems is due to SOM content.

Sorption of NORF by the Lexington silt loam soil showed the same trend of increased herbicide sorption with increasing SOM content. No-till surface soil adsorbed the greatest quantities of NORF at all concentrations followed by the CT and SUB soils, respectively (Figure 4.1). All three Freundlich isotherms are significantly different from each other (α=0.05). However, the Freundlich model indicates that sorption of NORF by NT soil (K_F = 1.13) would be less at unity (1μg L^{-1}) than sorption by CT soil (K_F = 1.28). The K_D values computed at C = 100 μg L^{-1} were 11.22 for NT, 5.75 for CT, and 2.45 for subsoil sorption. Plotting the K_D as a function of the equilibrium solution concentration

of herbicide shows the influence of concentration on the sorption of NORF by these soils (Figure 4.3). Sorption of NORF by NT surface soil, and subsoil does not appear to be effected by the equilibrium concentration of herbicide in solution. Conventional till sorption of NORF decreases with increasing herbicide concentration.

The computed K_{OC} values suggest that SOM is the primary sorbent in the CT and NT surface soil systems. That is, when NORF sorption is normalized by the organic carbon content, the sorption constants are very similar (CT K_{OC} = 405; NT K_{OC} = 458). The K_{OC} computed for the low organic carbon content SUB soil (K_{OC} = 663), also suggests that SOM significantly contributes to NORF sorption. However, SOM is not the only sorbent of herbicide in the SUB soil system.

Although the sorption constants for NORF are much greater than those for FLMT, the same trend of increased sorption with increasing SOM content is evident. Many studies have indicated that SOM is the primary sorbent for trace organic chemicals (Smith et al. 1988; Kile et al. 1995). The K_{OC} values for the NT and CT systems indicate that SOM is an important sorbent in these two systems. The K_{OC} for sorption of NORF by SUB soil indicates that SOM is an important sorbent of NORF; however, other sorbents also contribute to NORF sorption in these systems.

Effect of Dissolved Organic Carbon on Sorption

The influence of dissolved organic carbon (DOC) from poultry and dairy biosolid on the sorption of the FLMT and NORF to all three soils was analyzed. Four concentrations of poultry DOC and two concentrations of dairy DOC were introduced into the CT, NT, and SUB sorption systems. Poultry DOC concentrations were 920, 460,

205 or 102 mg DOC L^{-1} at the onset of the sorption process. Dairy DOC concentrations were 920 or 460 mg DOC L^{-1}. The effect of 75 or 37.5 mg NT DOC L^{-1} on the sorption of FLMT and NORF by SUB soil was also examined.

Fluometuron Sorption

Poultry Dissolved Organic Carbon

All four concentrations of poultry DOC reduced the sorption of FLMT by CT soil (Figure 4.4). Considerable scatter in the data for the 920 mg L^{-1} DOC system resulted no significant difference between the 0 mg L^{-1} and 920 mg L^{-1} isotherms (Table 4.3). The Freundlich models for the 460, 205, and 102 mg DOC L^{-1} isotherms were significantly different from the 0 mg L^{-1} system (α=0.05). The 205 and 102 mg L^{-1} DOC isotherms are not significantly different from each other. The isotherm N and K_F values could not be related to the concentration of poultry DOC in the equilibration solutions.

Sorption of FLMT by NT soil was also influenced by the presence of poultry DOC in the equilibration solutions (Figure 4.5). All four DOC isotherms were significantly different from the 0 mg L^{-1} system (Table 4.4). Sorption of FLMT by NT soil with poultry DOC was greater at the low initial herbicide concentrations, relative to the 0 mg L^{-1} sorption system. Conversely, FLMT sorption was reduced by poultry DOC at high FLMT concentrations, relative to the 0 mg DOC L^{-1} system. The slopes of the four poultry DOC isotherms increased with decreasing DOC concentration, although the 460, 205 and 102 mg L^{-1} isotherm slopes were not significantly different from each other (α=0.05). Fluometuron sorption isotherm intercepts in the poultry DOC-NT systems were significantly influenced by poultry DOC concentration. Overall, the poultry DOC

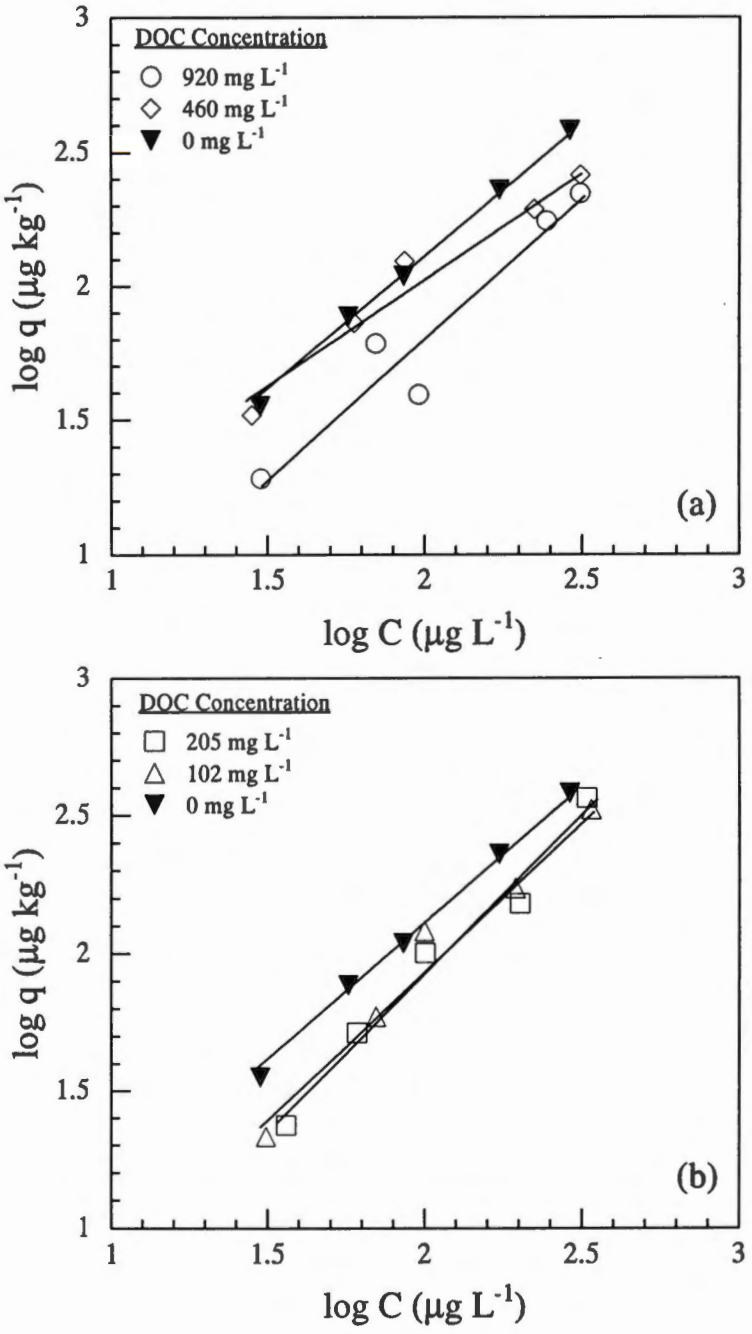


Figure 4.4. Freundlich isotherms showing the sorption of fluometuron by conventional tillage surface soil as a function of poultry litter DOC concentration.

Table 4.3. Freundlich isotherm parameters, distribution coefficients (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}), for the sorption of fluometuron by conventional tillage surface soil with poultry and dairy dissolved organic carbon (DOC).

DOC Concentration	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
mg L^{-1}						
0	0.14	0.99	a	0.9067**	1.32	92.8
			Poultry DOC			
920	-0.30	1.05	ab	0.8390**	0.63	44.4
460	0.79	0.44	c	0.9285**	0.47	32.9
205	-0.38	1.15	b	0.8928**	0.83	58.6
102	-0.22	1.08	b	0.9449**	0.87	61.3
			Dairy DOC			
920	-0.17	1.02	b	0.9859**	0.74	52.2
460	-0.13	1.01	ab	0.8764**	0.78	54.7

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level

§ *, ** indicate significance at the 0.05 and 0.01 levels.

¶ Distribution coefficients derived from the equation: $K_D = q/C$, C = 100 μg L^{-1}, and q computed from the Freundlich model

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D / foc$, where foc = 0.0142

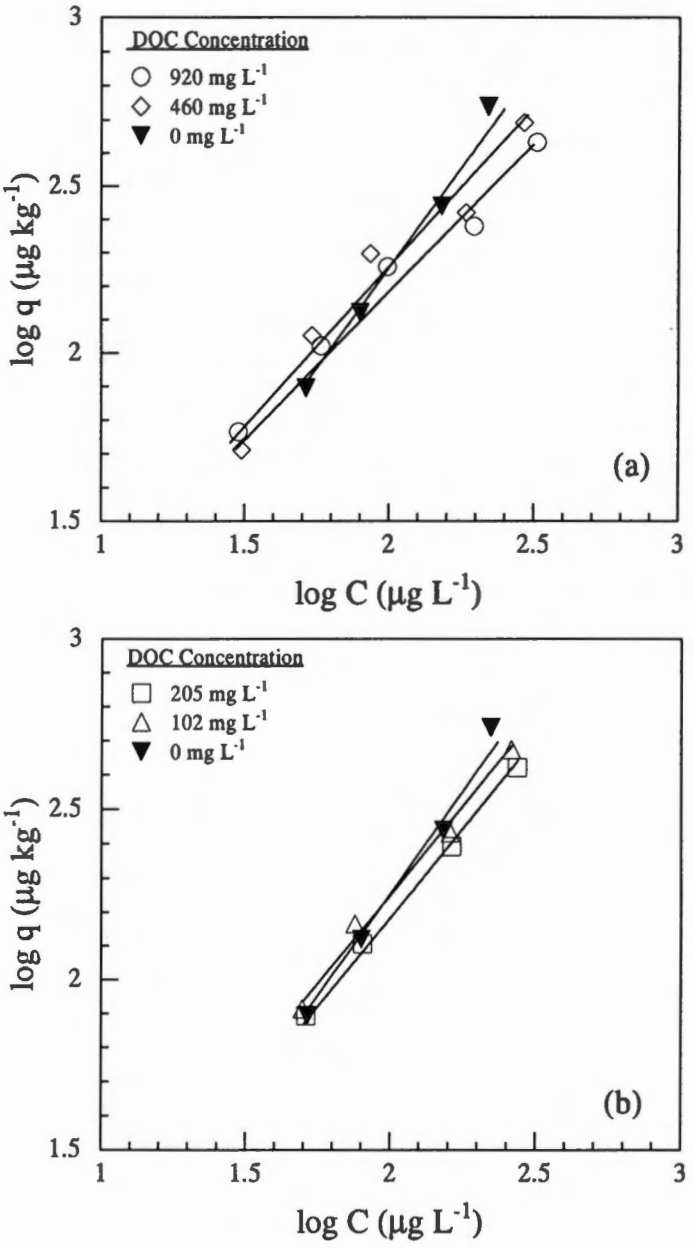


Figure 4.5. Freundlich isotherms showing the sorption of fluometruon by no-till surface soil as a function of poultry litter DOC concentration.

Table 4.4. Freundlich isotherm parameters, distribution constants (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}) for the sorption of fluometuron by no-till surface soil with poultry and dairy dissolved organic carbon (DOC).

DOC Concentration	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
mg L^{-1}						
0	-0.15	1.20	a	0.9941**	1.77	72.6
		Poultry DOC				
920	0.41	0.89	b	0.9049**	1.55	63.2
460	0.35	0.96	bc	0.9504**	1.86	76.0
205	0.09	1.05	d	0.9912**	1.55	63.2
102	0.16	1.04	cd	0.9961**	1.74	70.9
		Dairy DOC				
920	0.18	1.00	bcd	0.9257**	1.51	61.8
460	-0.03	1.11	acd	0.9354**	1.54	63.2

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level

§ *, ** indicate significance at the 0.05 and 0.01 levels.

¶ Distribution coefficients derived from the equation: $K_D = q/C$, C = 100 µg L-1, q computed from the Freundlich model

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D / foc$, where foc = 0.0245

decreased the slopes of the isotherms, making the poultry DOC isotherms significantly different from the 0 mg L^{-1} system. The concentration of poultry DOC in the equilibration solution was positively correlated with the decrease in FLMT sorption by NT surface soil, as shown by the decreasing K_D values (Table 4.4).

Poultry DOC decreased the slope of the SUB soil isotherms (Figure 4.6). The 920 and 460 mg DOC L^{-1} Freundlich isotherms exhibited less FLMT sorption at all herbicide concentrations (Table 4.5). Both the 920 and 460 mg poultry DOC L^{-1} isotherms were significantly lower than the 0 mg L^{-1} system. The 205 and 102 mg DOC L^{-1} systems indicated increased sorption of FLMT at low concentrations (50 $\mu g\ L^{-1}$) and decreased sorption at higher FLMT concentrations, relative to the 0 mg L^{-1} systems. However, the wide scatter in the sorption data indicates that the Freundlich model did not accurately describe the 205 mg poultry DOC L^{-1} systems ($r^2 = 0.47$).

Overall, the presence of poultry DOC in the sorption equilibration solution resulted in decreased sorption of FLMT by the Lexington silt loam soils. A trend of decreasing sorption with increasing poultry DOC concentration indicates that the poultry DOC interferes with the sorption process. The formation of a soluble complex between the relatively large DOC molecules and FLMT could explain the sorption results. Researchers have reported trace organic compound solubility enhancement in the presence of naturally occurring and commercial humic substances. They attributed the solubility enhancement to the formation of organic compound - DOC complexes. These soluble complexes reduce the concentration of trace organic molecules that are available

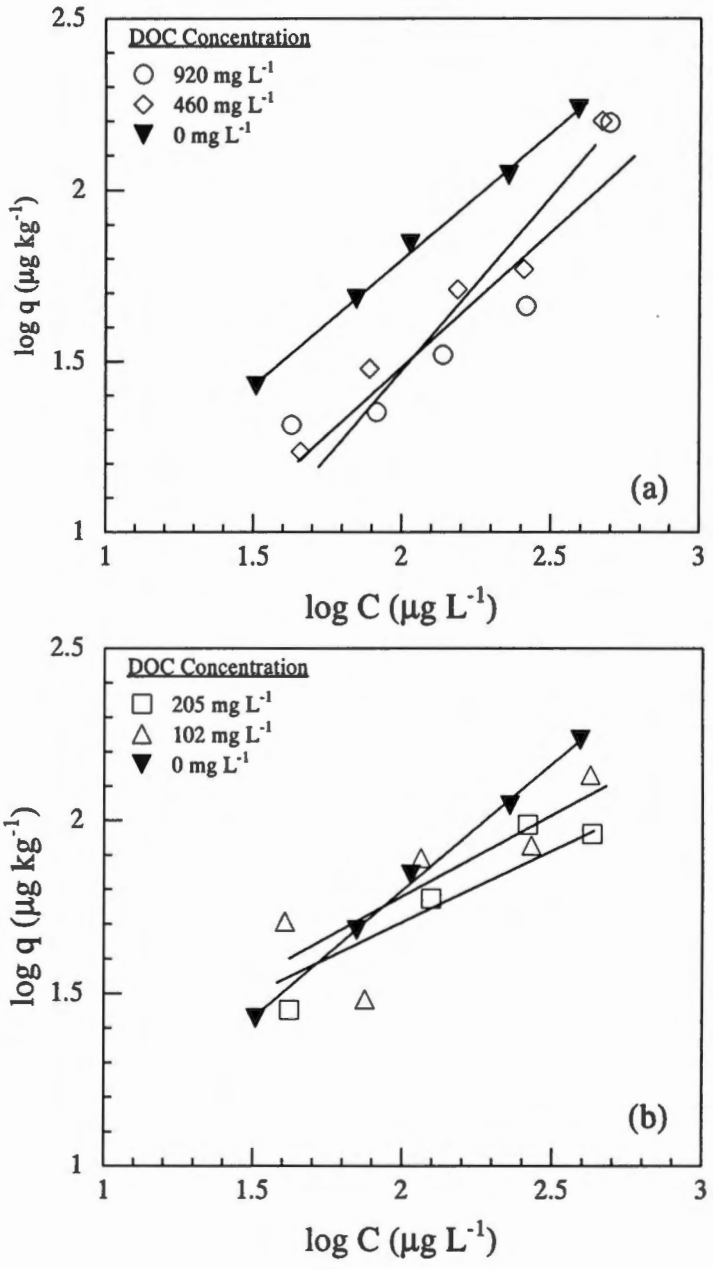


Figure 4.6. Freundlich isotherms showing the sorption of fluometuron by subsoil as a function of poultry litter DOC concentration.

Table 4.5. Freundlich isotherm parameters, distribution coefficients (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}), for the sorption of fluometruon by subsoil in the presence of poultry litter, dairy manure, and no-till surface soil dissolved organic carbon (DOC).

DOC Concentration	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
mg L^{-1}						
0	0.32	0.74	a	0.9921**	0.63	171
			Poultry DOC			
920	-0.10	0.79	b	0.8076**	0.30	81.6
460	-0.55	1.01	c	0.8881**	0.30	79.8
205	0.88	0.41	d	0.4711**	0.50	135
102	0.84	0.47	d	0.5733**	0.60	163
			Dairy DOC			
920	1.21	0.26	d	0.2510^{NS}	0.54	145
460	0.92	0.37	d	0.5230**	0.46	124
			No-till DOC			
75	-0.60	1.09	c	0.9427**	0.38	103
37.5	0.10	0.81	b	0.9752**	0.52	142

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level

§ *, ** indicate significance at the 0.05 and 0.01 levels; NS indicates not significant

¶ Distribution coefficients derived from the equation: $K_D = q/C$, $C = 100$ μg L^{-1}, q computed from the Freundlich model

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D / foc$, where foc = 0.0037

for sorption, resulting in reduced sorption. However, the solubility enhancement reported in the literature is primarily specific to hydrophobic compounds that are more soluble in the organic humic substances than in water. The relatively high water solubility of FLMT suggests that the hydrophobic partition of FLMT into DOC molecules, forming a soluble complex is unlikely. However, the sorption isotherm can be employed to evaluate the formation of a hydrophobic DOC - FLMT complex.

By defining the K_{DOC} parameter, it is possible to utilize the sorption data and estimate the influence of DOC on the sorption of trace organic compounds in soil systems (Essington et al., 1995). The K_{DOC} represents the difference between the sorption isotherm of a compound without added DOC and the sorption isotherm with DOC in the equilibration solution. The K_{DOC} parameter represents the hydrophobic partition of organic solute into the hydrophobic portion of DOC in a system. This requires that DOC molecules be sufficiently large and posses a sizable intramolecular nonpolar environment to promote herbicide binding. Further, the herbicide must exhibit very low water solubility and significant compatibility with DOC. Studies in the literature which utilize K_{DOC} computations commonly employ humic acid solutions and relatively hydrophobic trace organic solutes (Chiou et al., 1986, 1987; Lee and Farmer 1989; Lee et al., 1990; Essington et al., 1993). Fluometuron has little hydrophobic character, as does the DOC employed in this study. Therefore, because many of the assumptions of the K_{DOC} model have been broken, the K_{DOC} computation may not accurately describe herbicide - DOC association in these systems. Indeed, the hydrophobic character of DOC is much

less than that of solid phase organic carbon. Thus, K_{DOC} may be small, compared with K_{OC} (Essington, 1993).

The K_{DOC} predicted for the sorption of FLMT to CT soil in the presence of 920 mg poultry DOC L^{-1} was 945 L kg^{-1}. Figure 4.7 graphically depicts the 0 mg L^{-1} isotherm DOC system with the poultry DOC isotherm. Calculations of K_{DOC} for the 460, 205, and 102 mg poultry DOC L^{-1} systems result in K_{DOC} values of 1378, 2315, and 3941 L kg^{-1}, respectively. Because partitioning is implied, the K_{DOC} values are theoretical constants which represents the formation of DOC - herbicide complexes in a system. Thus, the K_{DOC} value should not vary with DOC concentration. Clearly, the computed K_{DOC} values increase with decreasing poultry DOC concentration, indicating that the partitioning of FLMT with DOC may not be occurring.

Bulk phase or solid SOM is estimated to be about twice as efficient as DOC in the uptake of trace organic solutes from aqueous solution (Smith et al., 1988). The K_{OC} constants for FLMT in the three soils range from 68 to 170 L kg^{-1}. Assuming that DOC has an affinity for the herbicide that is less than or equal to solid SOM, the K_{DOC} parameters should not exceed 170 L kg^{-1}. However, the K_{DOC} values for FLMT sorption by CT soil in the presence of poultry DOC exceed 900 L kg^{-1}. Lee et al (1989, 1990) found K_{DOC} values for prometryn, bromacil and napropamide to range from 1640 to 2000 L kg^{-1}. However, the experiments of Lee et al. (1989, 1990) were conducted with separative membranes in solution in the presence and absence of DOC with either no sorbent, or solid SOM sorbent present in the systems. Based on the observation that

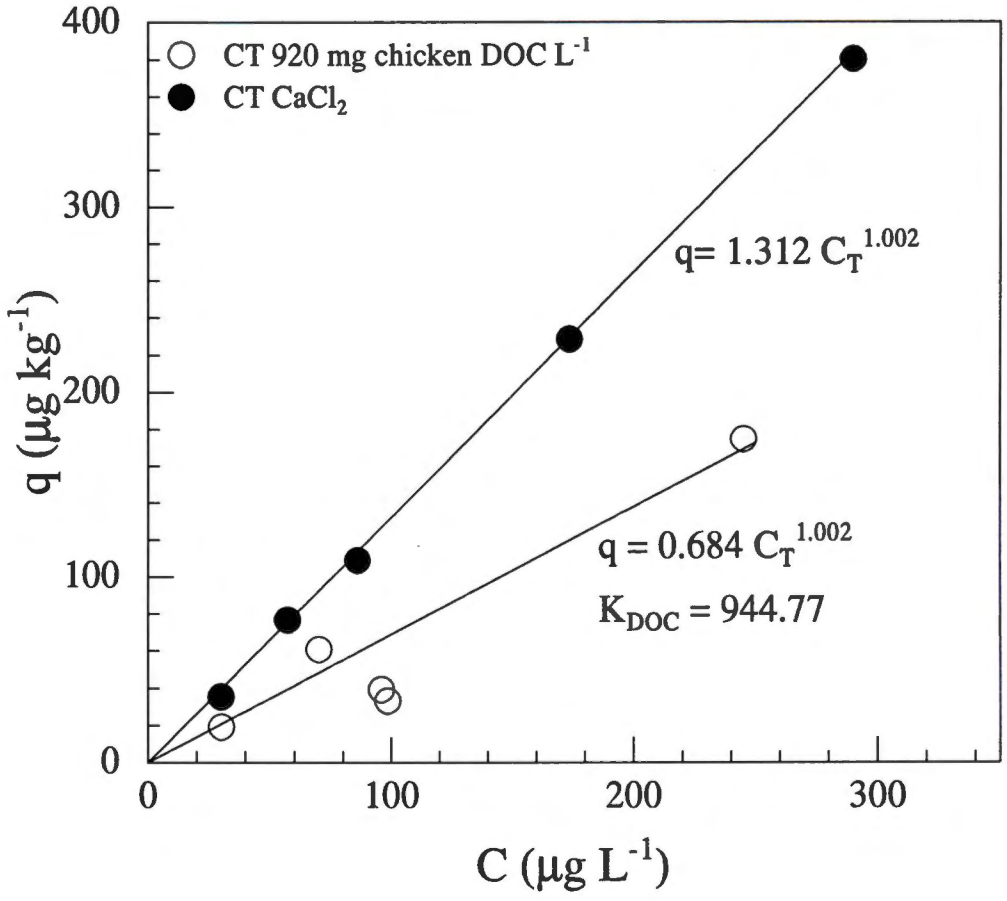


Figure 4.7. Predicted isotherm for the sorption of fluometuron by conventional tillage surface soil in the presence of 920 mg poultry litter DOC L^{-1} shown with the 0 mg DOC L^{-1} isotherm.

K_{DOC} varies with DOC concentration and the $K_{DOC} >> K_{OC}$, it is postulated that poultry DOC does not complex FLMT in the soil solutions.

The mechanism of herbicide sorption and the influence of DOC on those mechanisms is not determined in this study. Sorption isotherms alone can not indicate the physiochemical processes taking place in the soil systems. Detailed evaluation of the sorption surfaces and solution components is necessary to elucidate the mechanism of sorption. However, past research and experimental results can allow speculation about the sorption mechanisms. Because hydrophobic partitioning of herbicide into DOC forming soluble complexes does not adequately explain the reduced herbicide sorption in the presence of DOC, competition between the herbicides and DOC molecules for sorption sites must also be considered. Moreover, the DOC (which is several orders of magnitude greater in concentration in the experimental systems than the herbicides) may compete with the herbicides for surface sorption sites.

A non-partitioning mechanism, which implies competition between DOC and the herbicides for limited sorption sites, could explain the reduced sorption noted in the presence of poultry DOC. The poultry DOC is generally composed of large organic molecules (Figure 3.1). These DOC molecules may coat the soil surface with a hydrophobic organic layer, prohibiting the sorption of hydrophilic herbicide molecules. Further, the DOC concentrations ranged from 920 to 102 mg L^{-1}, approximately 200 to 18,400 times as concentrated as the herbicides. Thus, any competition or coating mechanism would reflect the immense difference between the DOC and herbicide concentrations.

Dairy Dissolved Organic Carbon

The presence of dairy DOC in the FLMT sorption systems resulted in reduced sorption of FLMT by all three soils. Sorption isotherms for FLMT sorption by CT indicate significantly lower sorption in the presence of dairy DOC, compared to the 0 mg DOC L^{-1} isotherm (Table 4.3) and (Figure 4.8). The K_D values indicate that FLMT sorption by CT soil with 460 and 920 mg dairy DOC L^{-1} was less than half that of the 0 mg DOC L^{-1} sorption isotherm (Table 4.3).

The sorption of FLMT by NT soil in the presence of dairy DOC is shown in Figure 4.8. Both dairy DOC isotherms appear to be similar to the 0 mg DOC L^{-1} isotherm. Indeed, considerable scatter in the 460 mg L^{-1} data points makes this isotherm statistically equivalent to the 0 mg L^{-1} DOC isotherm (Table 4.4). The K_D values for the NT-DOC isotherms also reflect the similar sorption of FLMT in the presence of dairy DOC (Table 4.4).

Dairy DOC decreased the sorption of FLMT by SUB soil (Figure 4.9). Sorption in the presence of 460 mg dairy DOC L^{-1} was significantly different from sorption in the presence of 920 mg DOC L^{-1} (Table 4.5). However, the K_D values for sorption of FLMT in the presence of dairy DOC are similar to the K_D value of the 0 mg L^{-1} system (Table 4.5).

The dairy DOC is composed of molecules larger than the herbicides. The dairy DOC also had a significant proportion of small molecules, represented by the eluting peak proximate to the herbicides (Figure 3.1). The poultry DOC, which influenced FLMT sorption to a greater extent, was primarily composed of larger DOC molecules.

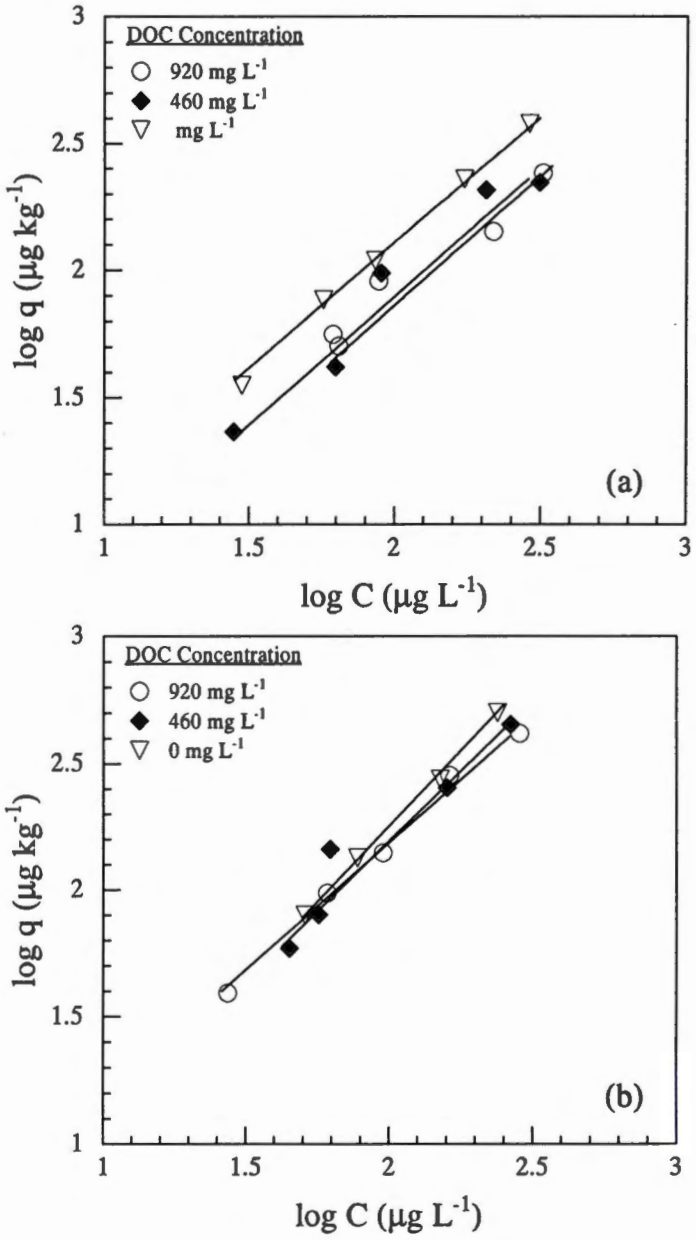


Figure 4.8. Freundlich isotherms showing the sorption of fluometuron by (a) conventional tillage and (b) no-till surface soil in the presence of dairy DOC.

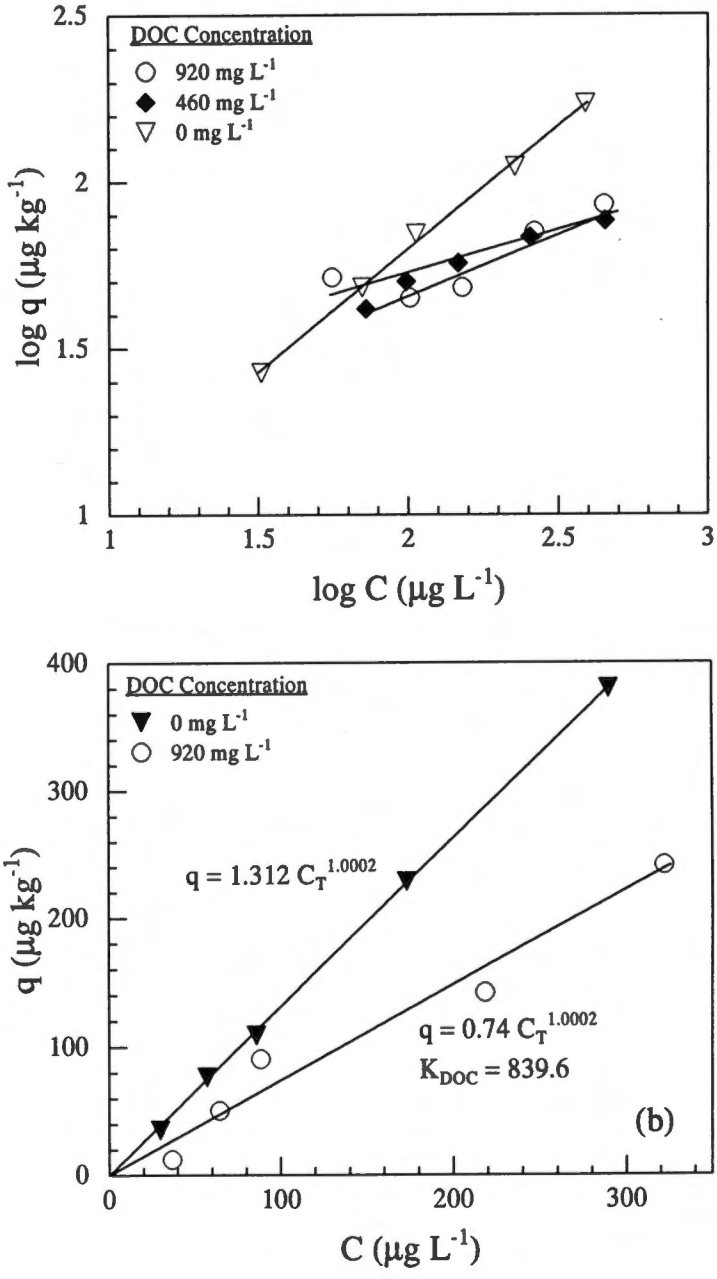


Figure 4.9. Freundlich isotherms showing the sorption of fluometuron by subsoil in the presence of (a) dairy DOC and (b) the predicted isotherm for fluometuron sorption by conventional tillage surface soil in the presence of 920 mg dairy DOC L^{-1}.

Correspondingly, these larger molecules may influence FLMT sorption to the greatest extent. As was postulated for the poultry DOC systems, the formation of soluble complexes between the large molecules of the dairy DOC and FLMT molecules could consume significant quantities of FLMT and reduce sorption. Alternatively, the large DOC molecules could be adsorbed to the soil surface and form a organic coating on the soil. This organic coating may present a hydrophobic surface to FLMT in the soil solution. Thus, FLMT molecules would remain in solution, and an overall reduction in FLMT sorption would be observed.

The K_{DOC} value, computed from the sorption data for FLMT sorption to CT soil in the presence of 920 mg dairy DOC L^{-1}, is 840 L kg^{-1} (Figure 4.9). The K_{DOC} for sorption of FLMT in the presence of 460 mg dairy DOC L^{-1} is 845 L kg^{-1}. The similarity in the two dairy K_{DOC} constants could indicate that hydrophobic partition of FLMT into dairy DOC may result in soluble complexes in these systems. However, these K_{DOC} values are more than 5 times greater than the K_{OC} (145) for this system. A greater computed K_{DOC} suggests that the formation of a FLMT - DOC complex is not occurring in these systems. It then follows that another mechanism, such as competition between DOC and herbicide molecules for surface sorption sites, is responsible for the reduced sorption of FLMT by CT and SUB soil in the presence of dairy DOC.

No-till Dissolved Organic Carbon

The effect of NT-DOC on the sorption of FLMT by SUB soil is shown in Figure 4.10. In general, the Freundlich isotherms indicate a decrease in FLMT sorption in the presence of NT DOC, relative to the 0 mg L^{-1} system. The NT DOC isotherms are

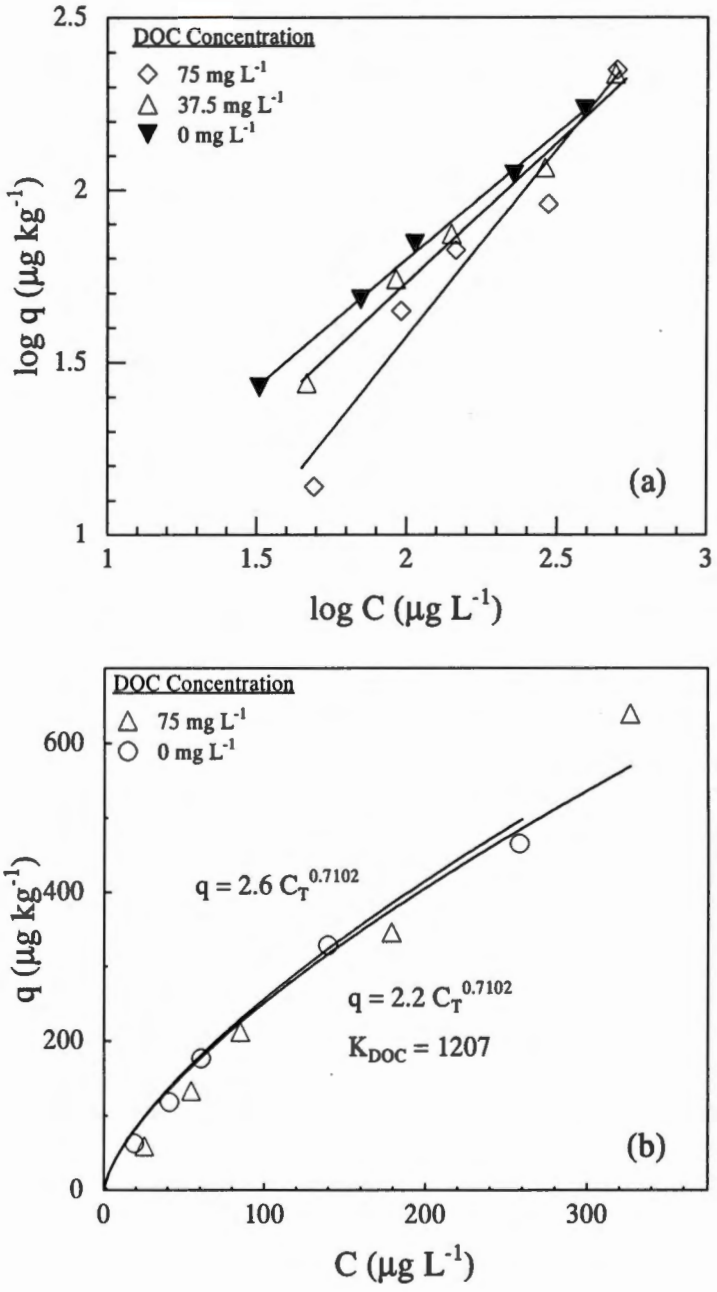


Figure 4.10. Freundlich isotherms showing the sorption of fluometuron by subsoil in the presence of (a) no-till surface soil DOC and (b) predicted sorption isotherms for the sorption of fluometuron in the presence of no-till DOC.

significantly different from each other and from the 0 mg L^{-1} DOC system. The K_F values suggest less sorption of FLMT at 1 μg L^{-1} in the presence of DOC than in the 0 mg L^{-1} DOC system (Table 4.5). However, the K_D values do not indicate a great reduction in FLMT sorption, relative to the sorption reduction observed in the dairy and poultry DOC systems (Table 4.5). Other researchers have reported no effect of soil derived DOC at concentrations less than 100 mg L^{-1} on the retention of trace organic compounds (Chiou et al. 1986; Madhun et al. 1986). However, this study indicates that concentrations of 75 and 37.5 mg L^{-1} can significantly alter the sorption of FLMT.

Dissolved organic carbon in the NT extract is composed of organic compounds that are similar in size to the herbicides examined in this study (Figure 3.1). Both the poultry and dairy DOC extracts had significant proportions of relatively high molecular weight compounds. Moreover, these two extracts had a greater influence on FLMT sorption. The 102 mg poultry DOC L^{-1} isotherms are probably most comparable to the NT DOC isotherms because of similar DOC concentrations. Poultry DOC caused a significant decrease in the slope of the SUB soil isotherm while NT DOC increased the isotherm slope. It is apparent that the difference in molecular size distribution between the NT and biosolid extracts results in different FLMT sorption response.

The K_{DOC} value computed for sorption of FLMT in the presence of 75 mg NT DOC L^{-1} in SUB soil is 1207 L kg^{-1} (Figure 4.10). The K_{DOC} for the 37.5 mg NT DOC system is 489 L kg^{-1}. Thus, K_{DOC} is not a constant in these NT DOC systems. The K_{DOC} values for these SUB systems do not indicate the formation of herbicide - DOC complexes in the presence of NT DOC. The K_{DOC} for FLMT sorption this system is only

124 (Table 4.5). Therefore, the formation of a DOC - herbicide complex is unlikely. Since the NT DOC molecules are relatively small and similar in size to the herbicides, they probably compete with FLMT for sorption sites.

Norflurazon Sorption

Poultry Dissolved Organic Carbon

The presence of poultry DOC reduced the sorption of NORF by CT surface soil (Figure 4.11). The 460 mg L^{-1} DOC isotherm is statistically equal to the 0 mg L^{-1} DOC isotherm (Table 4.6). However, the 920, 205, and 102 mg L^{-1} DOC isotherms exhibit significantly less NORF sorption by CT soil. The K_D values further illustrate the reduced sorption of NORF by CT soil in the presence of poultry DOC (Table 4.6). The K_D values also indicate that NORF sorption is generally inversely correlated to poultry DOC concentration in the equilibration solutions.

Sorption of NORF to NT surface soil was influenced the presence of poultry DOC in the sorption system (Figure 4.12). The four poultry DOC isotherms are statistically different from the 0 mg L^{-1} isotherm ($\alpha = 0.05$), with the exception of the 460 mg L^{-1} DOC isotherm (Table 4.7). Norflurazon sorption by NT surface soil was decreased by the poultry DOC. In general, the K_D values increased with decreasing poultry DOC concentrations.

All four concentrations of poultry DOC significantly decreased the sorption of NORF by SUB soil, relative to the 0 mg L^{-1} DOC system (Figure 4.13) and (Table 4.8). The K_D values (Table 4.8) indicate that sorption of NORF by SUB soil in the presence of poultry DOC was correlated to decreasing DOC concentration.

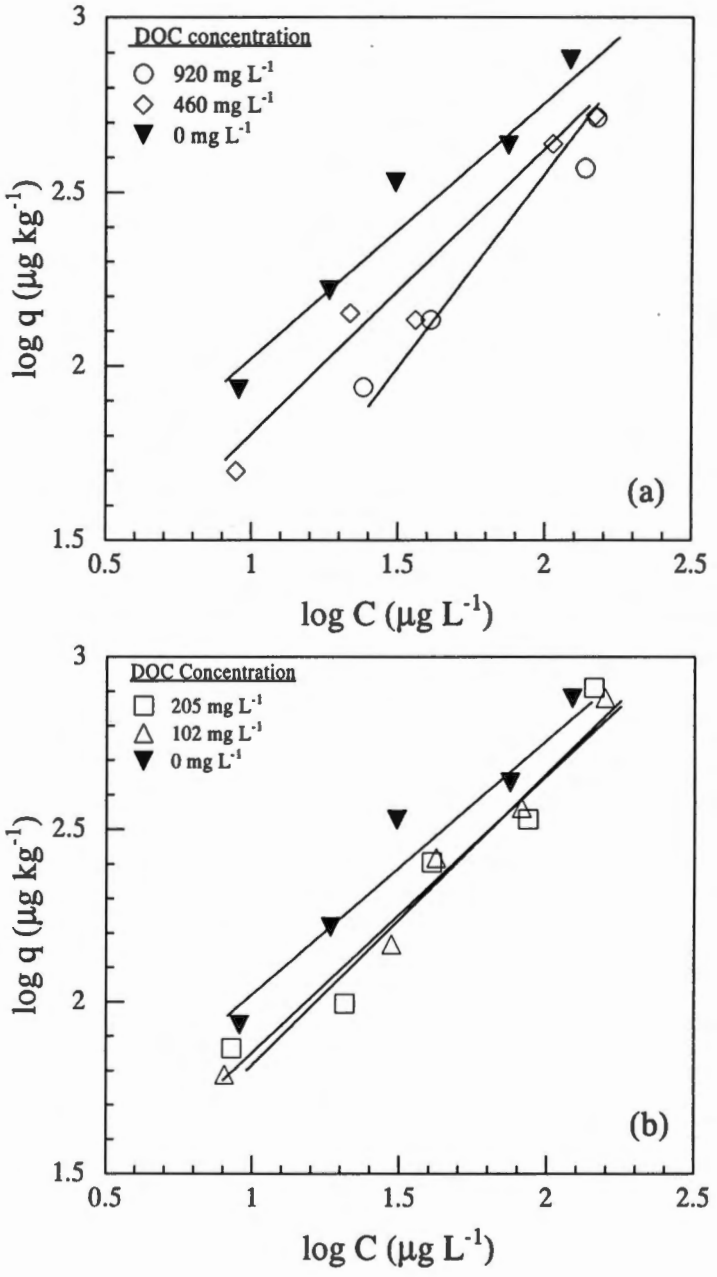


Figure 4.11. Freundlich isotherms showing the sorption of norflurazon to conventional tillage surface soil in the presence of poultry litter DOC.

Table 4.6. Freundlich isotherm parameters, distribution coefficients (K_D), and K_D values normalized for the fractional organic content of the sorbent (K_{OC}), for the sorption of norflurazon by conventional tillage surface soil with poultry and dairy dissolved organic carbon.

DOC Concentration mg L^{-1}	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
0	1.28	0.74	a	0.9344**	7.67	540
			Poultry DOC			
920	0.31	1.12	b	0.9746**	3.05	215
460	0.98	0.82	ac	0.9732**	5.07	357
205	0.97	0.84	c	0.9123**	5.31	374
102	1.05	0.80	c	0.9441**	5.56	391
			Dairy DOC			
920	1.19	0.70	ac	0.9231**	5.43	382
460	1.44	1.10	d	0.7989**	3.84	271

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level

§ *, ** indicate significance at the 0.05 and 0.01 levels.

¶ Distribution coefficients derived from the equation: $K_D = q/C$, C = 32 μg L^{-1} and q computed from the Freundlich model.

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D / foc$, where foc = 0.0142.

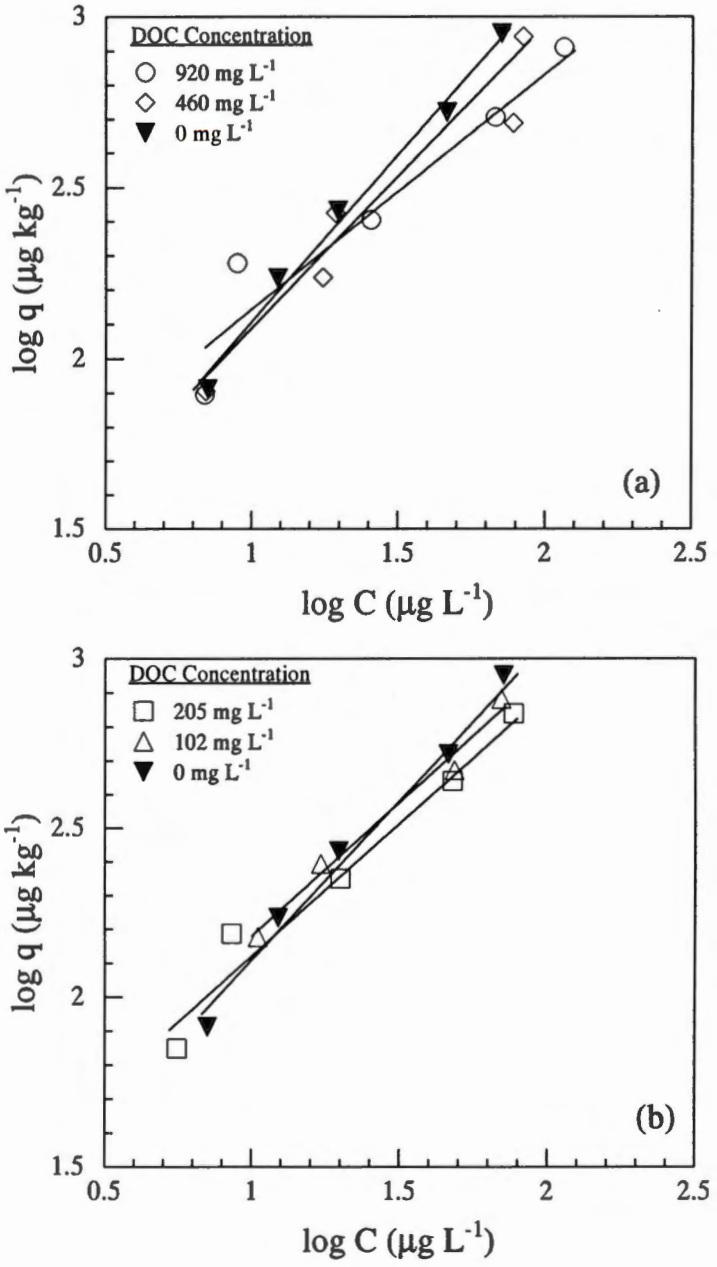


Figure 4.12. Freundlich isotherms showing the sorption of norflurazon to no-till surface soil in the presence of poultry litter DOC.

Table 4.7. Freundlich isotherm constants, sorption distribution coefficients (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}), for the sorption of norflurazon by no-till surface soil with poultry and dairy dissolved organic carbon.

DOC Concentration	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
mg L^{-1}						
0	1.13	0.98	a	0.9835**	12.44	508
			Poultry DOC			
920	1.43	0.69	b	0.8879**	9.12	372
460	1.20	0.89	ac	0.9299**	10.71	437
205	1.34	0.79	bc	0.9510**	10.47	427
102	1.39	0.79	bc	0.9745**	10.74	479
			Dairy DOC			
920	1.41	0.75	b	0.9643**	10.71	437
460	1.32	0.81	ab	0.7417**	10.71	437

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level.

§ *, ** indicate significance at the 0.05 and 0.01 levels

¶ Distribution coefficients derived from the equation: $K_D = q/C$, C = 32 μg L^{-1}, and q computed from the Freundlich model

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D$ / foc, where foc = 0.0245

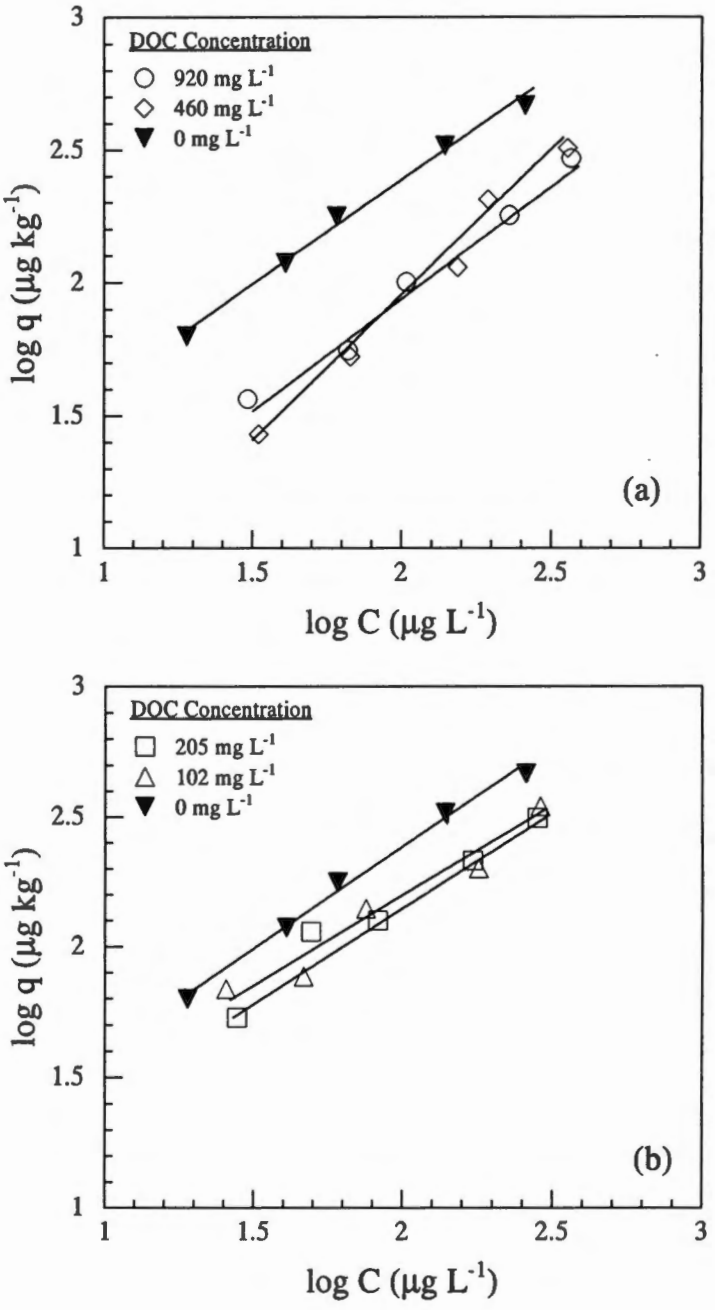


Figure 4.13. Freundlich isotherms showing the sorption of norflurazon to subsoil in the presence of poultry litter DOC.

Table 4.8. Freundlich isotherm constants, sorption distribution coefficients (K_D), and K_D values normalized for the fractional organic carbon content of the sorbent (K_{OC}), for the sorption of norflurazon by subsoil with poultry, dairy, and no-till dissolved organic carbon.

DOC Concentration mg L^{-1}	log K_F†	N†	Sorption Model‡	r^2§	K_D¶	K_{OC}#
0	0.81	0.79	a	0.9909**	2.45	663
			Poultry DOC			
920	0.25	0.84	b	0.9348**	0.85	230
460	-0.24	1.10	c	0.9289**	0.91	246
205	0.67	0.74	ad	0.9413**	1.41	382
102	0.81	0.70	d	0.9365**	1.62	438
			Dairy DOC			
920	0.63	0.75	abde	0.7306**	1.35	365
460	0.23	0.95	b	0.9397**	1.35	365
			No-till DOC			
75	0.53	0.91	e	0.9895**	2.24	605
37.5	0.81	0.79	a	0.9934**	2.25	663

† K_F and N are parameters in the Freundlich sorption isotherm model: $q = K_F C^N$, where q and C are sorbed and solution equilibrium concentrations of the herbicide

‡ Sorption models identified by the same letter are not significantly different at the 0.05 level

§ *, ** indicate significance at the 0.05 and 0.01 levels

¶ Distribution coefficients derived from the equation: $K_D = q/C$, C = 100 μg L^{-1}, q computed from the Freundlich model

Organic carbon normalized sorption distribution coefficient derived from the equation: $K_{OC} = K_D$ / foc, where foc = 0.0037

In general, sorption of NORF in the presence of poultry DOC was decreased, relative to the 0 mg L^{-1} DOC system. Although not evident with all poultry DOC concentrations, a general correlation between DOC concentration and decreased NORF sorption is evident with all three soils. The large poultry DOC molecules may have coated the soil surfaces and excluded the smaller more hydrophilic NORF and FLMT molecules from adsorbing to the soil surfaces. Moreover, the poultry DOC may have competed with the herbicides for sorption sites.

The K_{DOC} for NORF associated with poultry DOC are 2917, 4162, 6480, and 10,250 L kg^{-1} for the 920, 460, 205, and 102 mg poultry DOC L^{-1} systems, respectively. As with the sorption of FLMT in the presence of poultry DOC, the K_{DOC} values are not constant, and increase with decreasing DOC concentration. Further, K_{DOC} values should not exceed the K_{OC} values, as solid SOM is a much better sorbent of trace herbicides. The K_{DOC} values computed for the poultry DOC systems exceed 2917 L kg^{-1}, more than 4 times larger than the K_{OC} for this system (663) (Figure 4.14) and (Table 4.8). Therefore, the decrease in NORF sorption that is observed in the poultry DOC systems is a result of the large molecules of the poultry DOC coating the sorptive surfaces and forcing herbicide molecules to remain in the aqueous phase.

Dairy Dissolved Organic Carbon

Sorption of NORF by CT surface soil was decreased in the presence of dairy DOC, relative to the 0 mg L^{-1} DOC systems (Figure 4.15). Sorption of NORF in the 920 mg L^{-1} DOC system was not significantly different from that in the 0 mg L^{-1} DOC system (Table 4.6). However, the 460 mg L^{-1} DOC system showed significantly less sorption of

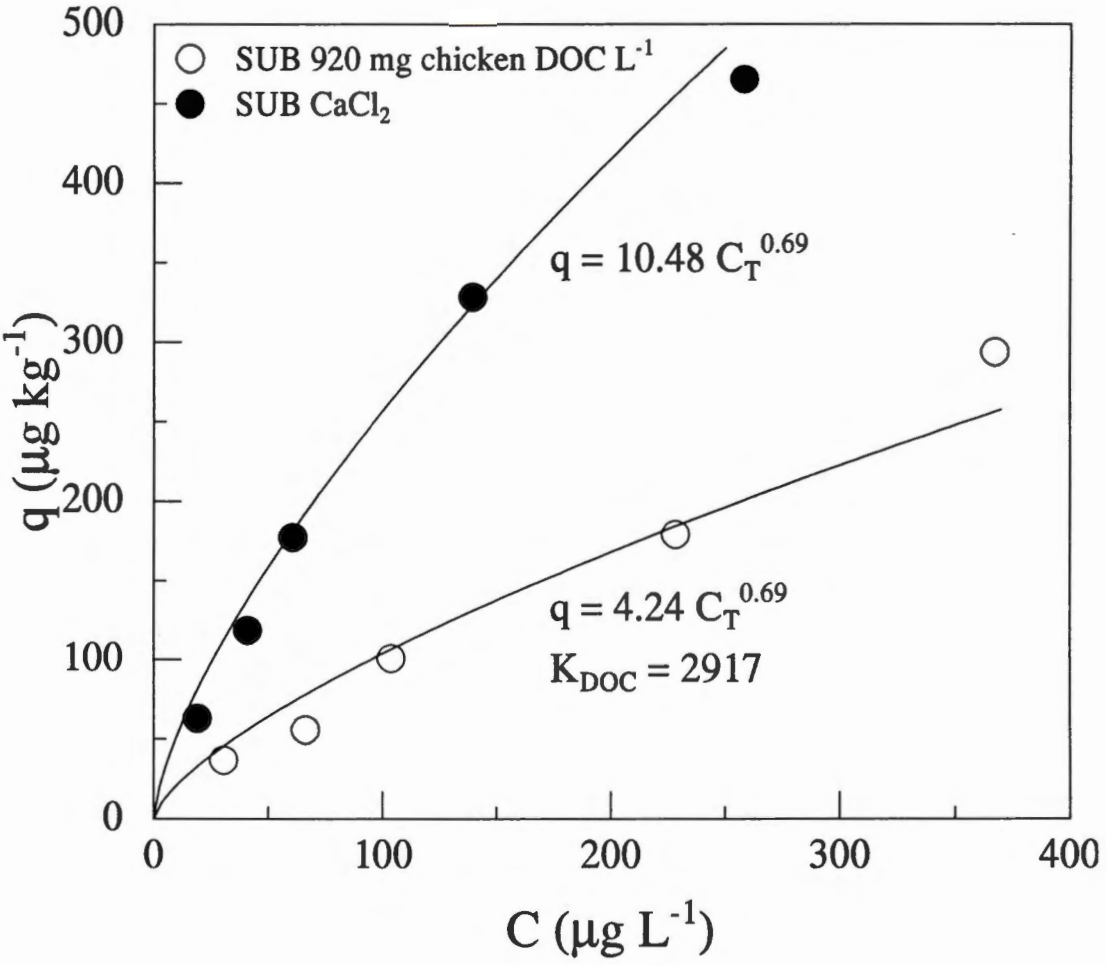


Figure 4.14. Predicted isotherm for the sorption of norflurazon by subsoil in the presence of 920 mg poultry litter DOC L^{-1} shown with the 0 mg DOC L^{-1} isotherm.

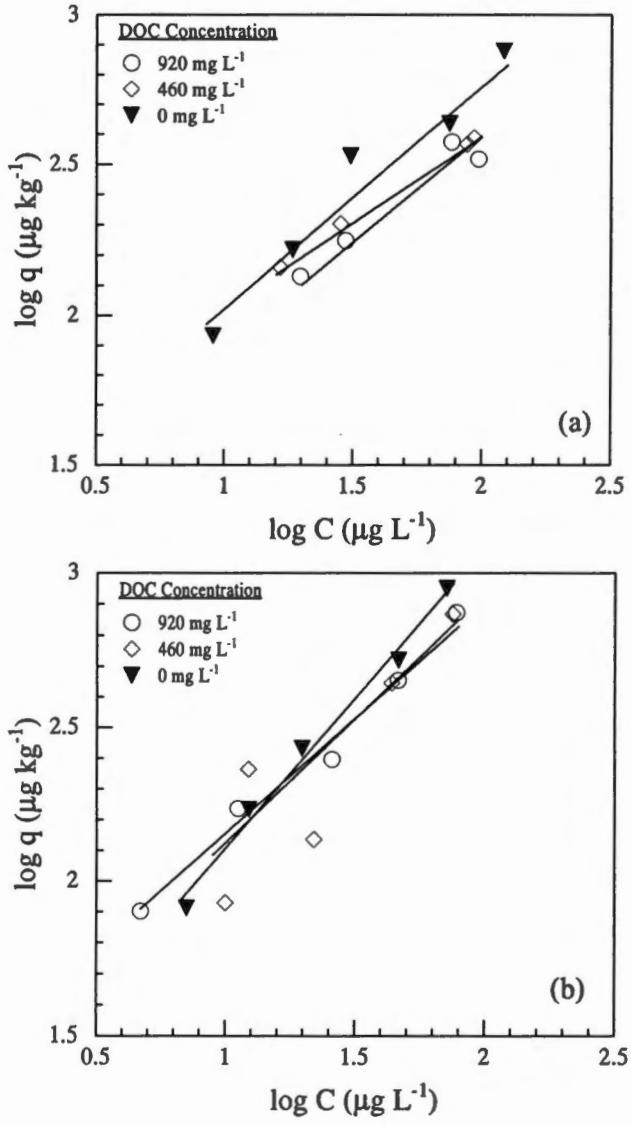


Figure 4.15. Freundlich isotherms showing the sorption of norflurazon by (a) conventional tillage and (b) no-till surface soil in the presence of dairy DOC.

NORF by CT surface soil at all herbicide concentrations. Although not statistically significant, K_D values for NORF sorption in the presence of dairy DOC indicate that sorption of NORF is correlated with decreasing dairy DOC concentration (Table 4.6).

Sorption of NORF by NT surface soil was influenced by the presence of dairy DOC in the sorption system (Figure 4.15). The 920 mg dairy DOC L^{-1} system shows enhanced NORF sorption at the lowest isotherm point, while NORF sorption decreased with increasing NORF concentration, relative to the 0 mg L^{-1} DOC system. Extreme scatter in the 460 mg L^{-1} dairy DOC isotherm data resulted in no significant difference from the 0 mg L^{-1} DOC system. Sorption distribution coefficients (K_D values) computed at C = 32 μg L^{-1} NORF did not vary with dairy DOC concentration (Table 4.7).

Sorption of NORF by SUB soil was decreased in the presence of dairy DOC, relative to the 0 mg L^{-1} DOC system (Figure 4.16). The 920 mg dairy DOC L^{-1} isotherm is not statistically different from the 0 mg L^{-1} DOC isotherm (Table 4.8). However, the 460 mg dairy DOC L^{-1} isotherm shows significantly less sorption of NORF at all herbicide concentrations (Table 4.8). The K_D values for the dairy DOC-SUB soil isotherms indicate that NORF sorption is inversely correlated to the DOC concentration in the system (Table 4.8).

Overall, sorption of NORF in the presence of dairy DOC was reduced, relative to the 0 mg L^{-1} DOC system. Although the trend was not statistically significant with all systems, NORF sorption was inversely correlated with DOC concentration. Poultry DOC effected NORF sorption to a greater extent in all sorption systems. Correspondingly, the poultry DOC had the greatest proportion of large size organic molecules (Figure 3.1).

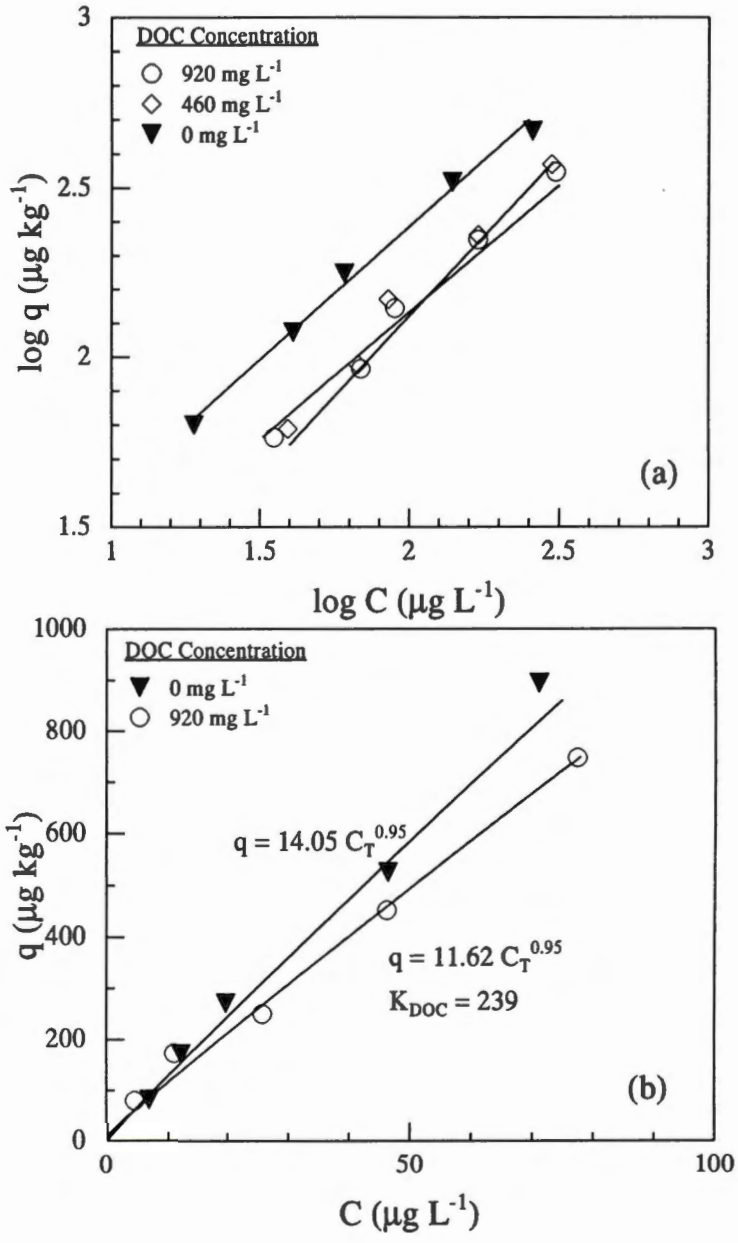


Figure 4.16. Freundlich isotherms showing (a) sorption of norflurazon by subsoil in the presence of dairy DOC and (b) the predicted isotherm for the sorption of norflurazon by no-till surface soil in the presence of 920 mg dairy DOC L^{-1}.

The dairy DOC had a distribution of both large and small DOC molecules. Thus, the larger humic acid molecules probably influenced NORF sorption in these systems.

The formation of a herbicide-DOC complex in solution can be assessed with K_{DOC} values. As with the FLMT systems, the K_{DOC} value for NORF sorption by NT soil in the presence of 920 mg dairy DOC L^{-1} suggests an unreasonably large influence of dairy DOC-herbicide complexation in these systems (Figure 4.16). The K_{DOC} values for NORF sorption in the presence of 920 and 460 mg dairy DOC are 239 and 361 L kg^{-1}, respectively. The K_{DOC} values are similar for both dairy DOC systems. Thus, it is possible that these values represent the formation of DOC - herbicide complexes in the NT surface soil systems. However, the K_{DOC} values are much greater than the K_{OC} for this system (365). Thus, the formation of DOC - herbicide complexes in solution does not occur to a significant extent.

No-till Dissolved Organic Carbon

Dissolved organic carbon from the NT surface soil had little effect on the sorption of NORF by SUB soil (Figure 4.17). The 37.5 mg L^{-1} NT-DOC concentration had no effect on the sorption of NORF. However, the 75 mg L^{-1} NT-DOC concentration isotherm exhibits significantly less NORF sorption than the 0 and 37.5 mg L^{-1} isotherms (Table 4.8). Although the K_D values for the NT DOC isotherms are very close, the 75 mg L^{-1} system exhibited significantly less sorption of NORF (Table 4.8).

The K_{DOC} value for the 75 mg NT DOC L^{-1} is 11079 L kg^{-1} (Figure 4.17). This K_{DOC} value is significantly larger than the K_{OC} for this system (605) (Table 4.8). Thus,

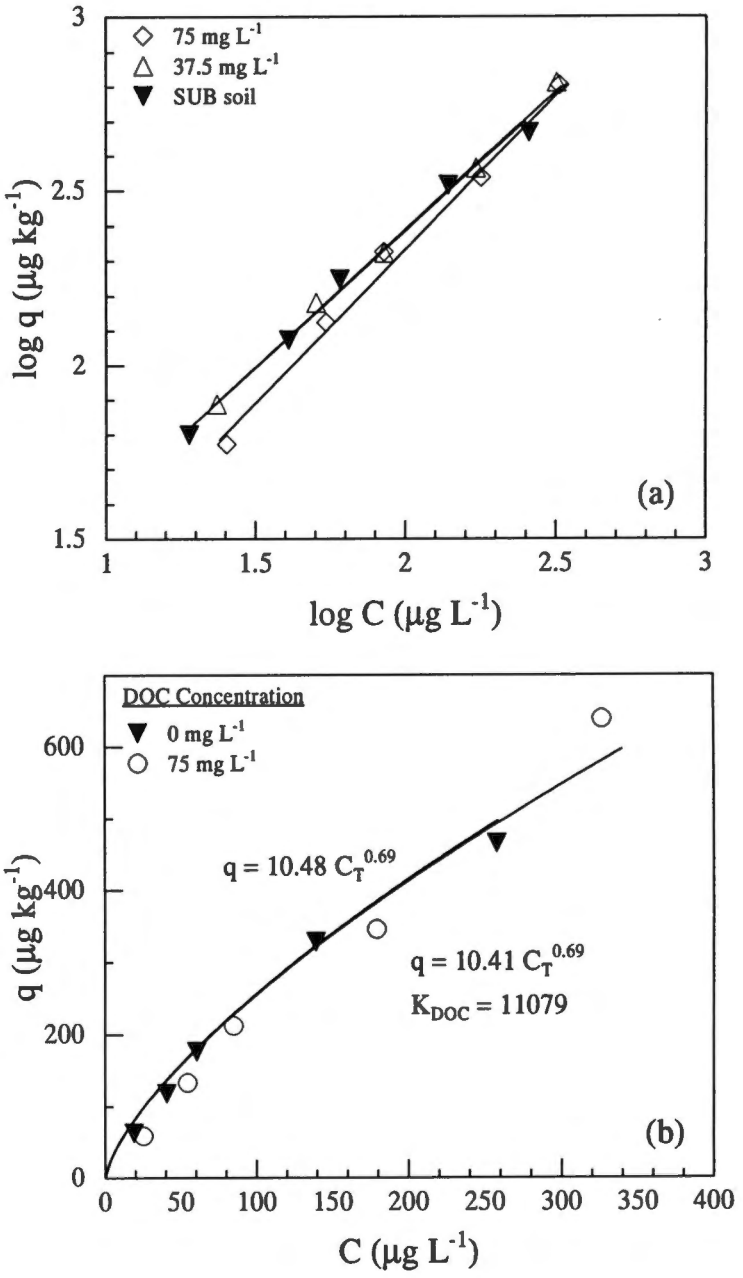


Figure 4.17. Freundlich isotherms showing (a) sorption of norflurazon by subsoil in the presence of no-till surface soil DOC and (b)the predicted isotherm for this same system.

the isotherm deflection noted with the NT DOC system is not attributed to the formation of a herbicide-DOC complex.

An overall reduction in herbicide sorption resulted from NT DOC in the equilibration solution. The small NT DOC molecules, similar in size to the herbicides, may have competed for sorption sites in the SUB soil matrix. The NT DOC gel chromatograph indicates that the NT DOC molecules are very similar in size to the NORF molecules. These DOC molecules could compete with the herbicides for sorption onto the limited soil surface sites.

Desorption of Fluometuron and Norflurazon

The desorption of FLMT and NORF from NT and CT managed surface soil and SUB soil was initiated by removing 5 ml of solution from the sorption systems having initial herbicide concentrations of 300 $\mu g\ L^{-1}$. This solution was replaced with 5 ml of the background electrolyte (with or without DOC) and equilibrated on a reciprocating shaker. The kinetics of the desorption equilibration was analyzed by determining the herbicide desorbed after 1, 3, 7, 14, or 28 days.

Three sets of desorption systems were created to determine the influence of tillage, DOC source and concentration, and kinetics on the desorption of FLMT and NORF from CT, NT, and SUB soil. The first set of desorption experiments was conducted without DOC in the sorption or desorption equilibration solutions. These systems were used as controls to determine the influence of DOC on the desorption processes in the other sets. A second set of experiments was conducted to assess the effects of DOC source and concentration on the desorption process. The two herbicides

were sorbed in the absence of DOC. Then, 5 ml of DOC solution was added at the desorption step to bring DOC concentrations to 460 and 230 mg DOC L^{-1}. The third set of experiments was conducted to determine the influence of DOC on the desorption of FLMT and NORF adsorbed in the presence of DOC. The poultry and dairy DOC concentrations in these sorption systems were 920 and 460 mg L^{-1}, while the DOC concentration in the desorption systems was 1150 and 575 mg DOC L^{-1}. An additional set of poultry DOC experiments was conducted where the initial DOC concentrations were 205 and 102 mg DOC L^{-1} and the desorption DOC concentrations were 255 and 130 mg DOC L^{-1}.

Because DOC concentrations are typically lower in the subsoil than in surface soil, additional SUB soil desorption systems with dilute DOC concentrations were analyzed. Systems with FLMT and NORF adsorbed to subsoil without added DOC were adjusted such that 20 mg L^{-1} and 10 mg L^{-1} poultry litter, dairy manure, or NT surface mulch DOC was present in the desorption system.

Statistical evaluation of the desorption points consisted of comparing the 90% confidence intervals about the sorption isotherms and the desorption points. If the two confidence intervals coincided, sorption was considered to be reversible (α=0.05). If the two confidence intervals did not overlap, desorption was considered incomplete at the same level of statistical significance and desorption hysteresis was reported. A least square means separation of the desorption points determined significant differences between the day 1, 3, 7, 14, and 28 desorption points for each system (α = 0.05).

Sorption - Desorption Without Dissolved Organic Carbon

Fluometuron Desorption

The desorption of FLMT from CT, NT, and SUB soils displayed hysteresis (Figures 4.18 and 4.19). Desorption FLMT from CT soil exhibits hysteresis after 3, 7, 14, and 28 days of desorption equilibration. Desorption after 1 day of equilibration does coincide with the 90% confidence interval about the sorption isotherm, suggesting non-hysteretic behavior. However, hysteresis increased with equilibration period, suggesting that sorption of FLMT is not complete in the 72 hour sorption equilibration period. Many other researchers have noted biphasic sorption kinetics, where the greatest amount of sorption occurs in the first 2 to 48 hours . However, a second much slower, sorption phase results in a continual uptake of organic compound from the aqueous phase (Cameron and Klute, 1977; Karickhoff, 1979; McCall and Agin, 1985, Scow, 1994). Fluometuron sorption kinetics were not studied in this experiment. Thus, incomplete sorption equilibrium is only a hypothesis offered to explain the increasing sorption of FLMT by CT surface soil in this system.

Desorption of FLMT from NT soil exhibited hysteresis after 1, 3, 7, and 28 days of equilibration. Figure 4.18 shows that desorption was complete on day 14, but all other desorption points show desorption hysteresis. Fluometuron desorption from SUB soil displayed hysteresis after 3, 7, and 28 days of equilibration (Figure 4.19). Fluometuron sorption to SUB soil was reversible 1 and 14 days after sorption equilibration. However, the majority of desorption time intervals for each soil exhibit extensive hysteresis.

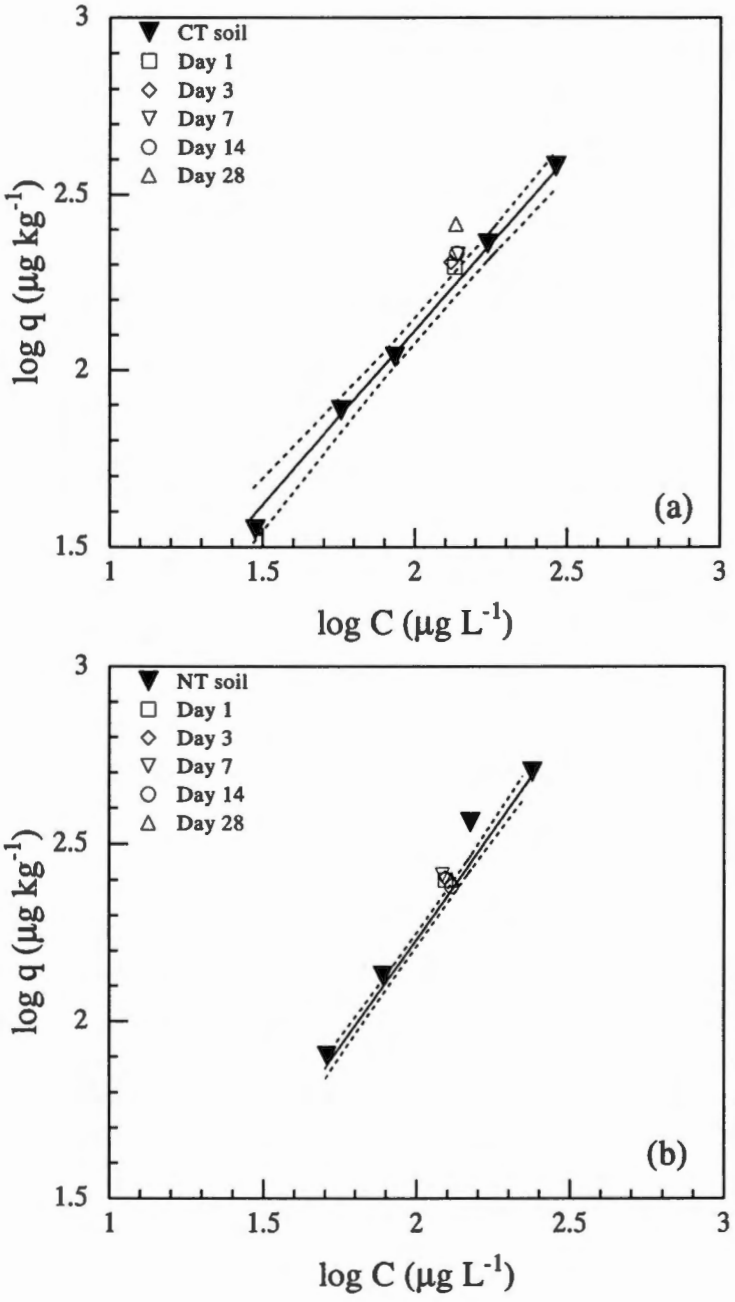


Figure 4.18. Desorption of fluometuron from (a) conventional tillage and (b) no-till surface soil.

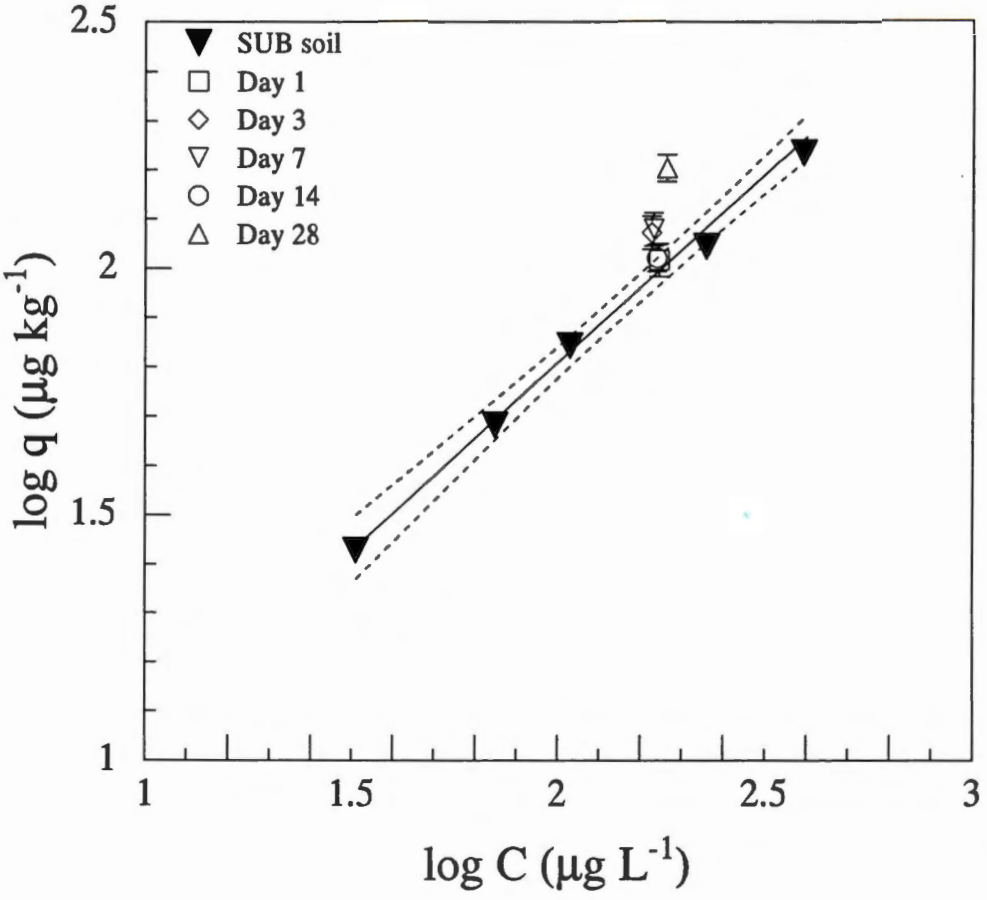


Figure 4.19. Desorption of fluometuron from subsoil.

In general, desorption of FLMT from CT, NT, and SUB soils displays hysteresis. The NT surface soil and SUB soil systems show a trend of increasing sorption of FLMT with desorption equilibration time. Hysteresis was greatest after 28 days of equilibration. Biphasic sorption kinetics result in a slow but continual sorption of FLMT by these soils throughout the desorption equilibration period.

Research indicates that FLMT and NORF persist beyond the growing season in soils under cotton cultivation (Rogers et al., 1985). This implies desorption hysteresis. Field soils are subject to many precipitation events each year that serve as desorption steps which could remove herbicide from the soil system. Essington et al. (1995) found that 10.7% and 6.4% applied FLMT in the surface 0-8 cm NT and CT soils one year after application, implying FLMT desorption hysteresis in these systems. Liu (1974) found less than 5.5% of total applied FLMT was leached below a depth of 20 cm in clay soils. Further, La Fleur et al. (1973) found that about 3.3% of applied FLMT was leached to shallow groundwater from a silty field soil. Baldwin et al. (1975) also found low runoff losses of FLMT from conventional till cotton fields. Moreover, the researchers found that FLMT sorbed by the sediment particles did not desorb from sediment. Thus, low leaching losses of FLMT and considerable carryover of adsorbed FLMT residues in soil, indicate that desorption of FLMT displays hysteresis.

Norflurazon Desorption

Hysteresis was also evident with NORF desorption from CT, NT, and SUB soils. Desorption of NORF from CT surface soil shows hysteresis after 1, 3, 7, and 28 days of equilibration (Figure 4.20). The same trend was noted with NORF desorption from NT

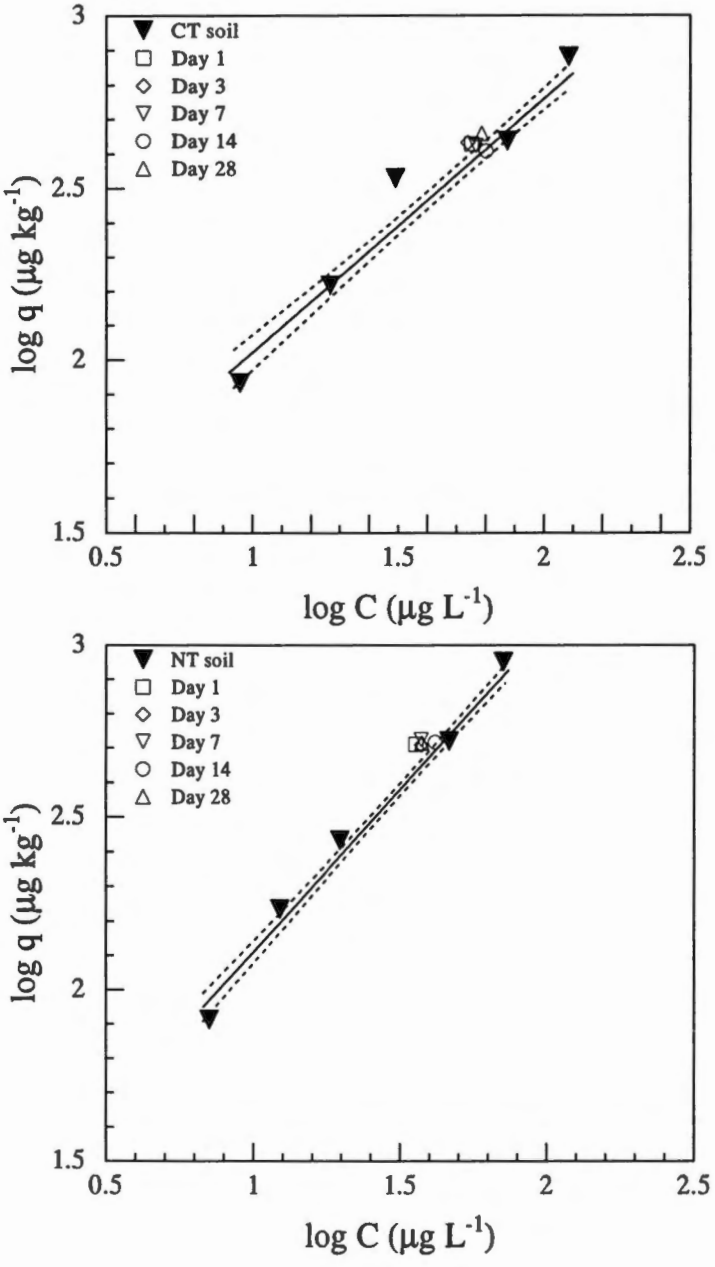


Figure 4.20. Freundlich isotherm and desorption of norflurazon from (a) conventional tillage and (b) no-till surface soil.

surface soil (Figure 4.20). Desorption of NORF from SUB soil in a background electrolyte solution displayed hysteresis with all equilibration time periods (Figure 4.21). No statistical trend of desorption equilibration time is evident with CT and NT soil. However, retention of NORF from SUB increases with desorption equilibration time (α=0.05). Increasing hysteresis with equilibration time indicates that NORF sorption continues throughout the desorption equilibration period. As with FLMT, the biphasic sorption process results in a small but continual sorption of NORF with time.

Overall, desorption of NORF from Lexington silt loam displays hysteresis. These findings are consistent with NORF in field studies. Schroder and Banks (1986) found that Bradford clay loam (2.83 g organic matter kg^{-1}) treated with 0.6 kg ha^{-1} NORF retained 0.5 mg kg^{-1} of the herbicide for 10 months. Subsequent treatment of the soil with 0.6 kg ha^{-1} NORF after 297 days resulted in the retention of 0.27 mg kg^{-1} NORF. Southwick et al. (1993) reported low leaching losses of NORF from field soils. They found that NORF runoff and leaching losses range from 0.07 to 2.3% of the applied herbicide, regardless of rainfall timing. Due to the relatively low water solubility of NORF, less leaching of the herbicide and more SOM and clay sorption causes NORF residues to persist in surface horizons of soil (Singh et al., 1985). Schroder and Banks (1986) found that NORF leaching was inversely related to SOM content. Hubbs and Lavy (1990) report that NORF sorption was positively correlated with organic matter and montmorillonite clay content of the 4 soils used in their study. The present study shows that sorption of NORF is not a reversible process. The behavior of FLMT and NORF

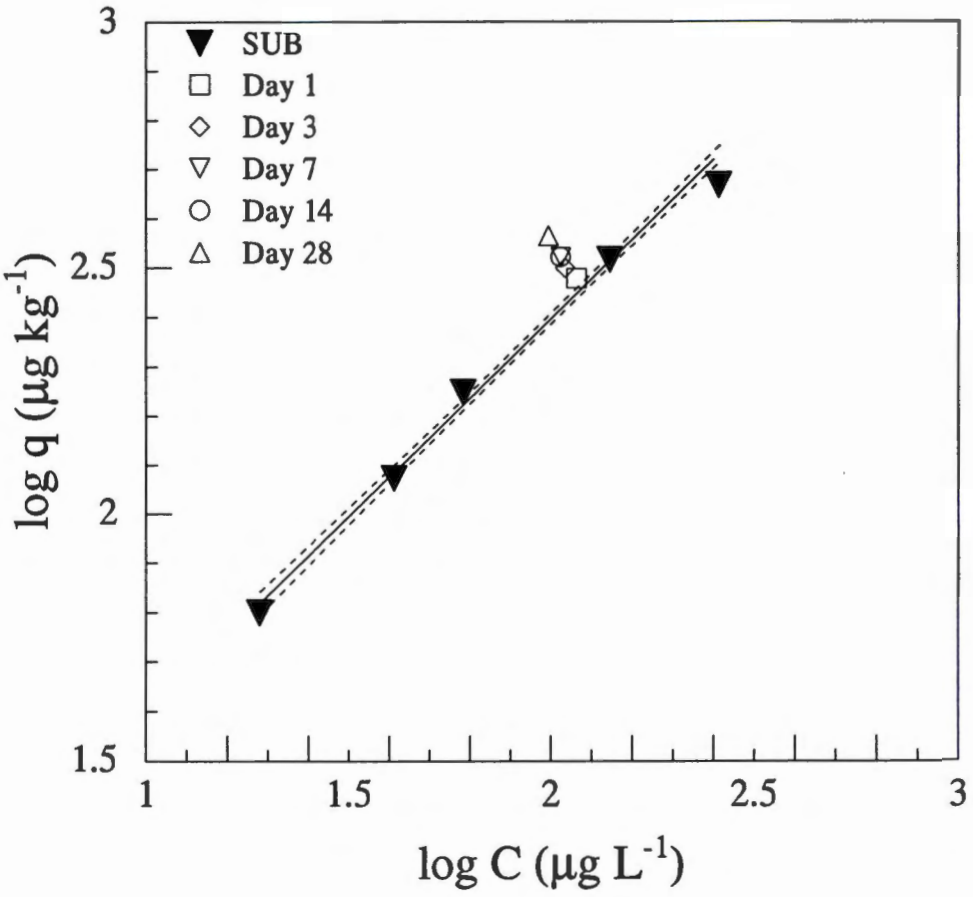


Figure 4.21. Desorption of norflurazon from subsoil.

documented in the literature confirms desorption hysteresis an important mechanism governing the fate of these herbicides.

Effect of Dissolved Organic Carbon in Desorption Solution Only

Fluometuron Desorption

Poultry Dissolved Organic Carbon:

Desorption of FLMT from CT, NT, and SUB soil was enhanced by the presence of both 460 and 230 mg poultry DOC L^{-1} in the desorption systems, compared to the 0 mg L^{-1} DOC isotherms (Figure 4.22, Figure 4.23, and 4.24). However, the addition of DOC in the desorption step changed the chemistry of the systems. The 0 mg DOC L^{-1} sorption isotherm does not represent the sorption equilibrium in the presence of poultry DOC. Therefore, desorption of FLMT should revert to a sorption isotherm of comparable DOC concentration.

Desorption of FLMT from CT surface soil was enhanced by the addition of 460 mg L^{-1} poultry DOC (Figure 4.22). Fluometuron sorption appears reversible, when compared to the 0 mg L^{-1} sorption isotherm. However, the addition of poultry DOC at the desorption step should force FLMT desorption to follow the 460 mg poultry DOC sorption isotherm. The confidence interval about the DOC isotherm was not included in this figure; however, FLMT sorption is reversible after 1 day of equilibration. A trend of increasing sorption with equilibration time characterizes the remainder of the desorption systems. Similarly, desorption of FLMT from CT appears to be complete when compared with the 0 mg DOC L^{-1} sorption isotherm. However, hysteresis is evident when desorption data are compared to the 205 mg poultry DOC L^{-1} isotherm.

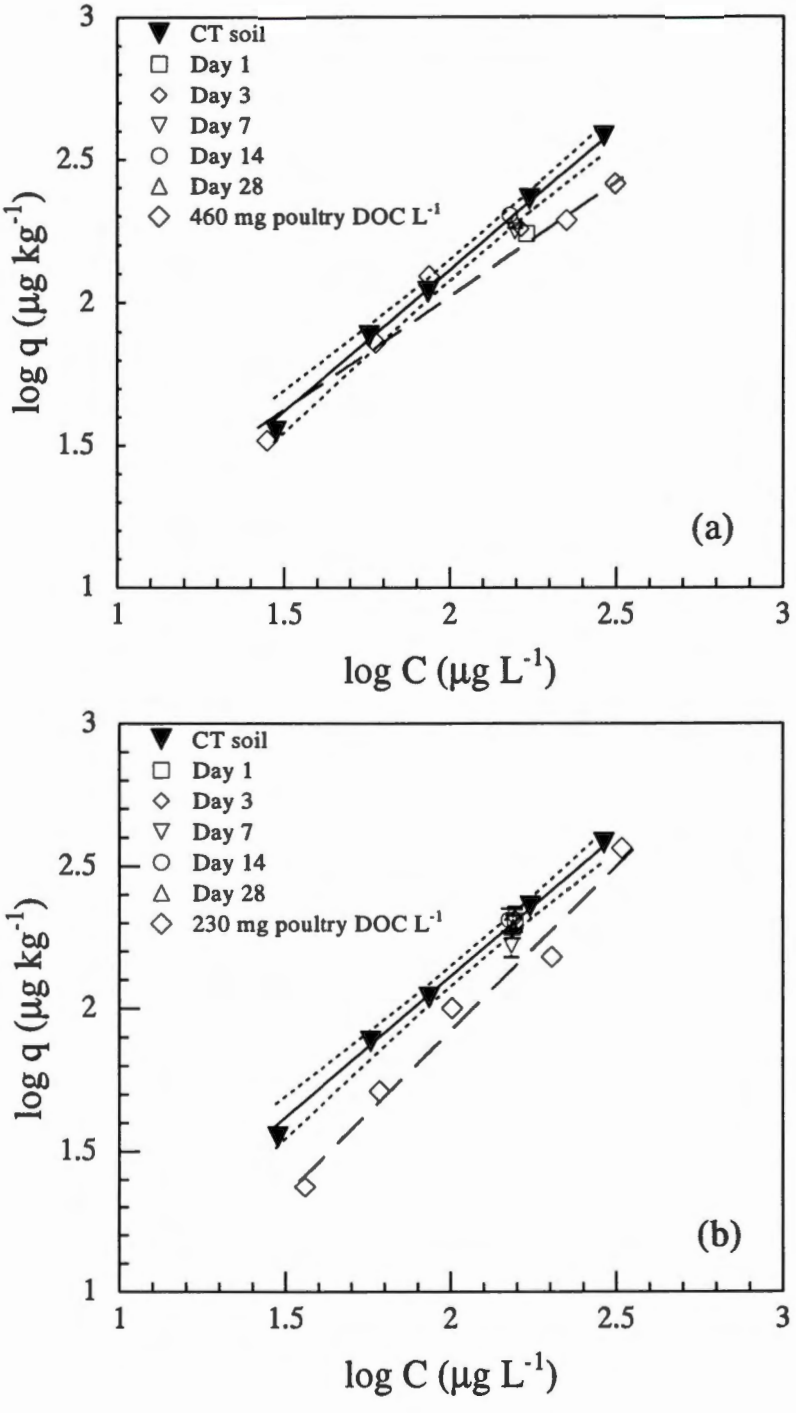


Figure 4.22. Desorption of fluometuron from conventional tillage surface soil with (a) 460 mg poultry litter DOC L^{-1} and (b) 230 mg poultry DOC L^{-1} in the desorption solution diamonds illustrate fluometruon sorption in the presence of poultry DOC.

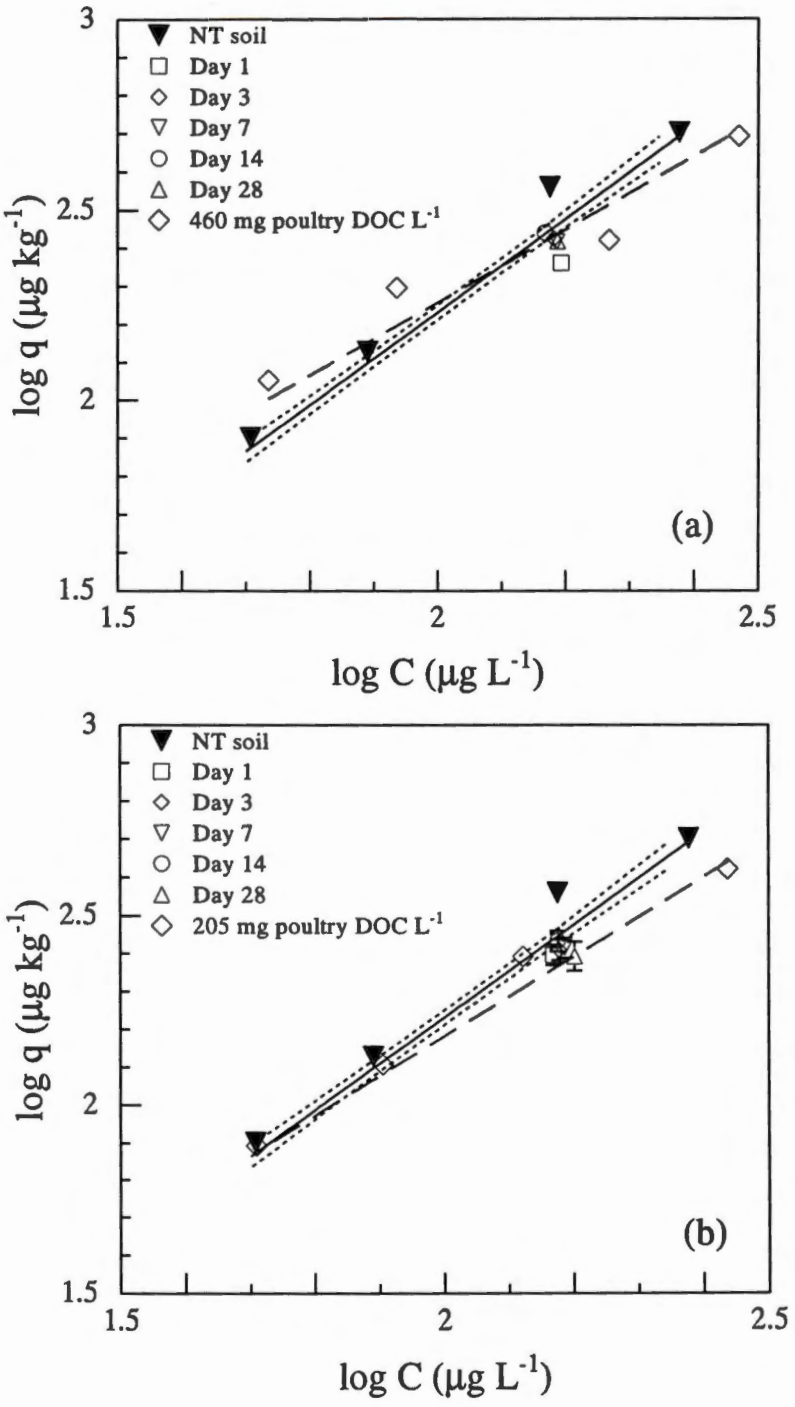


Figure 4.23. Desorption of fluometuron from no-till surface soil with (a) 460 mg poultry litter DOC L^{-1} and (b) 230 mg poultry DOC L^{-1} in the desorption solution, diamonds illustrate fluometuron sorption in the presence of poultry DOC.

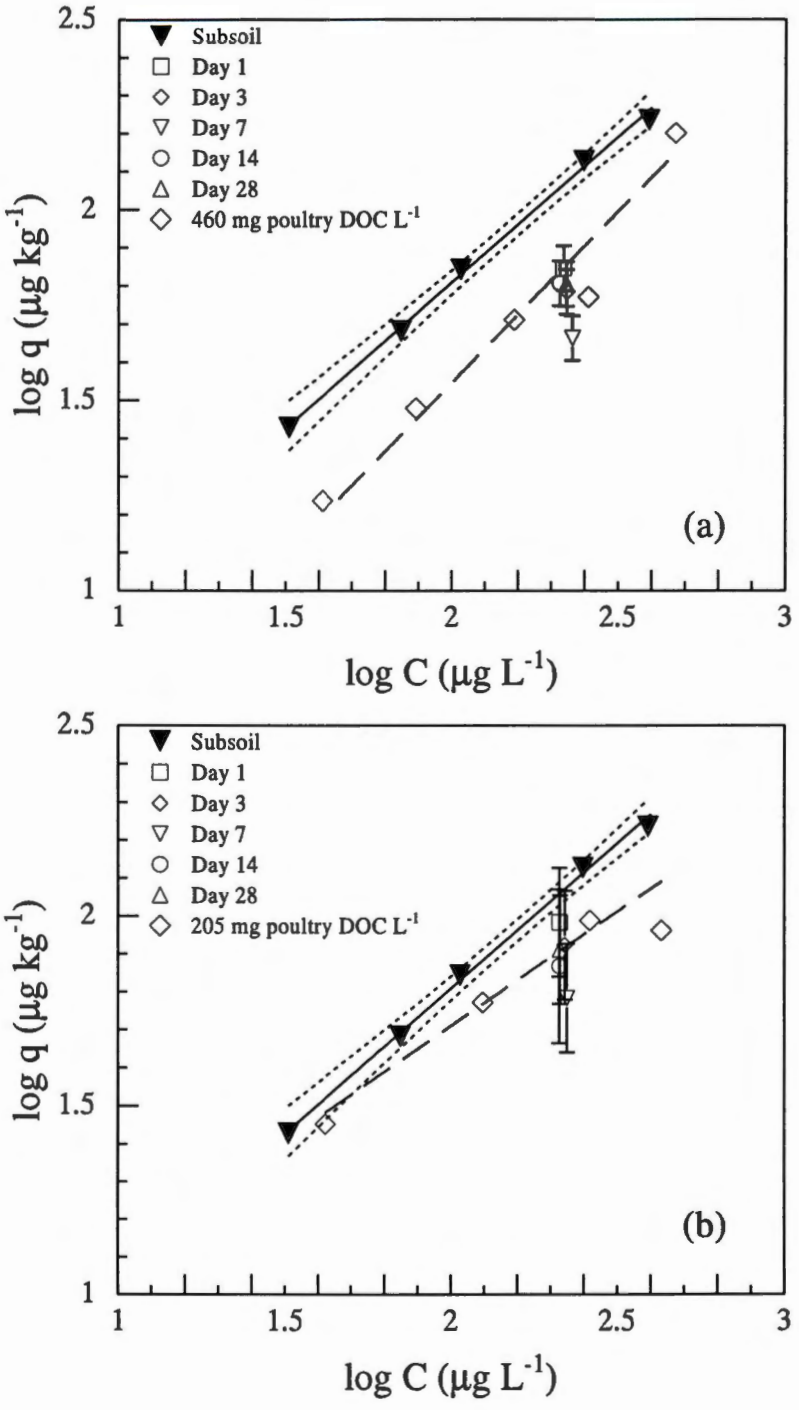


Figure 4.24. Desorption of fluometuron from subsoil with (a) 460 mg poultry DOC L^{-1} and (b) 230 mg poultry litter DOC L^{-1} in the desorption solution, diamonds illustrate fluometruon sorption in the presence of DOC.

Sorption of FLMT by NT surface soil is reversible with respect to both the 0 and 460 mg L^{-1} DOC isotherm (Figure 4.23). The desorption systems reflect FLMT sorption with desorption equilibration time. Similarly, the desorption of FLMT from NT in the presence of 230 mg poultry DOC is reversible with respect to the DOC and no-DOC isotherms (Figure 4.23). There is no effect of desorption equilibration time on the sorption equilibrium of FLMT in this system.

Desorption of FLMT from SUB soil shows the most dramatic effect of poultry DOC in the desorption solution (Figure 4.24). The presence of 460 mg poultry DOC L^{-1} in the desorption solution forces sorbed FLMT molecules into solution. Similarly, the 230 mg poultry DOC L^{-1} system shows that FLMT sorption reverts to the 205 mg DOC L^{-1} isotherm with the addition of poultry DOC in the desorption solution.

Fluometuron was sorbed without added DOC in the soil systems. The addition of poultry DOC into the desorption solution facilitated the desorption of FLMT, according to the DOC sorption isotherms. Initially, herbicide molecules occupied soil sorption sites in the sorption step without DOC. The addition of DOC molecules resulted in competition for the sorption sites. The more concentrated, less soluble DOC molecules had a greater affinity for the sorption sites. Thus, the hydrophilic FLMT molecules were displaced by the DOC.

Dairy dissolved organic carbon:

The addition of 460 and 230 mg dairy DOC L^{-1} in the desorption solution influenced the desorption of FLMT from CT surface soil (Figure 4.25). Sorption appears to be reversible with respect to the 0 mg dairy DOC L^{-1} isotherm. However, the 430 mg

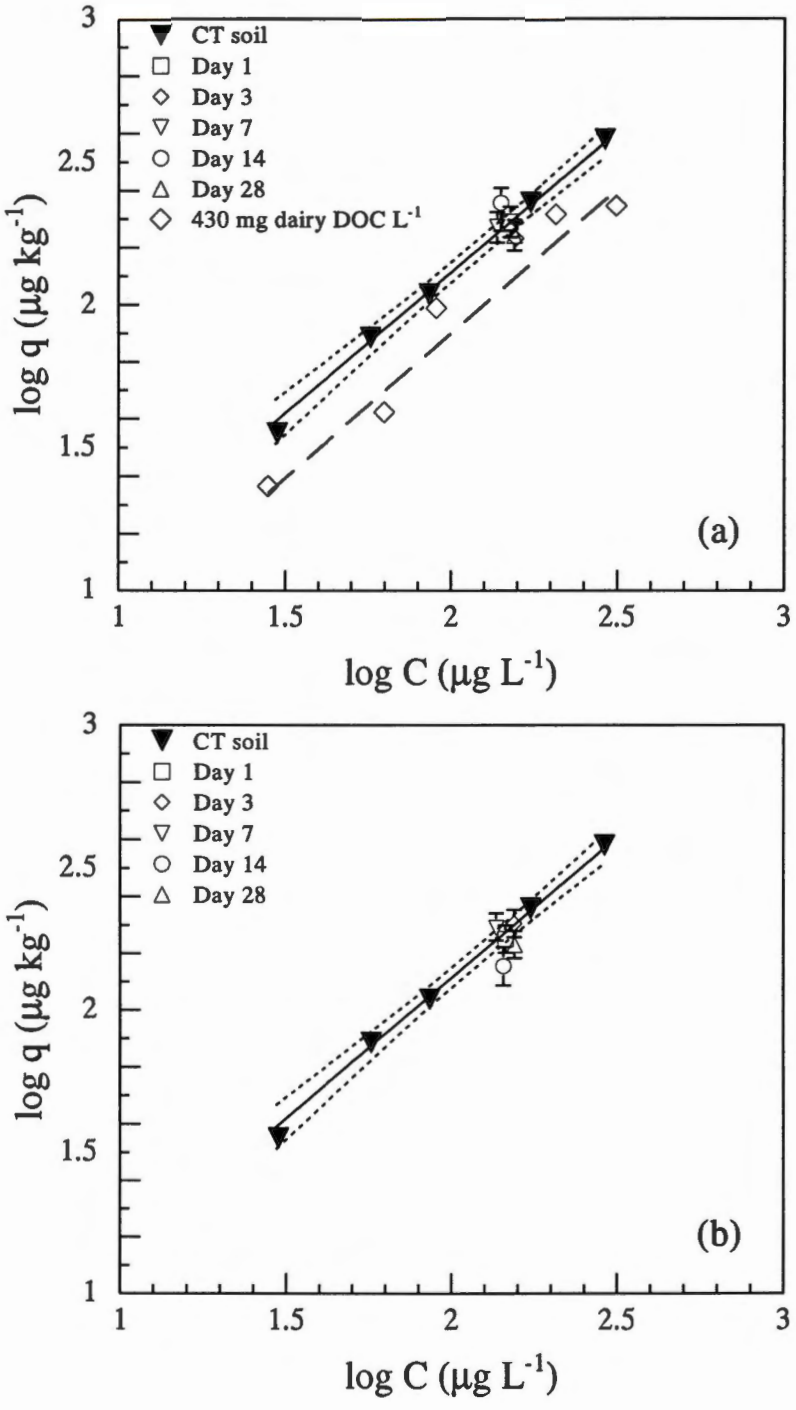


Figure 4.25. Desorption of fluometuron from conventional tillage surface soil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate fluometuron sorption in the presence of dairy DOC .

dairy DOC L^{-1} isotherm indicates FLMT desorption hysteresis. While no dairy DOC isotherm of comparable DOC concentration was investigated, one can infer that desorption in the 230 mg dairy DOC system also displayed hysteresis.

The 460 and 230 mg dairy DOC L^{-1} systems indicate significant desorption hysteresis for FLMT retention by NT surface soil (Figure 4.26). Fluometuron sorption to NT soil is not reversible with respect to the 0, 460, or 230 mg dairy DOC L^{-1} isotherms. Sorption of FLMT by SUB soil appears reversible with respect to the 0 mg L^{-1} DOC isotherm (Figure 4.27). However, significant hysteresis is evident when the appropriate dairy DOC isotherm is considered.

The dairy DOC extract in this study had a significant distribution of both large humic and smaller fulvic acid molecules. Thus, the dairy DOC had comparatively less large molecules than the poultry DOC extract. This difference in molecular size distribution may account for the different sorption trends. Perhaps the large DOC molecules had a stronger affinity for the soil sorption sites. Because there were more large DOC molecules in the poultry DOC systems, a greater competitive effect resulted in more desorption of FLMT in these systems. The bimodal size distribution of the dairy DOC had proportionally less large humic acid character molecules. Thus, less FLMT was displaced from the sorbed state.

Soluble humic substances can increase the apparent water solubility, bind by means of hydrogen, charge transfer, and van der Waals interactions, hydrolyze, photosensitize, or reduce the bioavailibility of nonpolar trace organic compounds in solution (Landrum, et.al., 1984). Abdul et al. (1990) used humic acid solutions to

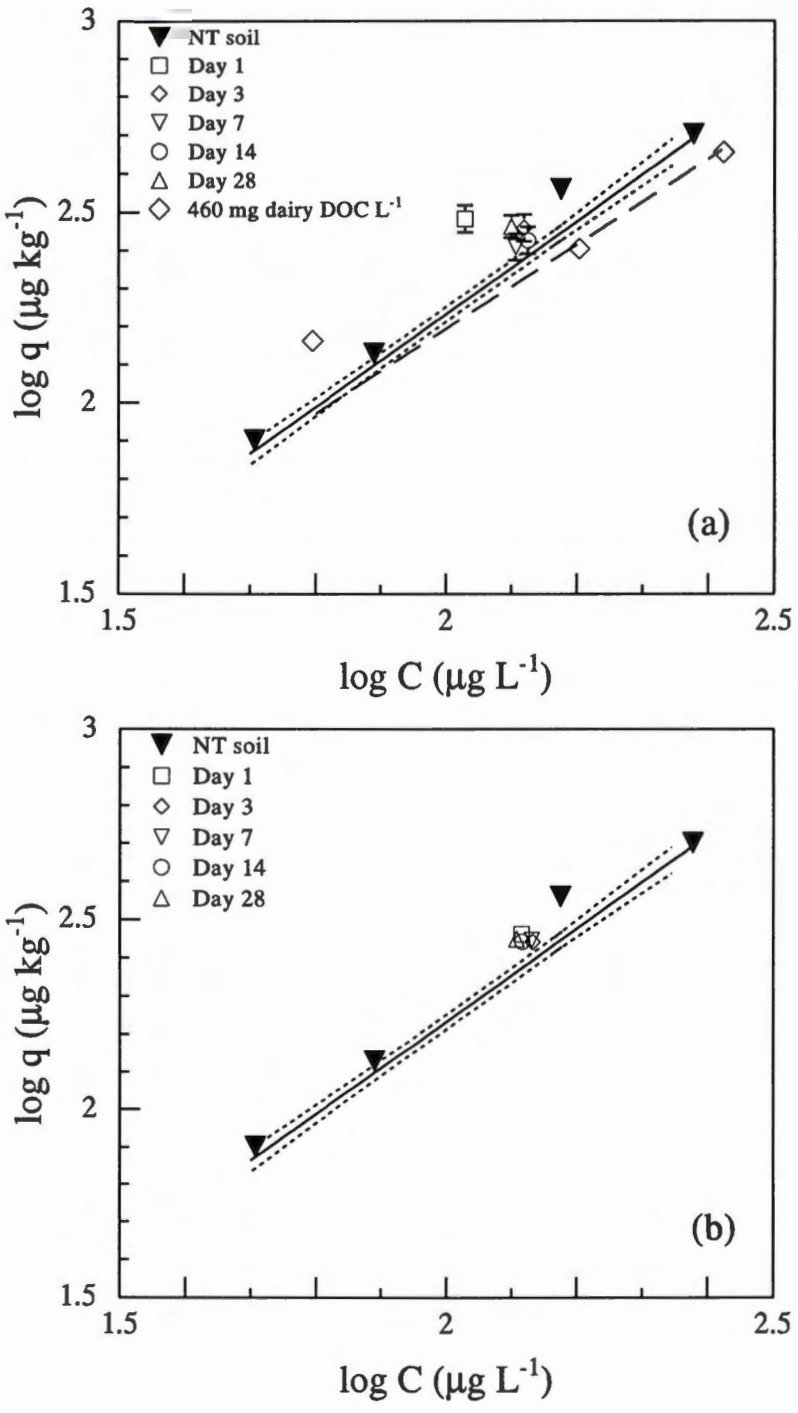


Figure 4.26. Desorption of fluometuron from no-till surface soil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate fluometuron sorption in the presence of DOC.

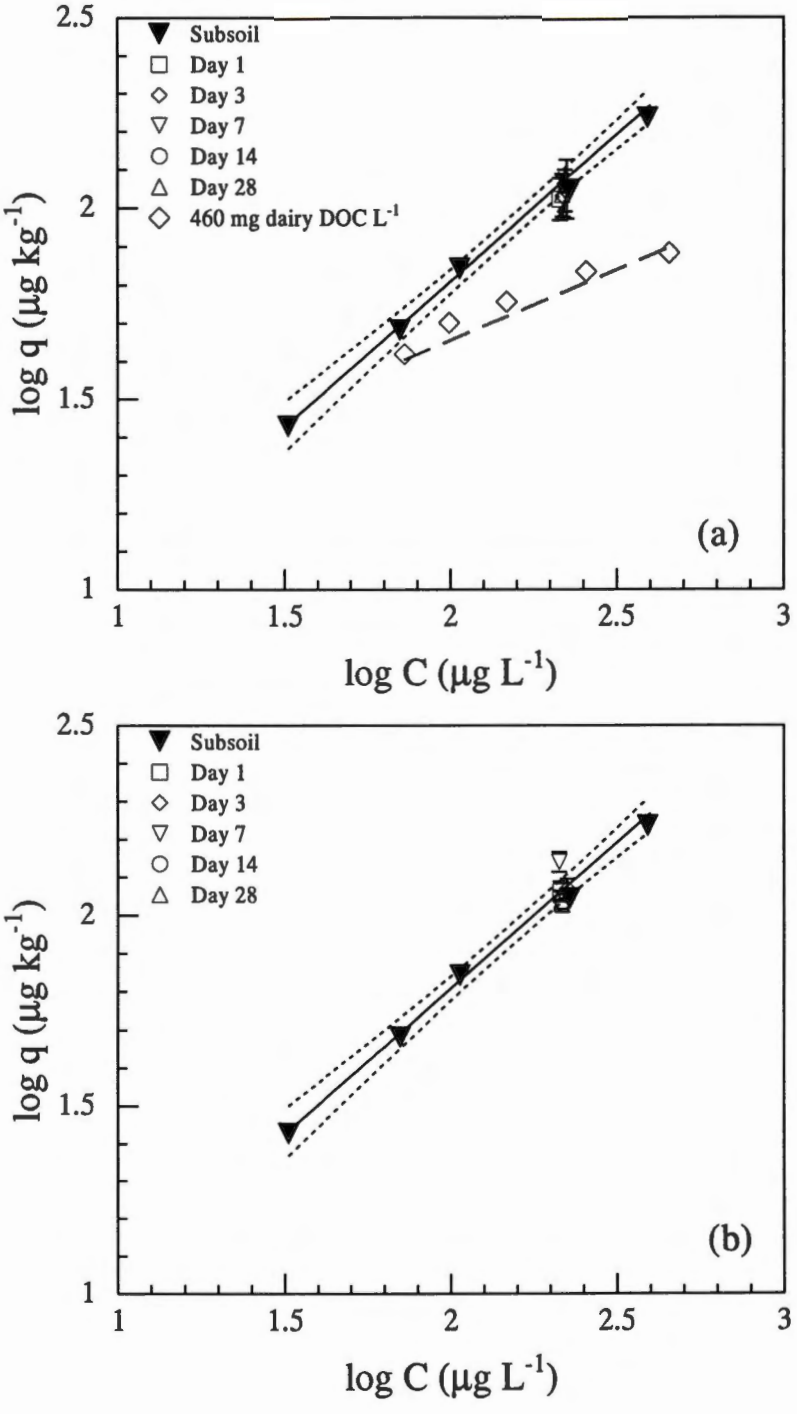


Figure 4.27. Desorption of fluometuron from subsoil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate fluometuron sorption in the presence of dairy DOC.

remove highly hydrophobic contaminants from a shallow sandy aquifer system. The 29 mg commercial humic acid L^{-1} solution removed 1.4 to 43% of toluene, benzene, and xylene applied to the simulated aquifer system. The authors attributed desorption to hydrophobic partition of the trace organic contaminants into the dissolved humic acid phase. However, the sand of the simulated aquifer system contained only silicate surface sorption sites. Organic compound sorption onto these sites is known to be minimal and easily reversed. Soil surfaces present a variety of SOM, clay, and amorphous surface sorption sites that may interact with trace organics differently than the pure sand system. Thus, there is limited research on the mechanism and nature of DOC interactions with hydrophilic organic compound sorption.

Dilute Poultry, Dairy, and No-till Dissolved Organic Carbon:

The addition of 10 or 20 mg diluted DOC extract L^{-1} into the desorption system effected the desorption of FLMT from Lexington silt loam soil. No sorption isotherms for these DOC concentrations were determined. Thus, desorption in these systems can only be compared to the no-DOC isotherms. These studies elucidate the effect of DOC concentration on the desorption of FLMT. Sorption of FLMT from SUB soil increased with equilibration time with 20 mg poultry DOC L^{-1} in the desorption solution while the 10 mg poultry DOC L^{-1} system showed significant FLMT hysteresis (Figure 4.28). These small DOC concentrations would probably exert a limited influence on FLMT sorption. Further, the results indicate that the concentration of DOC necessary to effect FLMT desorption lies between 10 and 20 mg poultry DOC L^{-1}. Fluometuron desorption increased with equilibration time with 20 mg dairy DOC L^{-1} (Figure 4.29). The 10 mg

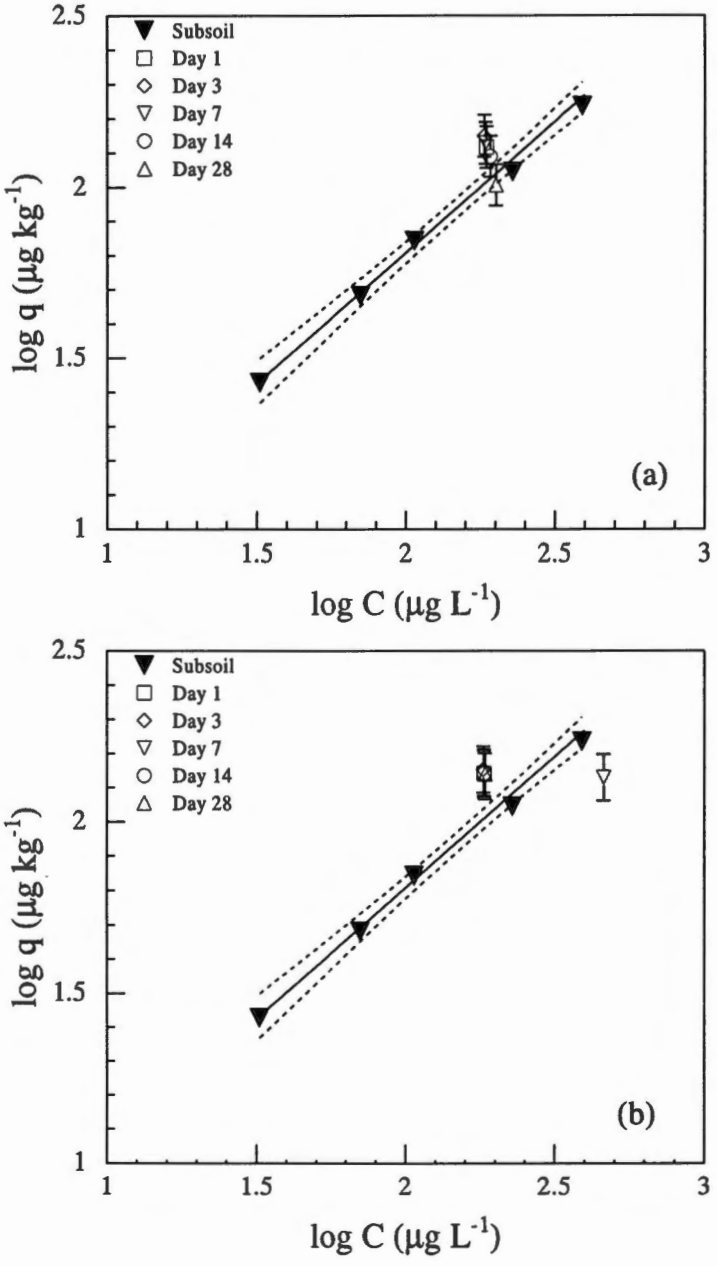


Figure 4.28. Desorption of fluometuron from subsoil with (a) 20 mg poultry litter DOC L^{-1} and (b) 10 mg poultry litter DOC L^{-1} in the desorption solution.

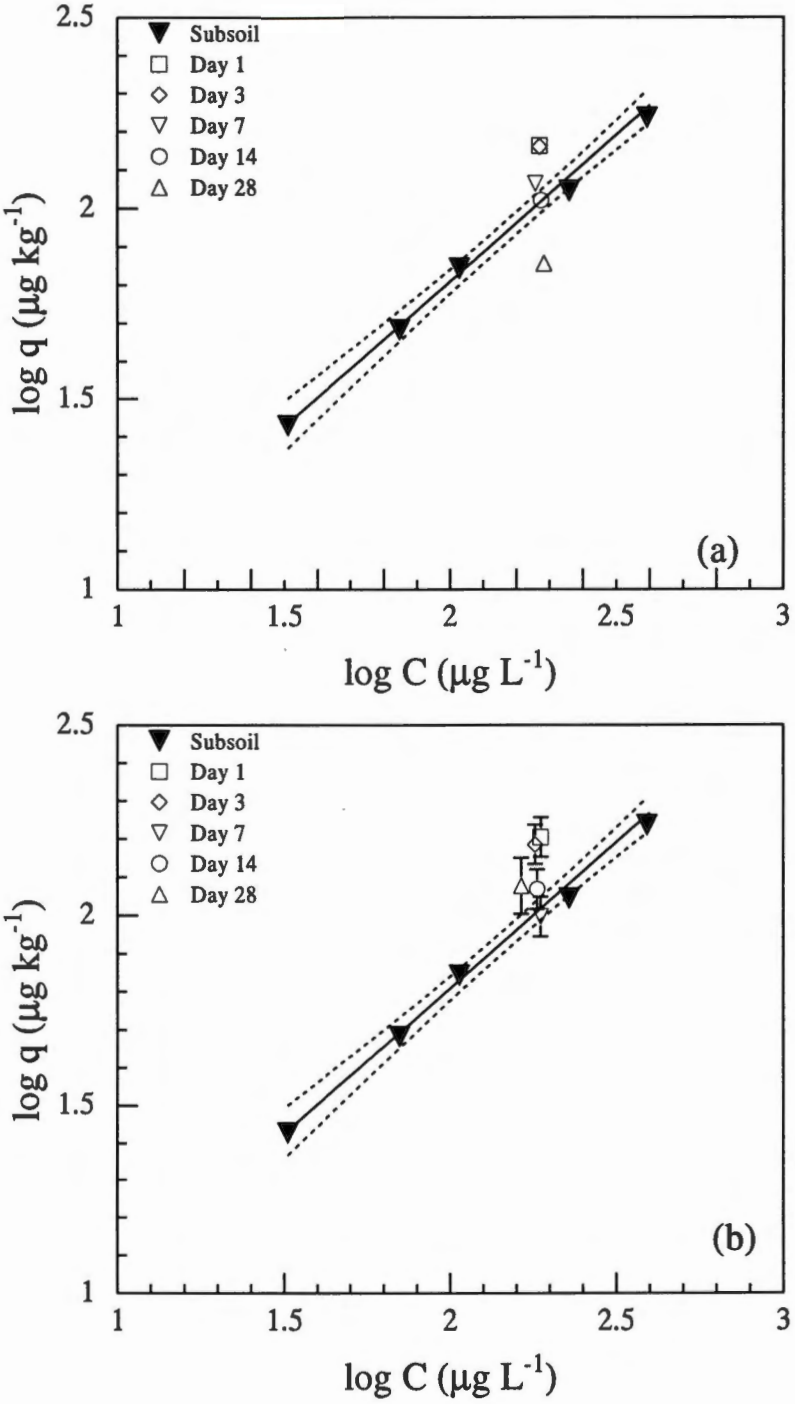


Figure 4.29. Desorption of fluometuron from subsoil with (a) 20 mg dairy manure DOC L^{-1} and (b) 10 mg dairy manure DOC L^{-1} in the desorption solution.

dairy DOC L^{-1} and both NT DOC systems show no effect of FLMT desorption from SUB soil (Figures 4.29, and 4.30).

In general, the addition of 10 mg DOC L^{-1} in the SUB soil desorption systems did not facilitate the desorption of FLMT from SUB soil. The concentration of DOC necessary to influence FLMT sorption appears to be much lower than the 100 mg DOC L^{-1} previously indicated (Madhun et al, 1986; Chiou et al., 1986 and 1987; Lee and Farmer, 1989). However, it is evident with these systems that DOC concentrations must be greater than 20 mg L^{-1} to facilitate sorption reversibility. Desorption is correlated with desorption equilibration time (α=0.05). This trend is opposite that of the no-DOC systems where herbicide sorption increases with equilibration time. Perhaps the DOC, which is about 1000 times more concentrated than the herbicides in these systems, requires time to access and compete with adsorbed herbicide molecules. The greater the time elapsed, the more time the DOC has to reach all the sorption sites and displace the herbicide molecules on the soil surface.

Norflurazon Desorption

Poultry Dissolved Organic Carbon:

Desorption of NORF was influenced by the presence of poultry DOC in the desorption system (Figures 4.31, 4.32, and 4.33). Upon initial inspection, NORF sorption to CT surface soil appears to be reversible, with respect to the 0 mg L^{-1} DOC system (Figure 4.31). However, desorption of NORF in these systems exhibits hysteresis with respect to the NORF sorption isotherms obtained in the presence of DOC. Both the NT surface and subsoil isotherms show that NORF sorption is reversible with both 460 and

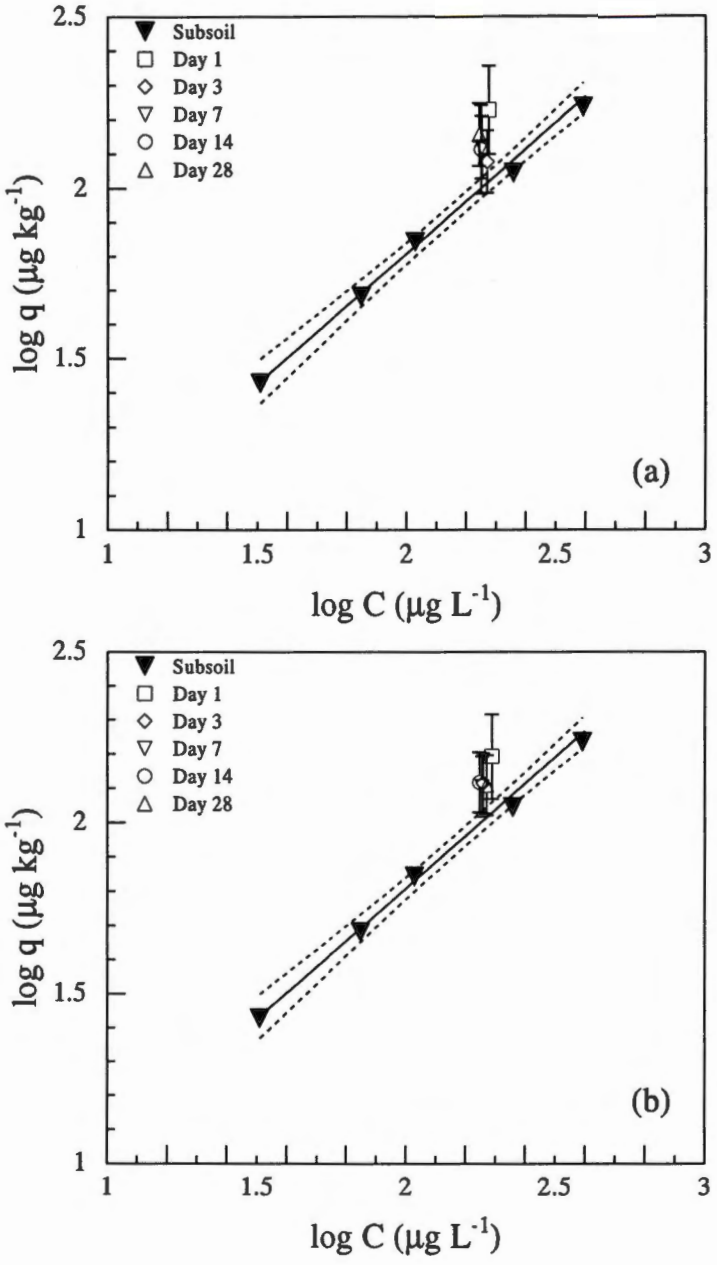


Figure 4.30. Desorption of fluometuron from subsoil with (a) 20 mg no-till surface soil DOC L^{-1} and (b) 10 mg no-till surface soil DOC L^{-1} in the desorption solution.

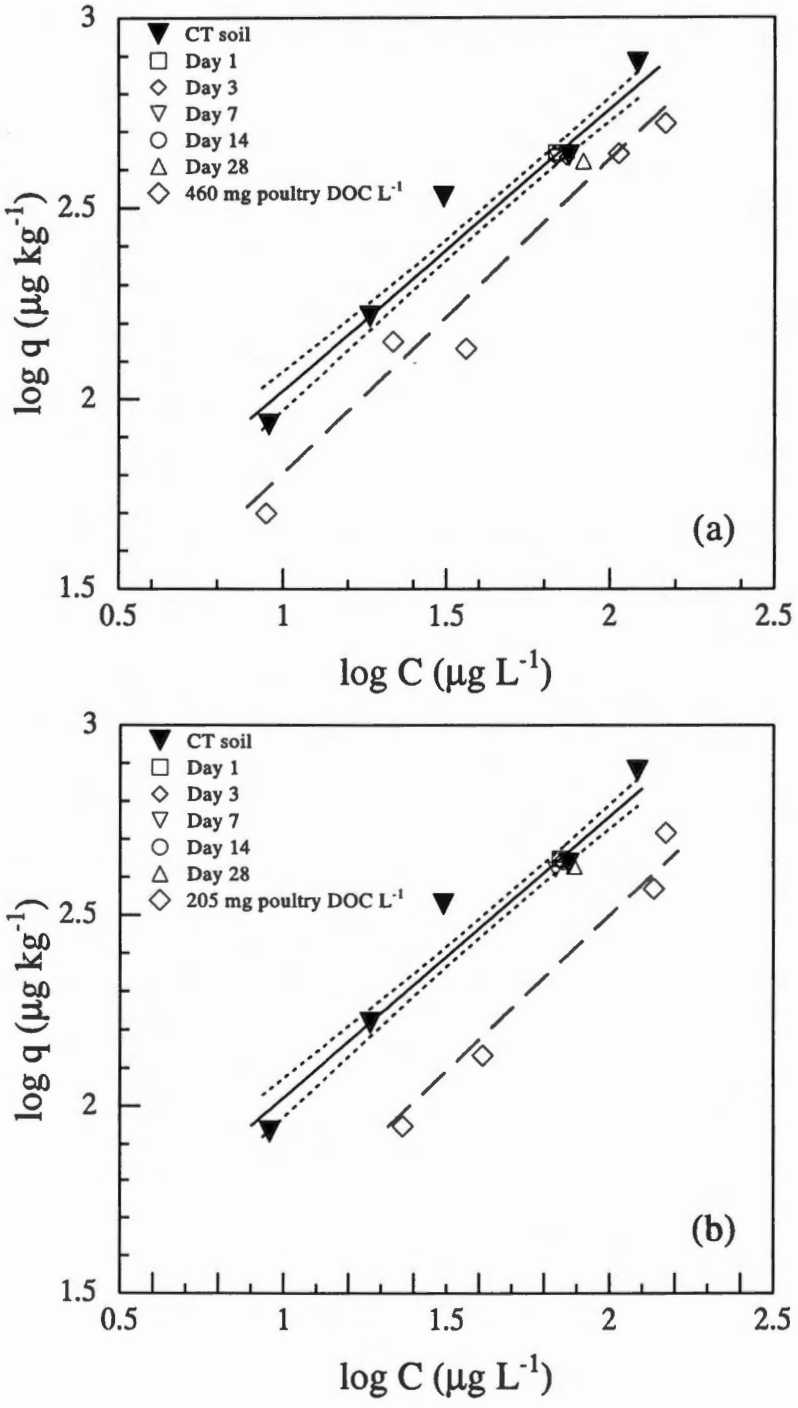


Figure 4.31. Desorption of norflurazon from conventional tillage surface soil with (a) 460 mg poultry DOC L^{-1} and (b) 230 mg poultry DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of poultry DOC.

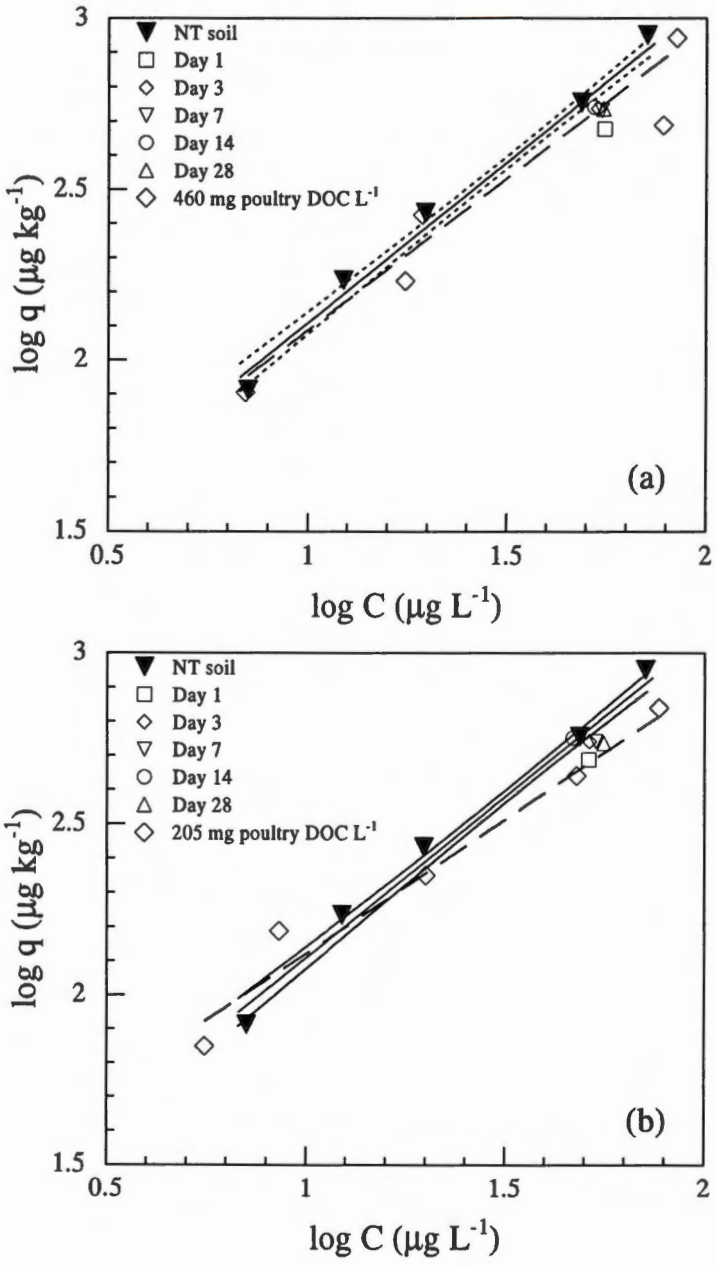


Figure 4.32. Desorption of norflurazon from no-till surface soil with (a) 460 mg poultry DOC L^{-1} and (b) 230 mg poultry DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of poultry DOC.

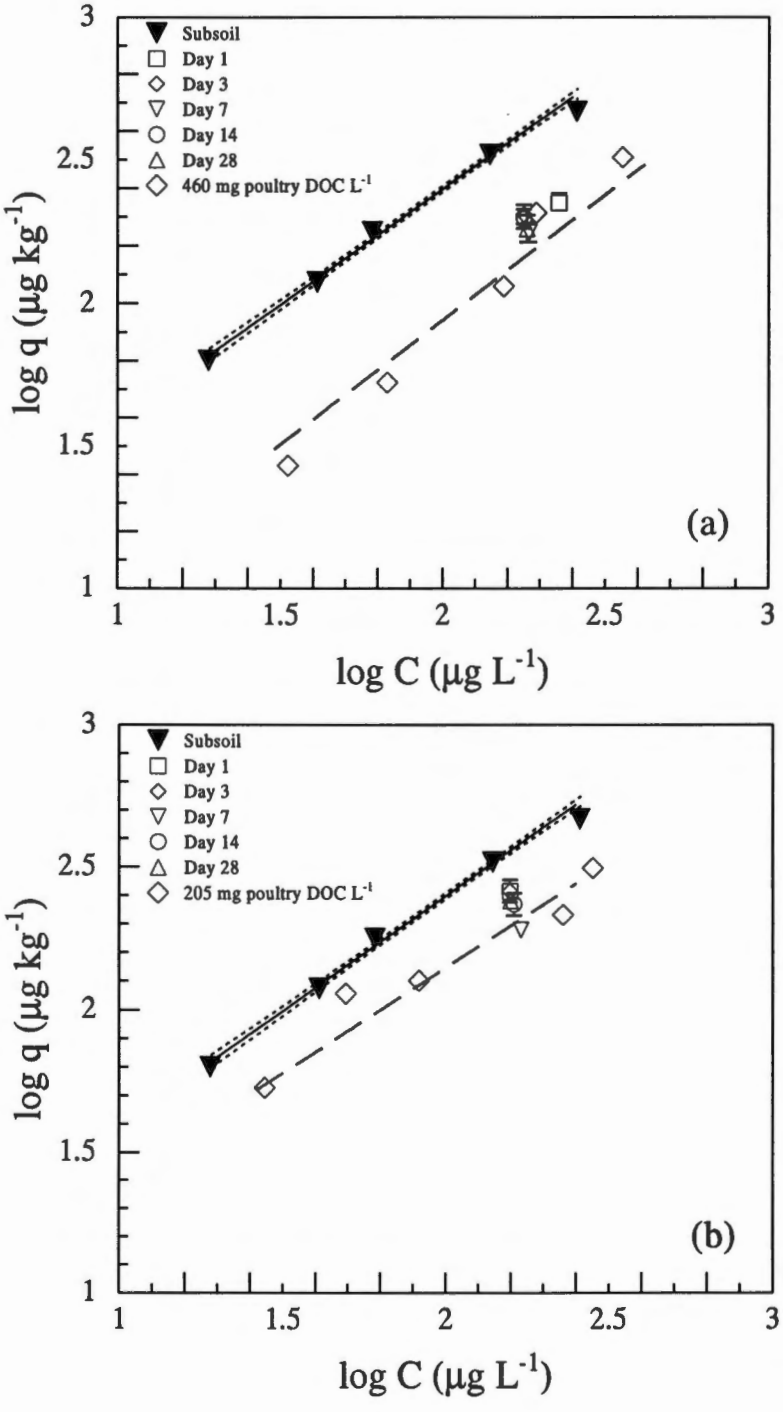


Figure 4.33. Desorption of norflurazon from subsoil with (a) 460 mg poultry DOC L^{-1} and (b) 230 mg poultry DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of poultry DOC.

230 mg poultry DOC L^{-1} in the desorption system, relative to the respective DOC isotherms (Figure 4.32 and 4.33).

Dairy Dissolved Organic Carbon:

Dairy DOC in the desorption solution influenced the desorption of NORF from Lexington silt loam soil. The 460 mg dairy DOC L^{-1} desorption systems resulted in reversible NORF sorption from CT and NT soil systems, relative to the respective DOC isotherm (Figures 4.34 and 4.35). Hysteresis characterizes NORF desorption from SUB soil with 460 mg dairy DOC L^{-1} in the system (Figure 4.36). Sorption of NORF appears to be reversible with 230 mg poultry DOC L^{-1} in the desorption solution (Figures 4.34, 4.35, and 4.36). However, the NORF sorption isotherms in the presence of DOC are not available for comparison.

Dilute Poultry, Dairy, and No-till Dissolved Organic Carbon:

Dilute DOC extracts exerted little influence on the desorption of NORF from subsoil. Desorption reversibility of NORF with 20 mg poultry DOC L^{-1} was approached with increasing equilibration time (Figure 4.37). However, desorption became more hysteretic in the 10 mg DOC L^{-1} system. These sorption trends indicate that the 20 mg L^{-1} system behaves like the more concentrated DOC systems, while the 10 mg DOC L^{-1} system resembles the no-DOC systems. The dilute dairy DOC systems behaved similar to the more concentrated DOC systems (Figure 4.38). Further, 10 mg dairy L^{-1} had no apparent influence on the desorption of NORF from SUB soil (Figure 4.38). Moreover, DOC extracted from NT surface soil did not effect the desorption of NORF from SUB soil (Figure 4.39).

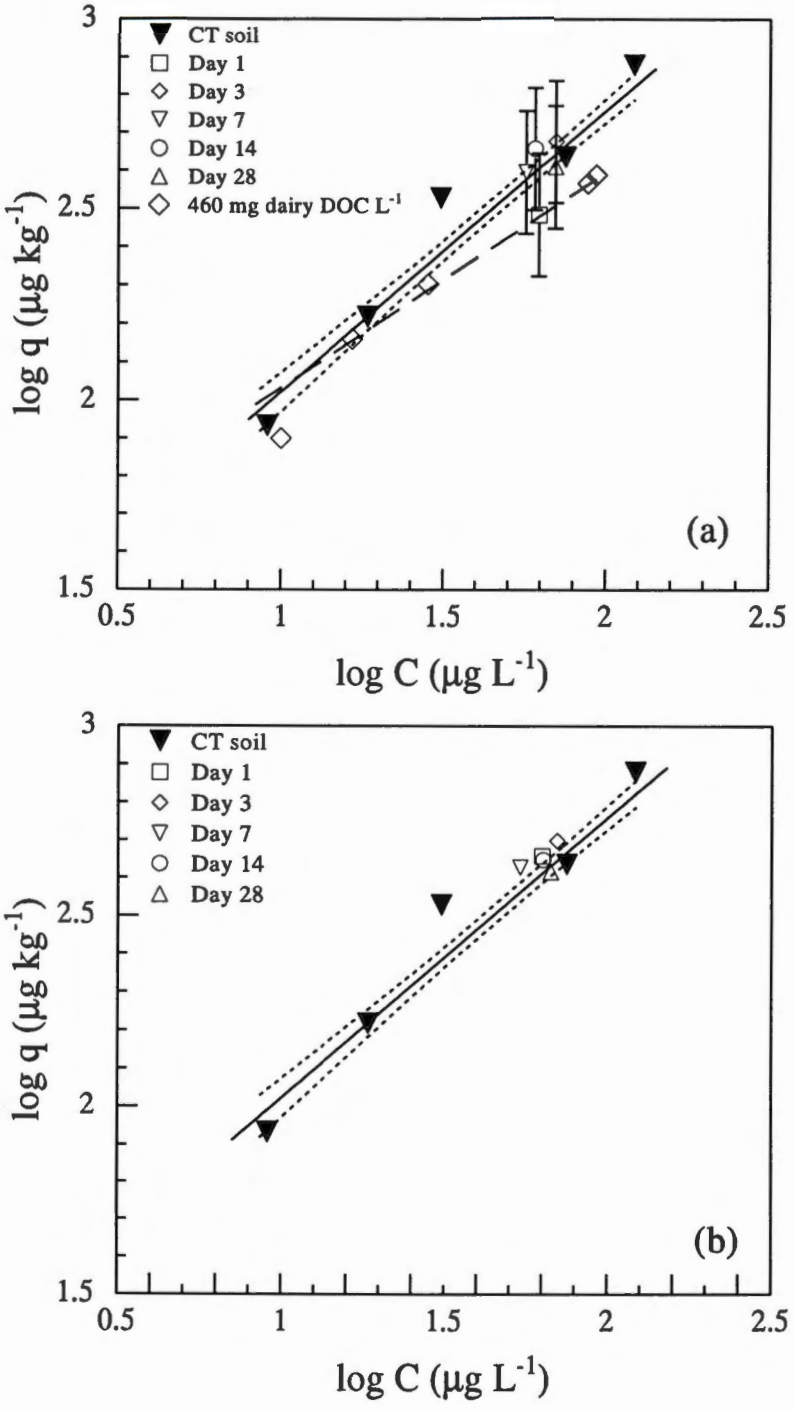


Figure 4.34. Desorption of norflurazon from conventional tillage surface soil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of dairy DOC.

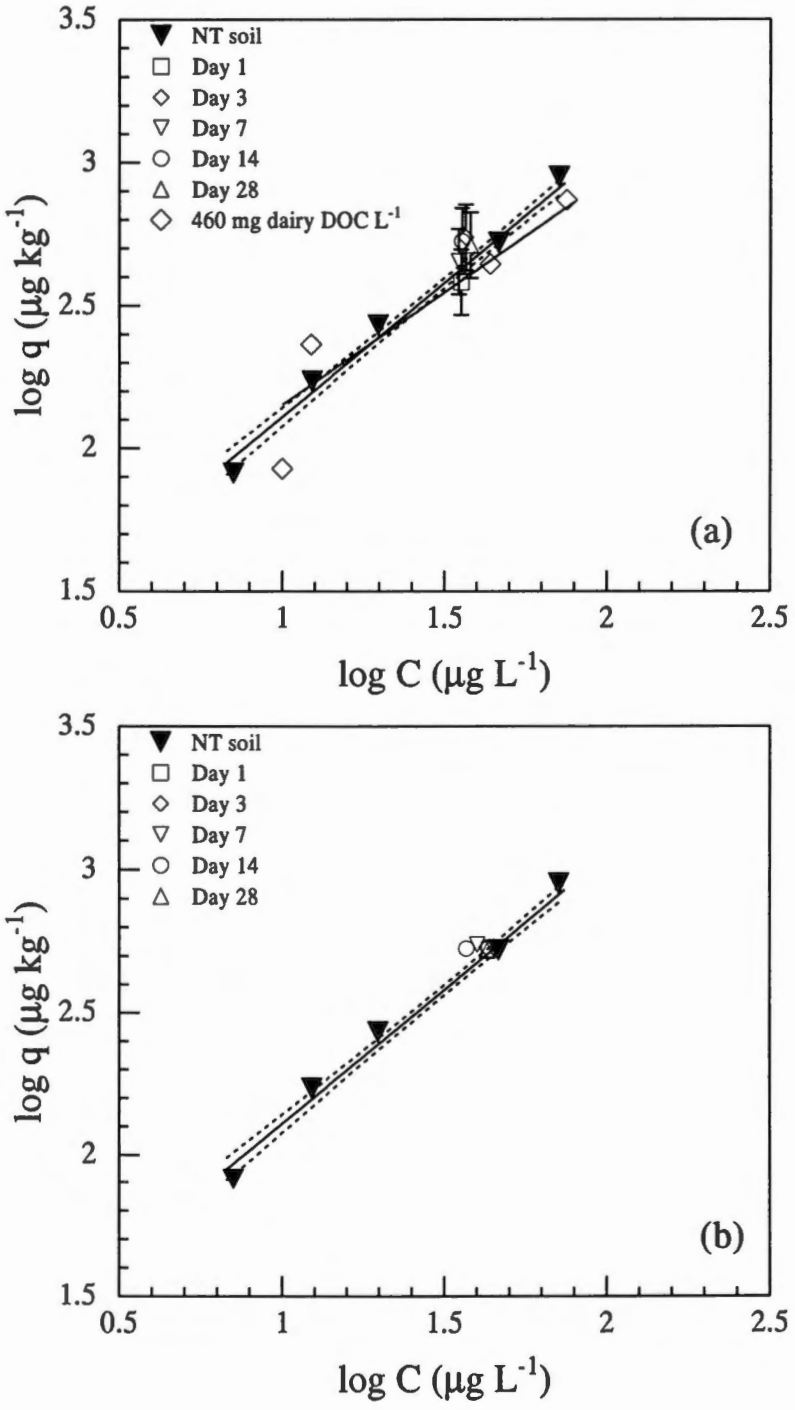


Figure 4.35. Desorption of norflurazon from no-till surface soil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of dairy DOC.

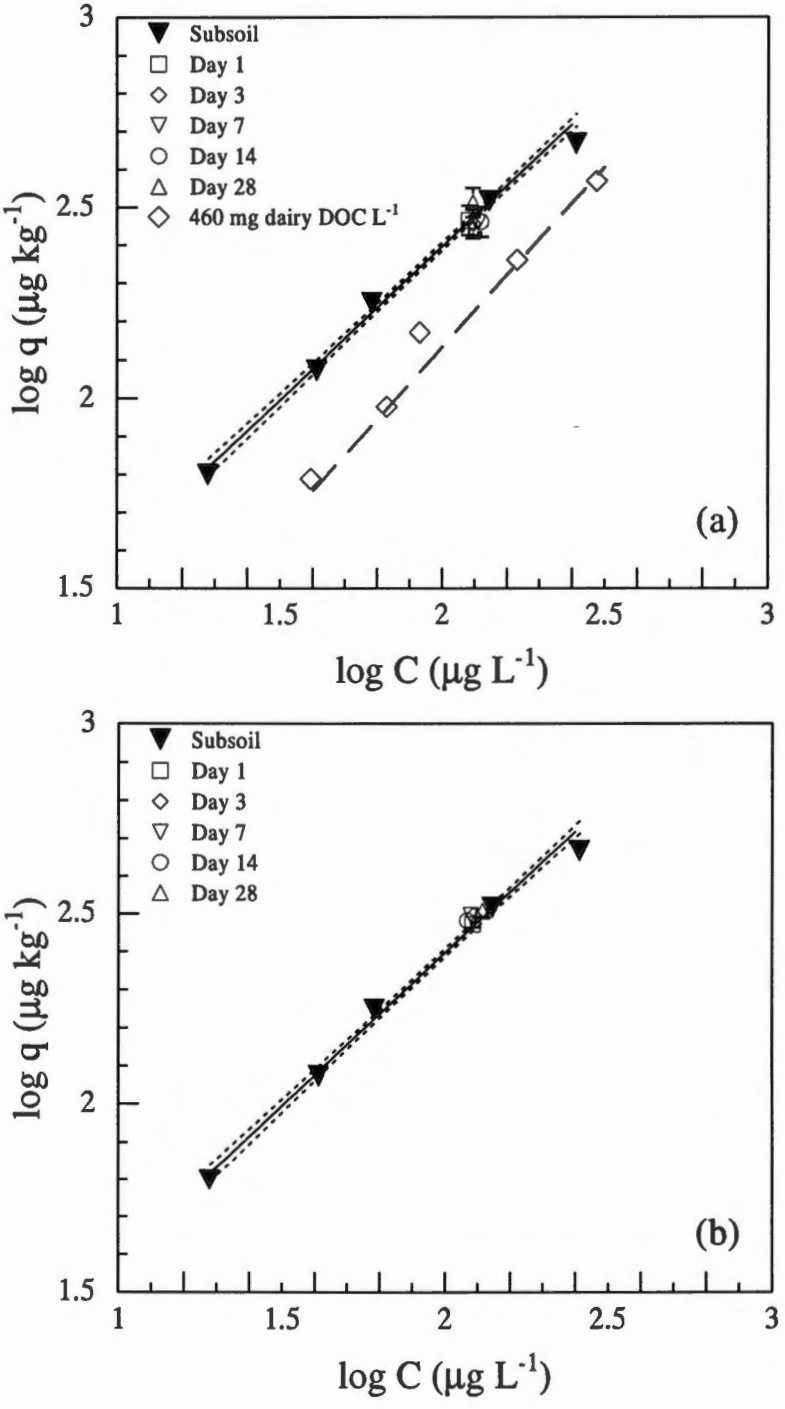


Figure 4.36. Desorption of norflurazon from subsoil with (a) 460 mg dairy DOC L^{-1} and (b) 230 mg dairy DOC L^{-1} in the desorption solution, diamonds illustrate norflurazon sorption in the presence of dairy DOC.

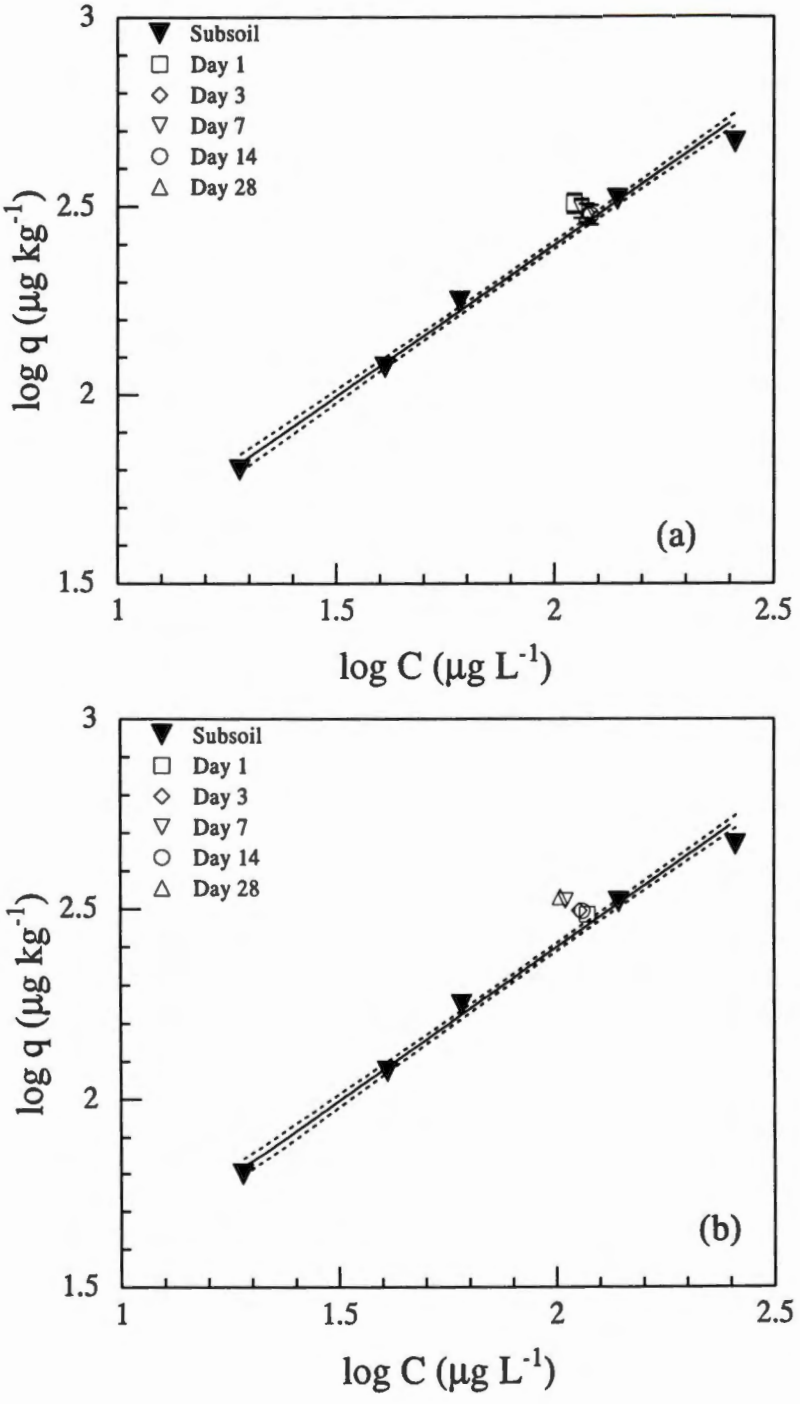


Figure 4.37. Desorption of norflurazon from subsoil with (a) 20 mg poultry litter DOC L^{-1} and (b) 10 mg poultry litter DOC L^{-1} in the desorption solution

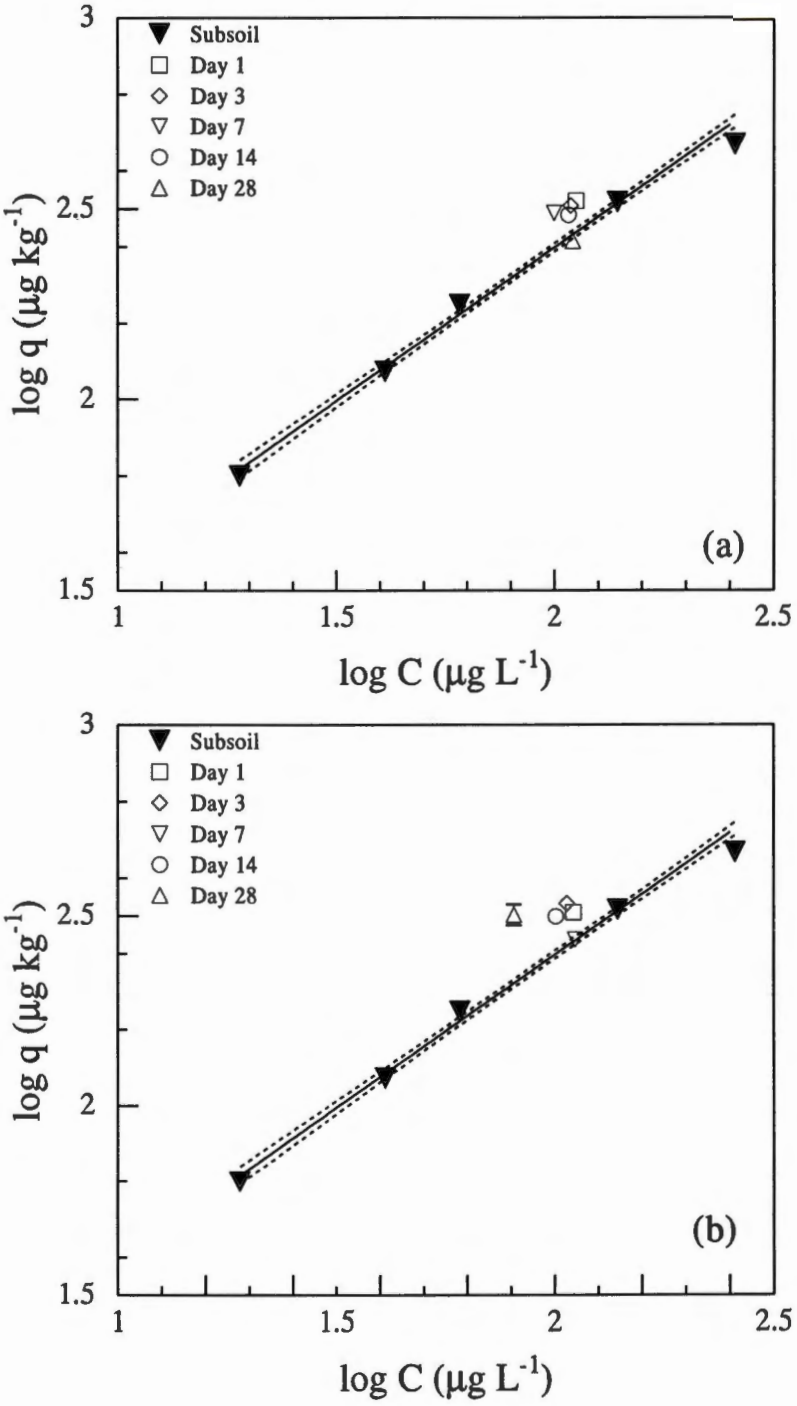


Figure 4.38. Desorption of norflurazon from subsoil with (a) 20 mg dairy manure DOC L^{-1} and (b) 10 mg dairy manure DOC L^{-1} in the desorption solution.

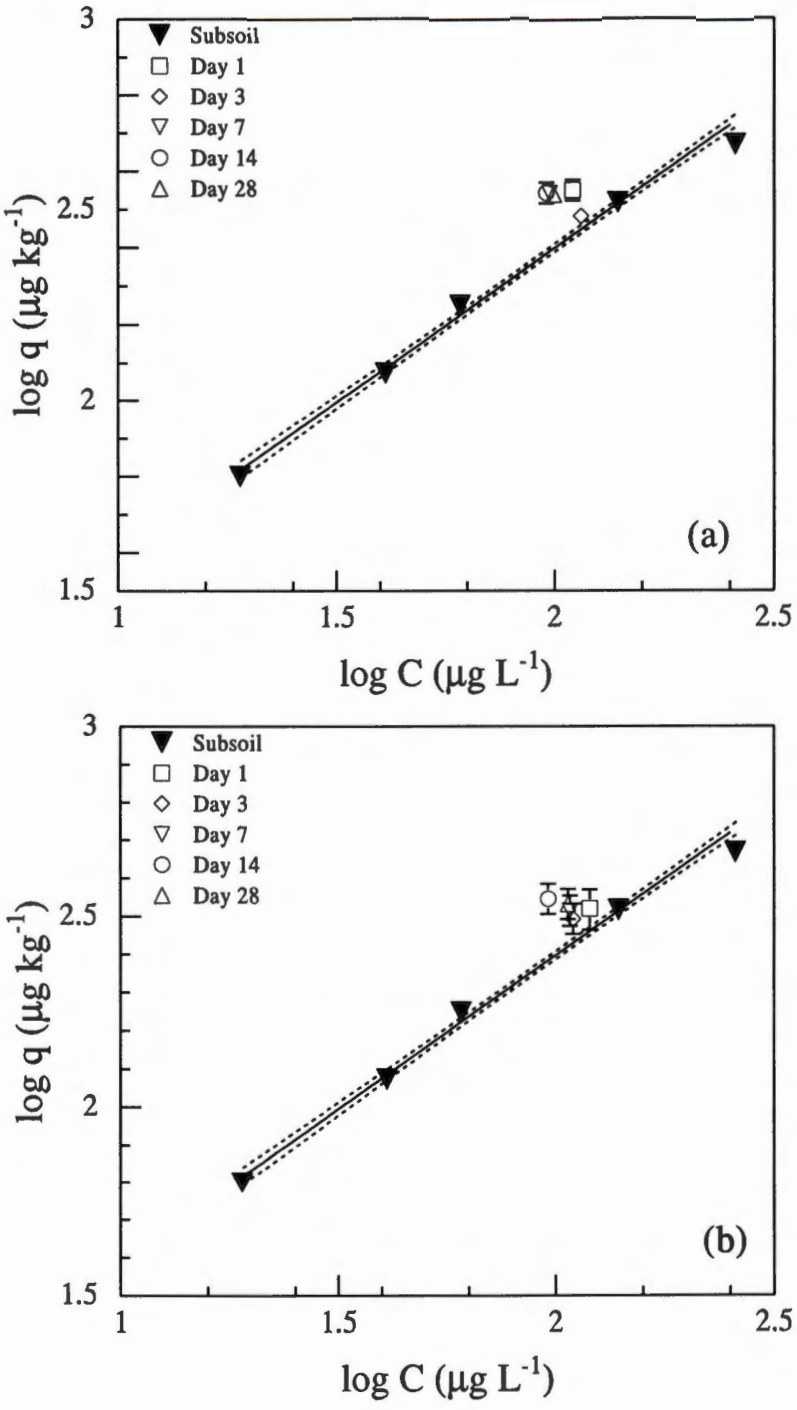


Figure 4.39. Desorption of norflurazon from subsoil with (a) 20 mg no-till surface soil DOC L^{-1} and (b) 10 mg no-till surface soil DOC L^{-1} (b) in the desorption solution.

Many researchers have found an increase in an irreversibly sorbed fraction of organic compound with time (Pignatello, 1989; McCall and Agin, 1985; Scow, 1993). Other authors have noted that organic compounds sorbed by DOC and suspended colloids tend to move to SOM or soil particulate sorbed states with time (Karickhoff, 1980; Karickhoff and Morris, 1985). The kinetic influence reported in the literature trends toward increased sorption of trace organic compound with time. The results of this study indicate that sorption of FLMT and NORF exhibits hysteresis with no added DOC and less than 20 mg DOC L^{-1} in the equilibration solution. However, with concentrations of DOC greater than 20 mg L^{-1} in the desorption solution, desorption becomes reversible with equilibration time. Apparently a concentration threshold exists in these DOC sorption systems. At DOC concentrations above the threshold, DOC molecules successfully compete for sorption sites. At DOC concentrations just above the threshold, time is required for the DOC molecules to force the desorption of the herbicides. At low DOC concentrations, below the theoretical threshold, DOC does not influence the sorptive equilibria of FLMT and NORF.

Effect of Dissolved Organic Carbon in Sorption and Desorption Solutions

Fluometuron Desorption

Poultry Dissolved Organic Carbon:

Sorption of FLMT by CT soil in the presence of 1150, 575, 255, and 130 mg poultry DOC L^{-1} was generally reversible (Figures 4.40 and 4.41). Desorption of FLMT from NT surface soil with is also reversible (Figures 4.42 and 4.43). The 1150 and 575 mg poultry DOC L^{-1} desorption points were significantly lower than the 920 and 460 mg

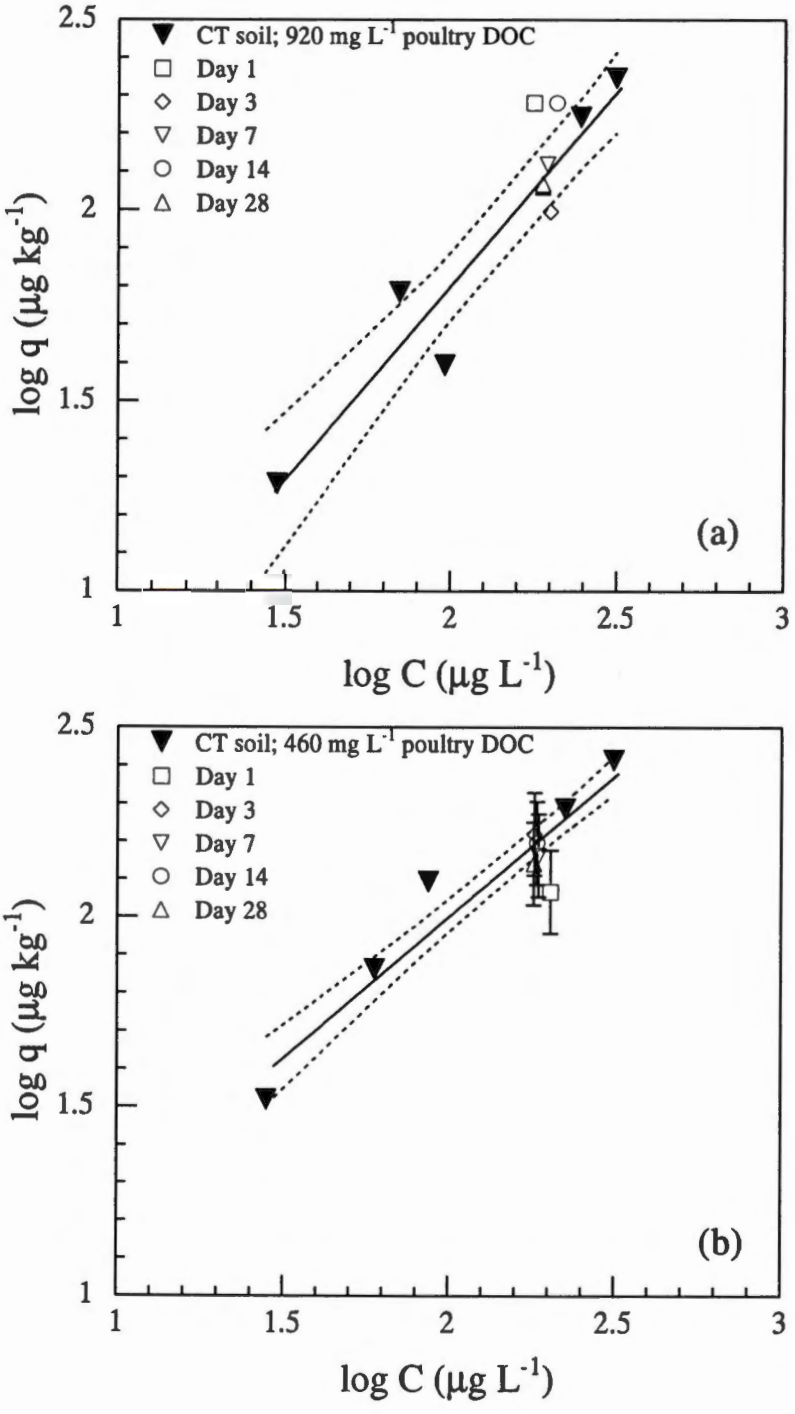


Figure 4.40. Desorption of fluometuron from conventional tillage soil in the presence of (a) 1150 mg L^{-1} poultry DOC and (b) 575 mg L^{-1} poultry litter DOC.

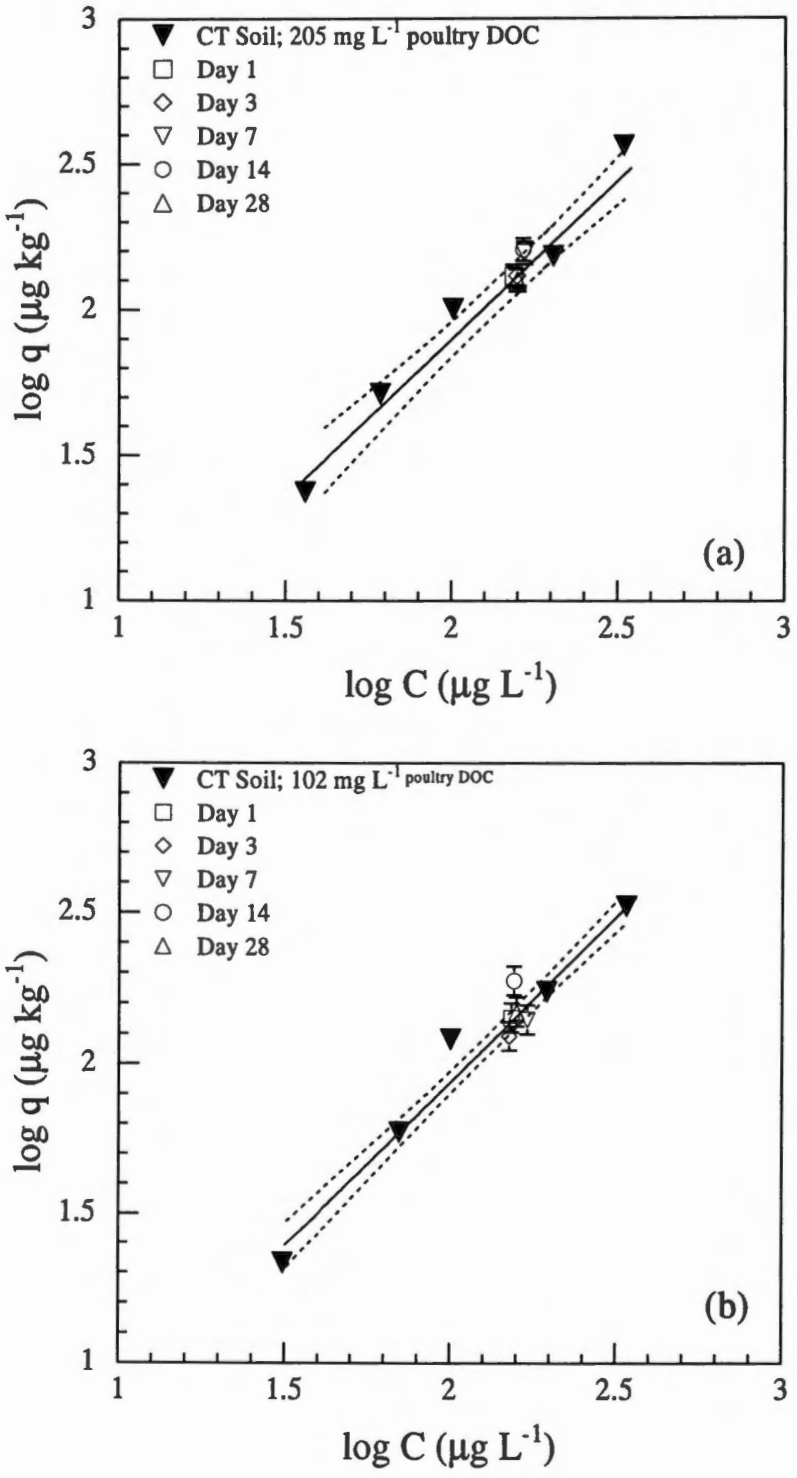


Figure 4.41. Desorption of fluometuron from conventional tillage surface soil with (a) 255 mg poultry litter DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

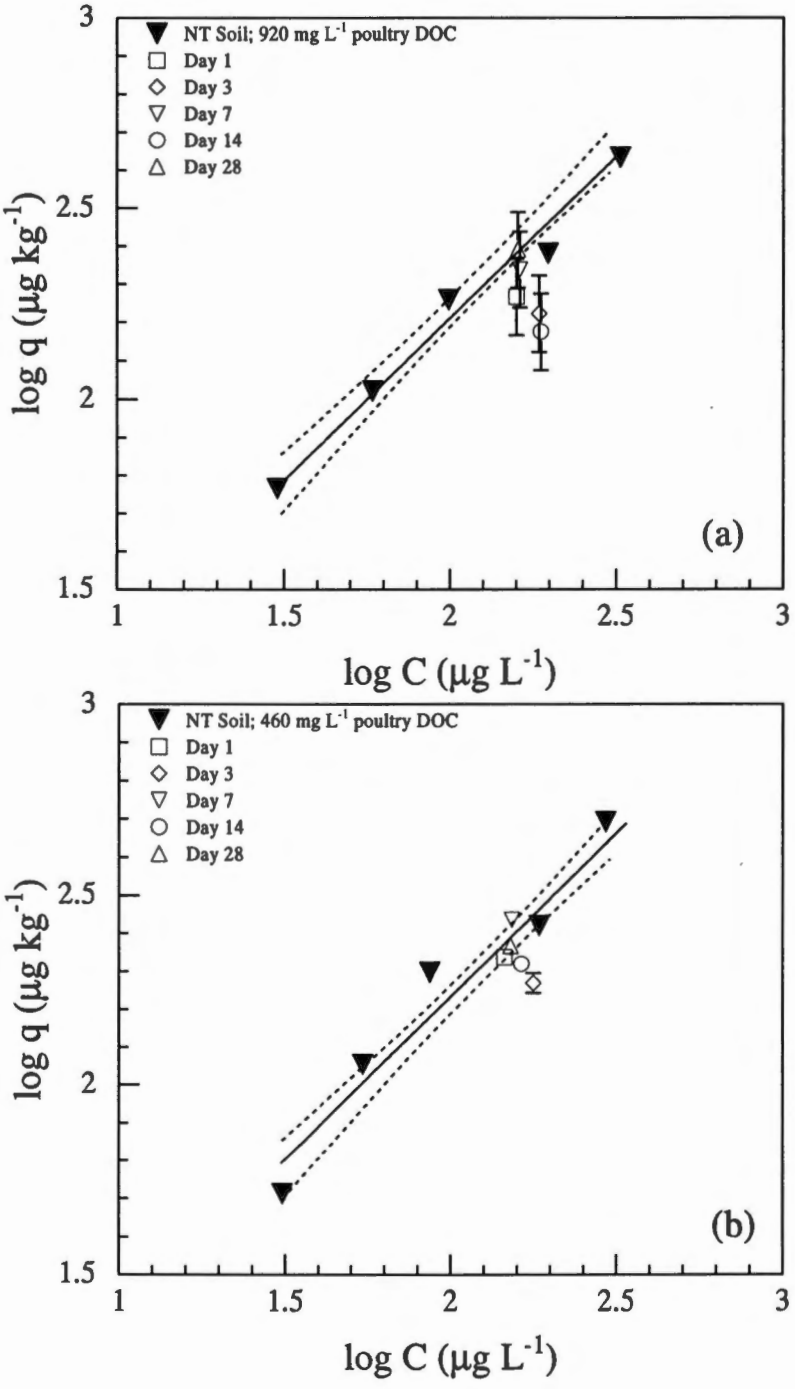


Figure 4.42. Desorption of fluometuron from no-till surface soil with (a) 1150 mg poultry litter DOC L^{-1} and (b) 575 mg poultry DOC L^{-1}.

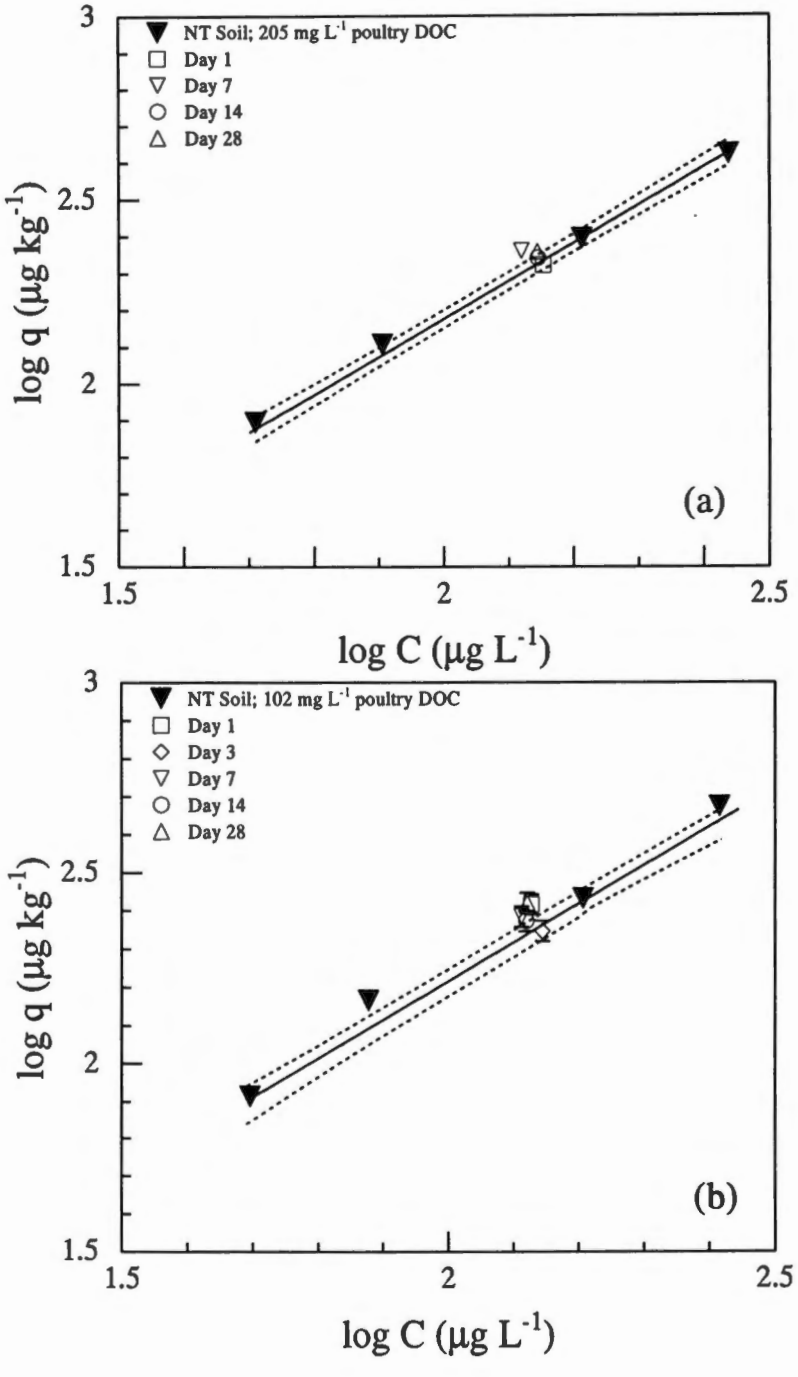


Figure 4.43. Desorption of fluometuron from no-till surface soil with (a) 255 mg poultry litter DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

L^{-1} DOC FLMT sorption isotherms. It is possible that these desorption systems are conforming to a different sorption isotherm. The sorption isotherms were determined with 920 and 460 mg poultry DOC L^{-1}. Perhaps the desorption systems reflect sorption of 300 μg FLMT L^{-1} with 1150 or 575 mg DOC L^{-1} in solution. There does not appear to be a trend in FLMT desorption with time during the 28 day period. Desorption data at days 1 and 28 lie within the 90% confidence interval of the sorption isotherms, while at intermediate time periods the desorption data lie outside the 90% confidence intervals. Sorption of FLMT from NT surface soil with 255 and 130 mg poultry DOC L^{-1} was reversible at all desorption time intervals (Figure 4.43).

Sorption of FLMT to subsoil is reversible at all desorption times with all 4 concentrations of poultry DOC in the desorption solution (Figures 4.44 and 4.45). However, scatter in the sorption isotherm data, and the desorption systems, results in large 90% confidence intervals about the isotherm and desorption systems.

Dairy Dissolved Organic Carbon:

The presence of dairy DOC in the desorption system enhanced the desorption of FLMT from CT, NT, and SUB soil. Figure 4.46 shows that FLMT sorption to CT surface soil is reversible (α=0.05). Moreover, FLMT desorption was positively correlated with equilibration time in both systems. Sorption of FLMT to NT surface soil and subsoil was generally reversible with 1150 and 575 mg dairy DOC L^{-1} in the desorption solution (Figures 4.47 and 4.48). However, no influence of desorption equilibration time was evident.

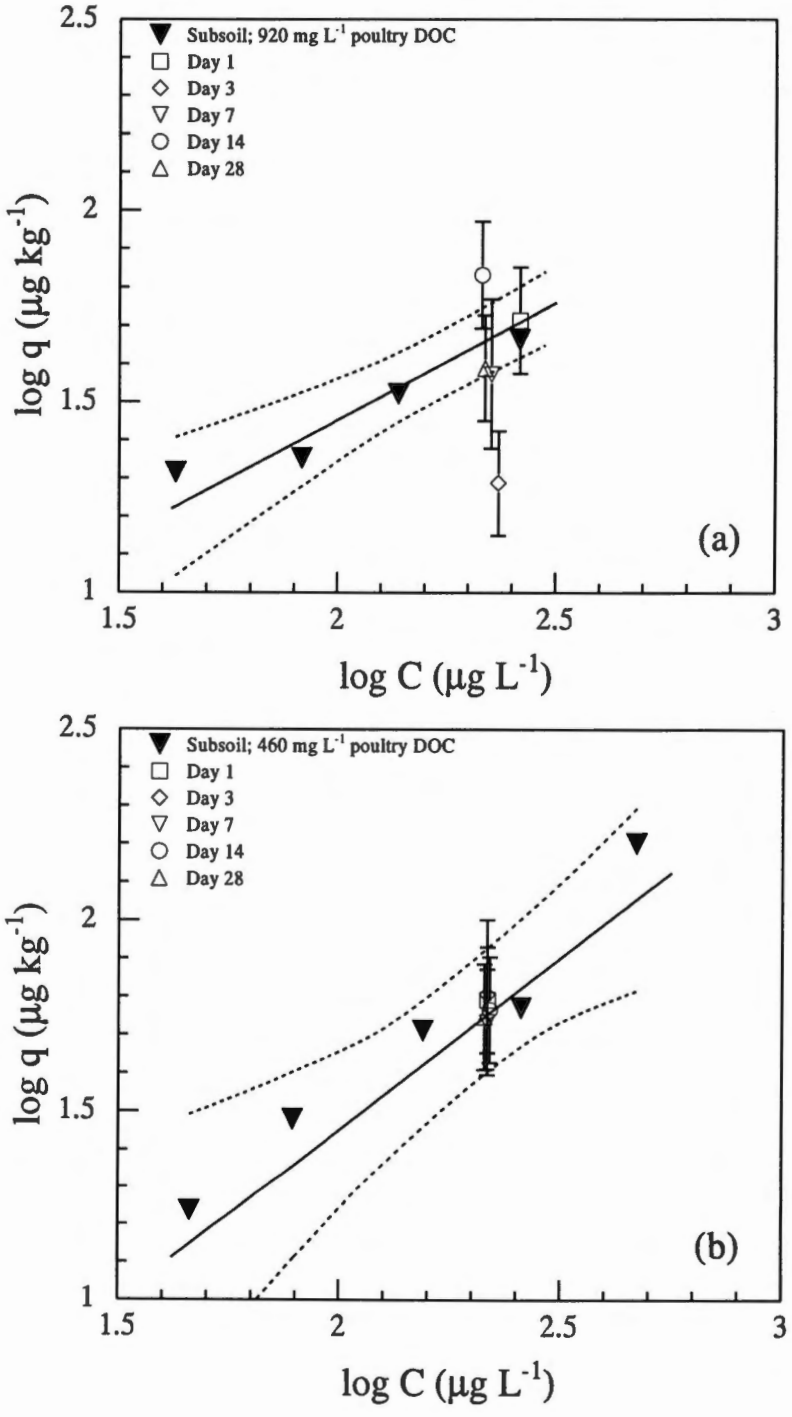


Figure 4.44. Desorption of fluometuron from subsoil with (a) 1150 mg poultry DOC L^{-1} and (b) 575 mg poultry DOC L^{-1}.

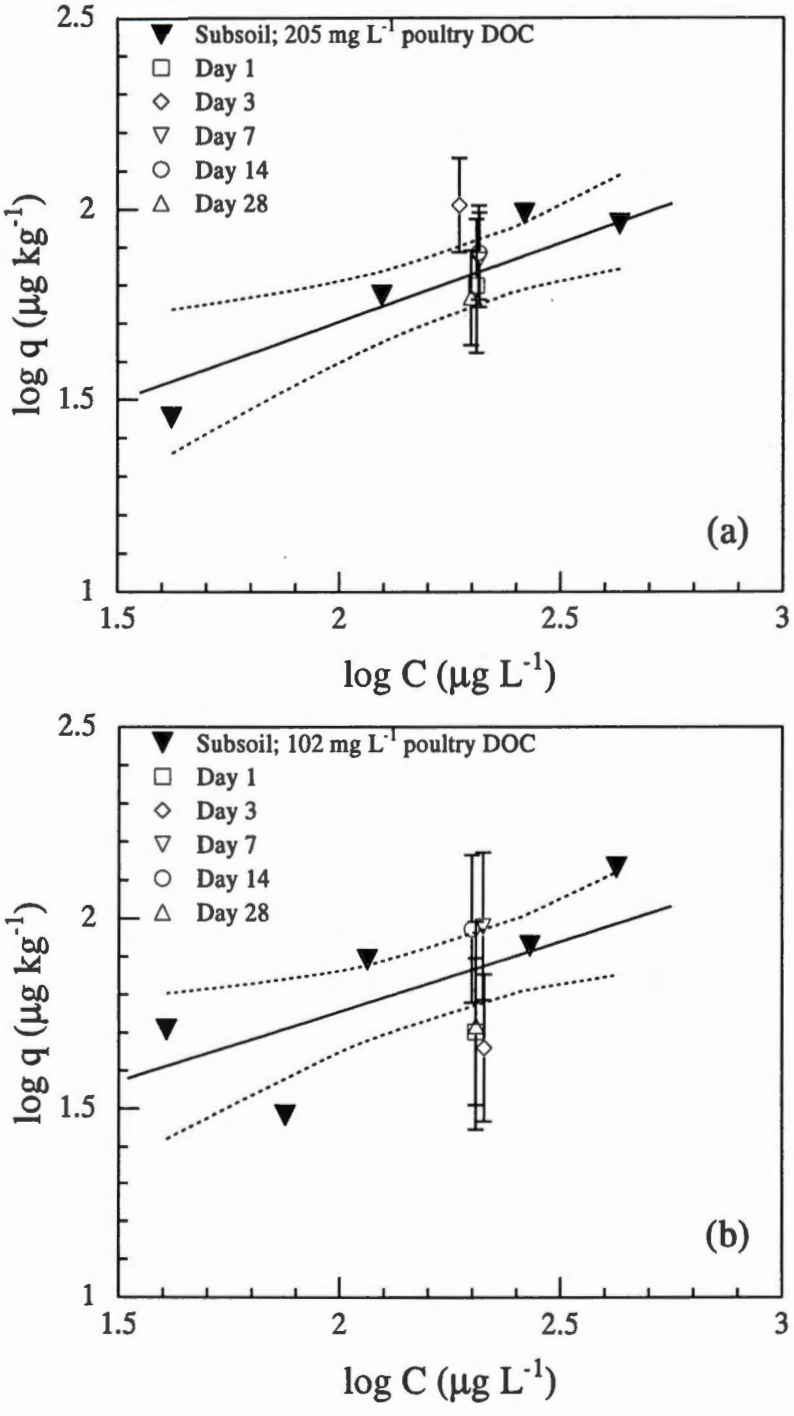


Figure 4.45. Desorption of fluometuron from subsoil with (a) 255 mg poultry DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

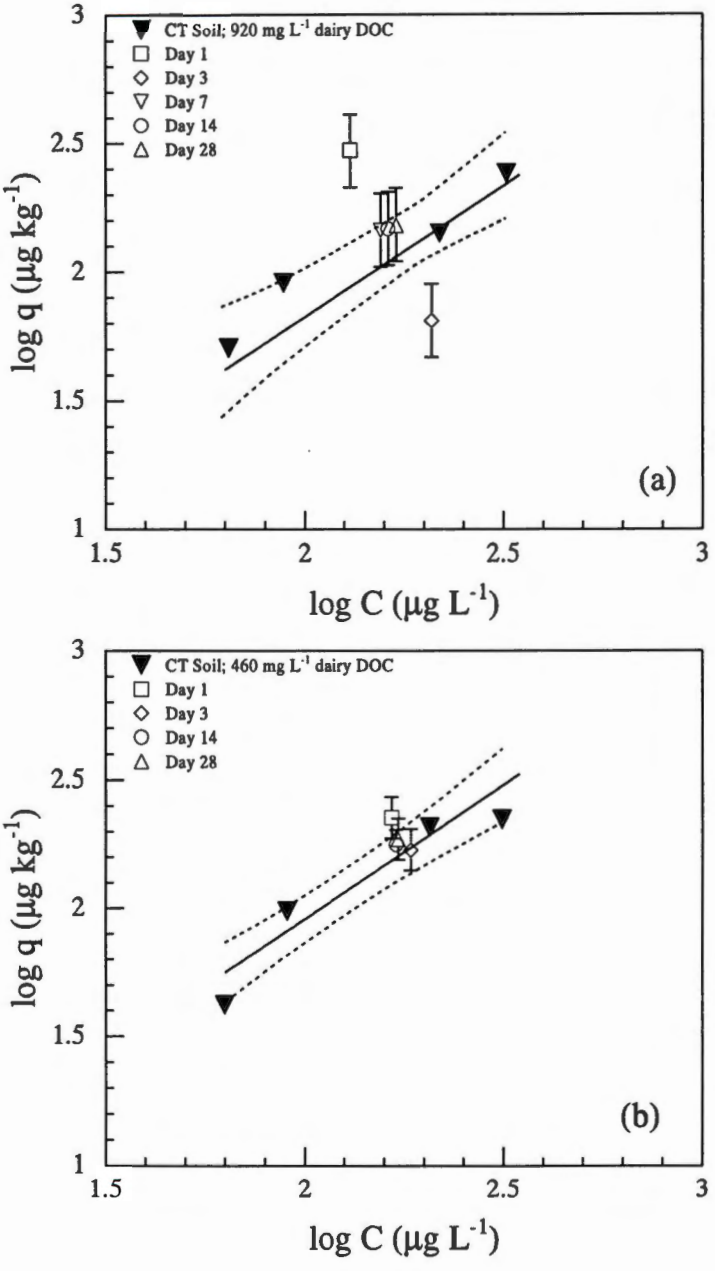


Figure 4.46. Desorption of fluometuron from conventional tillage surface soil with (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

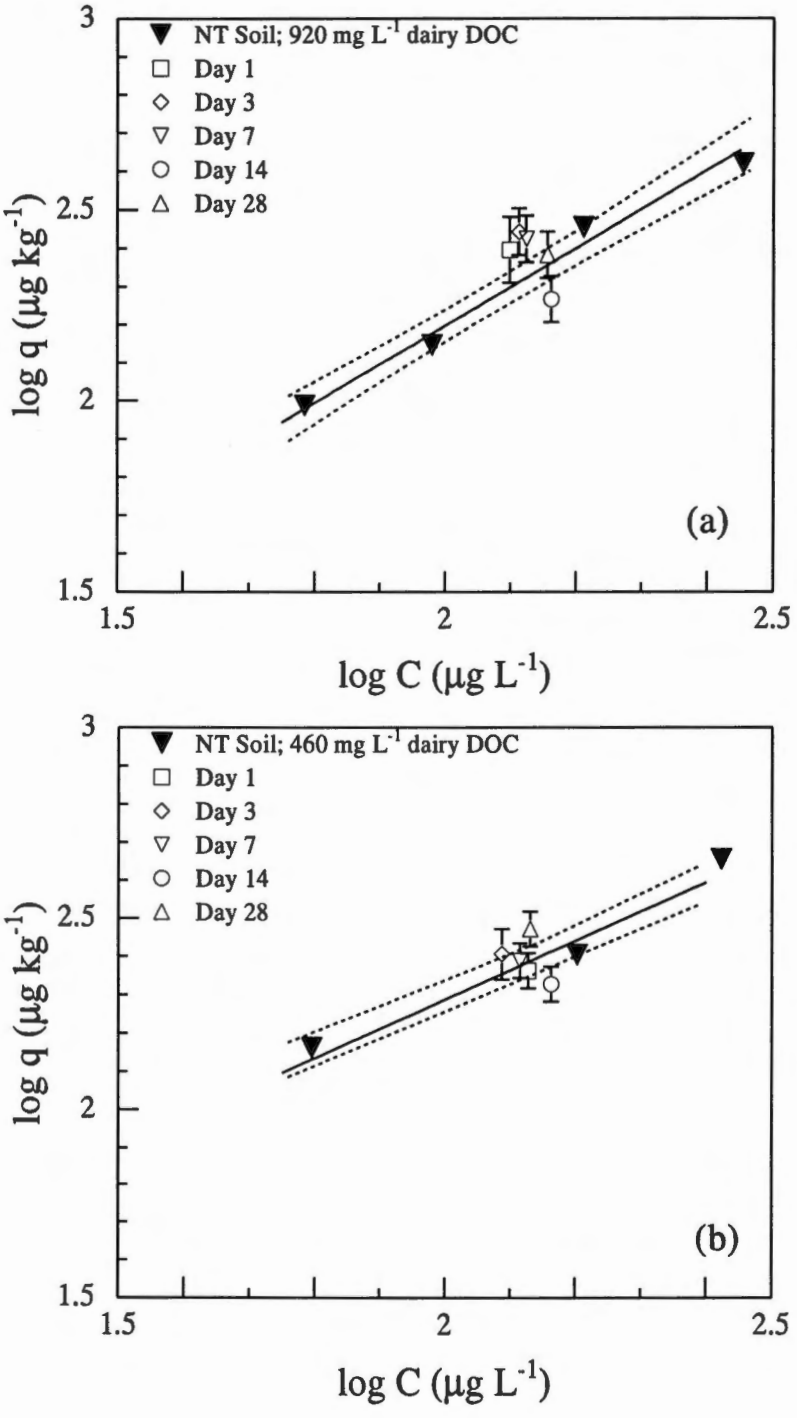


Figure 4.47. Desorption of fluometuron from no-till surface soil in the presence of (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

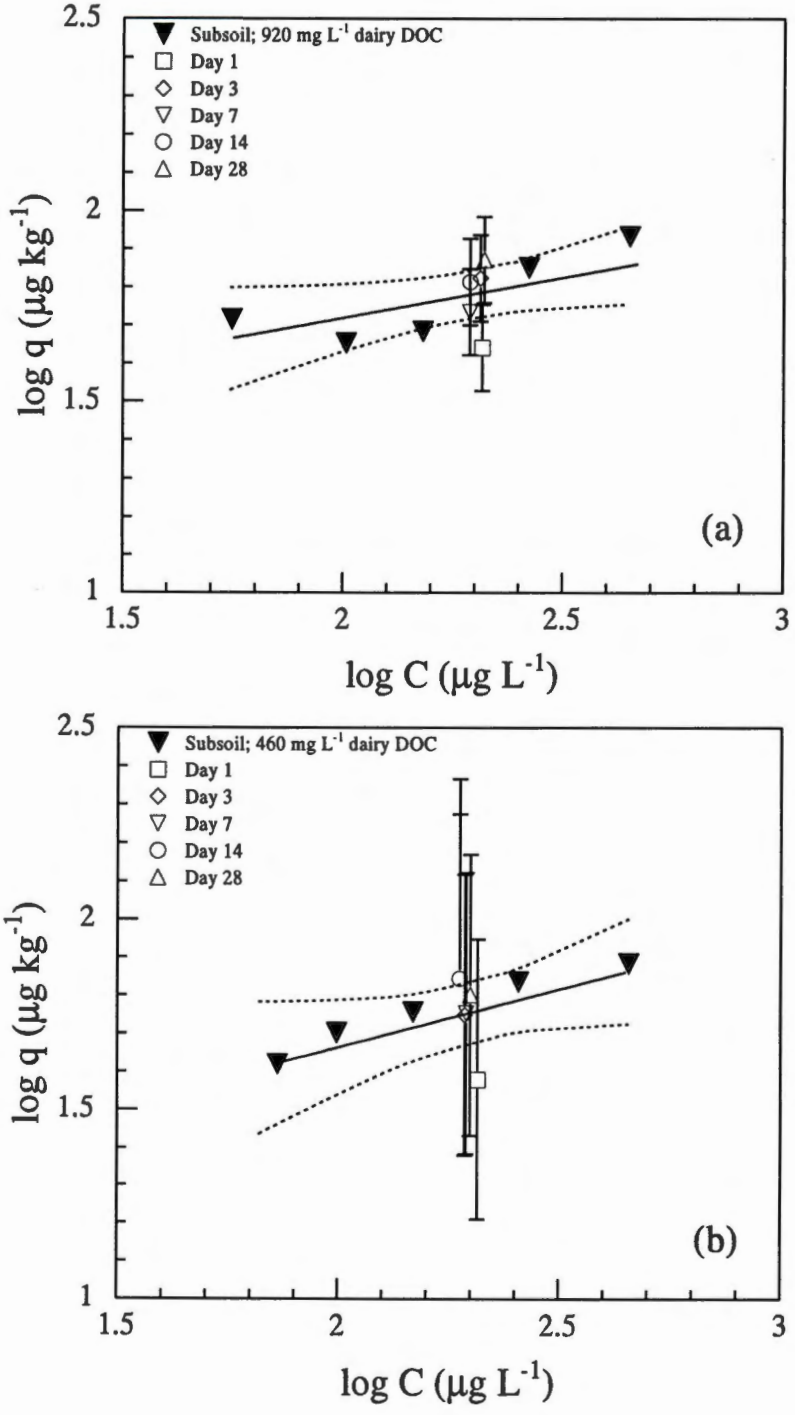


Figure 4.48. Desorption of fluometuron from subsoil in the presence of (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

No-till Dissolved Organic Carbon:

The sorption of FLMT to SUB soil in the presence of NT DOC is reversible (Figure 4.49). Although hysteresis is approached as equilibration time increases, the overall desorption of FLMT from SUB soil was complete with both DOC concentrations.

Norflurazon Desorption

Poultry Dissolved Organic Carbon:

Desorption of NORF was also enhanced by DOC in the sorption and desorption equilibration systems. Figures 4.50 and 4.51 show reversible NORF sorption in the CT soil systems. The sorption of NORF by NT soil was also reversible (Figures 4.52 and 4.53). Day 7 desorption of NORF from NT soil showed hysteresis with 1150, 575 and 255 mg poultry DOC L^{-1}. However, a general trend of sorption reversibility is evident. Similarly, sorption of NORF to SUB soil was generally reversible (Figures 4.54 and 4.55). Overall, desorption of NORF from Lexington silt loam in the presence of poultry DOC was reversible. Poultry DOC reduced the sorption of both FLMT and NORF by CT, NT, and SUB soil. Moreover, herbicide sorption was reversible in the presence of poultry DOC.

Dairy Dissolved Organic Carbon:

Dissolved organic carbon extracted from dairy manure influenced the desorption of NORF from Lexington silt loam soil. Sorption of NORF by CT surface soil was reversible with dairy DOC in the sorption and desorption systems (Figure 4.56). Desorption of NORF from NT surface soil displayed hysteresis after 1, 3, and 7 days of equilibration in a 1150 mg dairy DOC L^{-1} solution (Figure 4.57). However, sorption

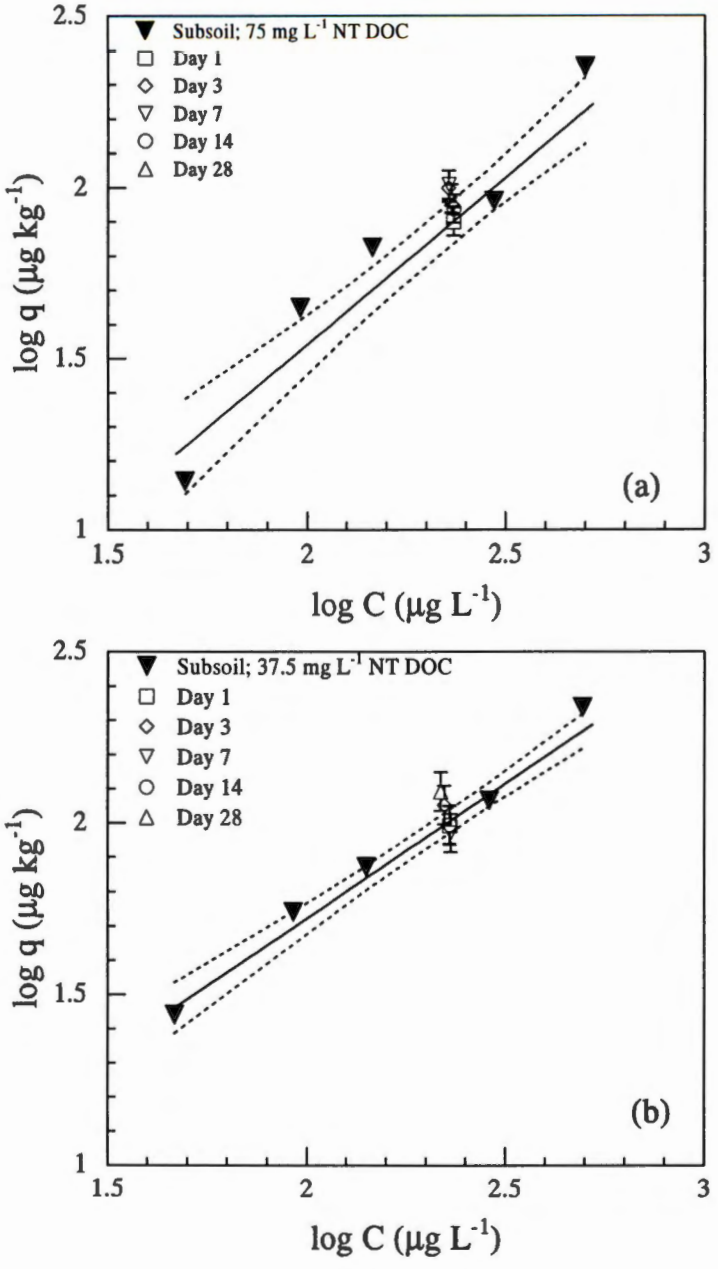


Figure 4.49. Desorption of fluometuron from subsoil with (a) 95 mg no-till DOC L^{-1} and (b) 47 mg no-till DOC L^{-1}.

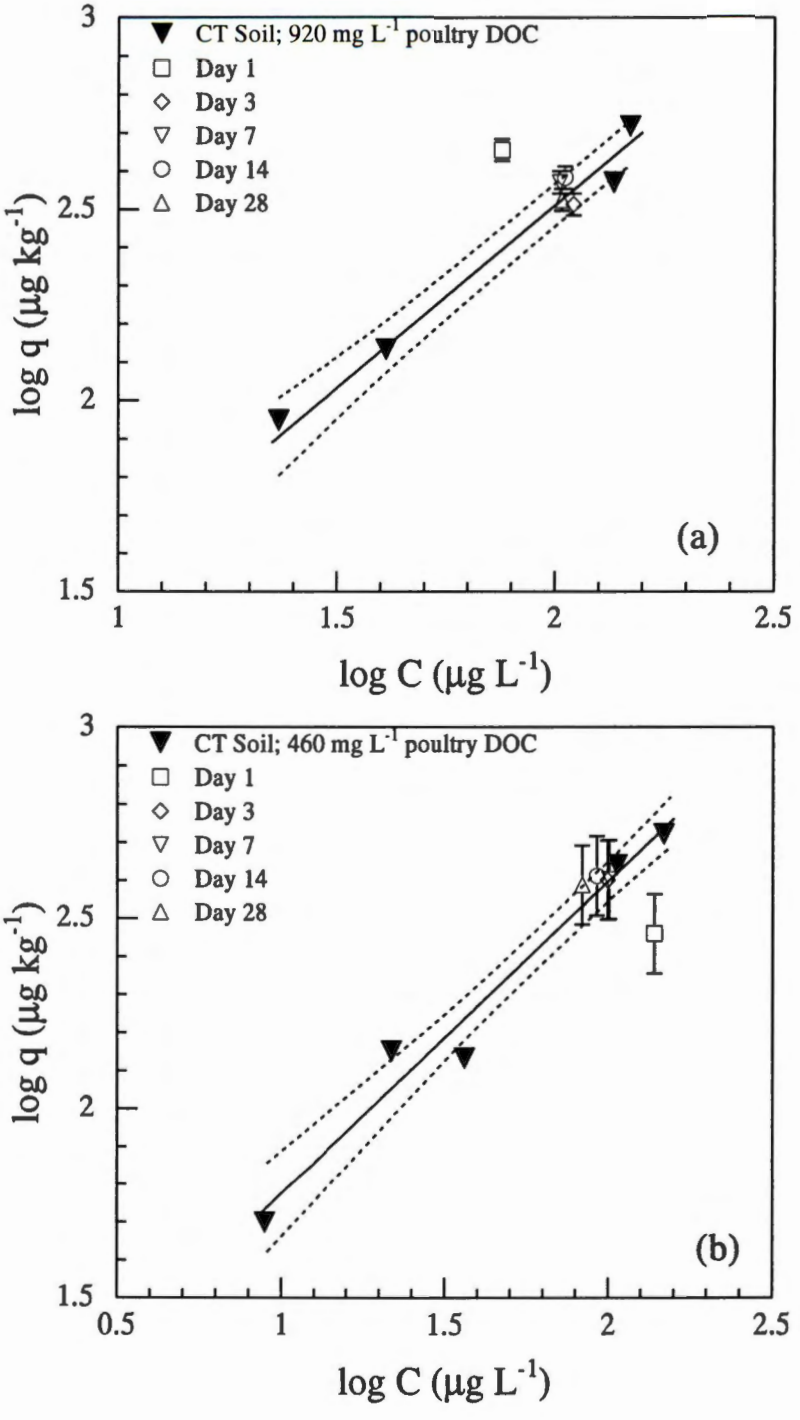


Figure 4.50. Desorption of norflurazon from conventional tillage surface soil with (a) 1150 mg poultry DOC L^{-1} and (b) 575 mg poultry DOC L^{-1}.

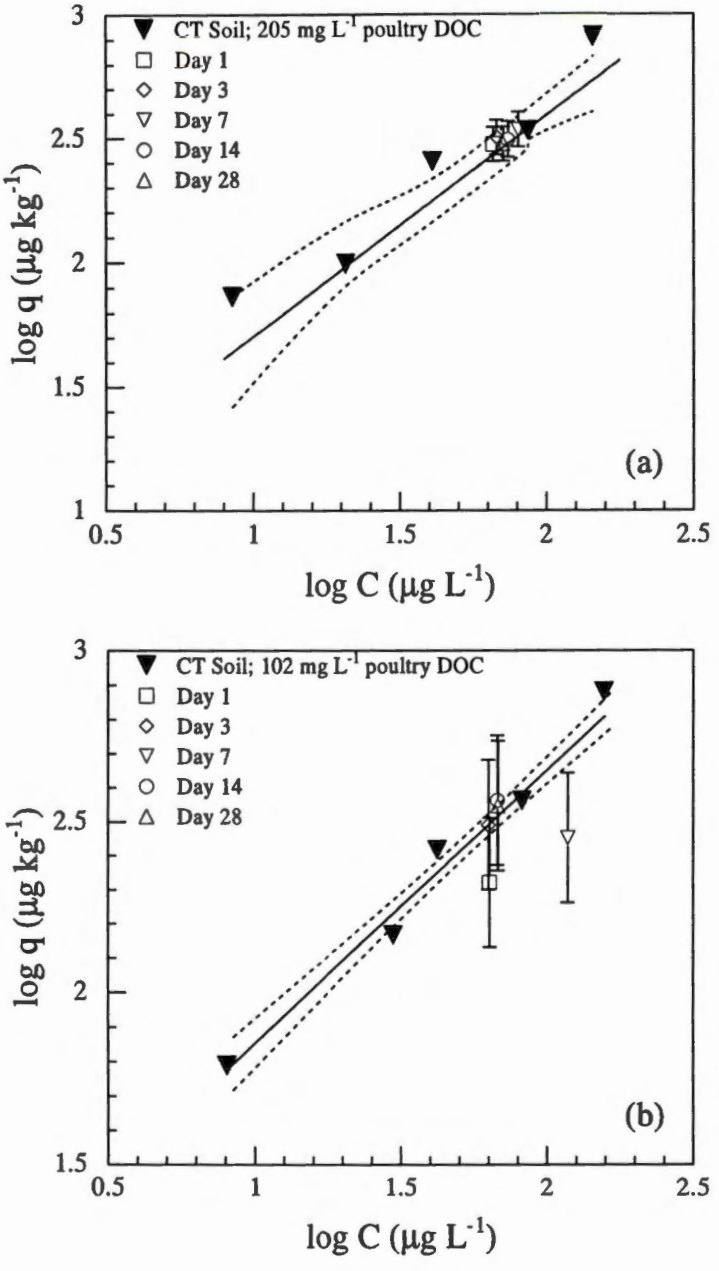


Figure 4.51. Desorption of norflurazon from conventional tillage surface soil with (a) 255 mg poultry DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

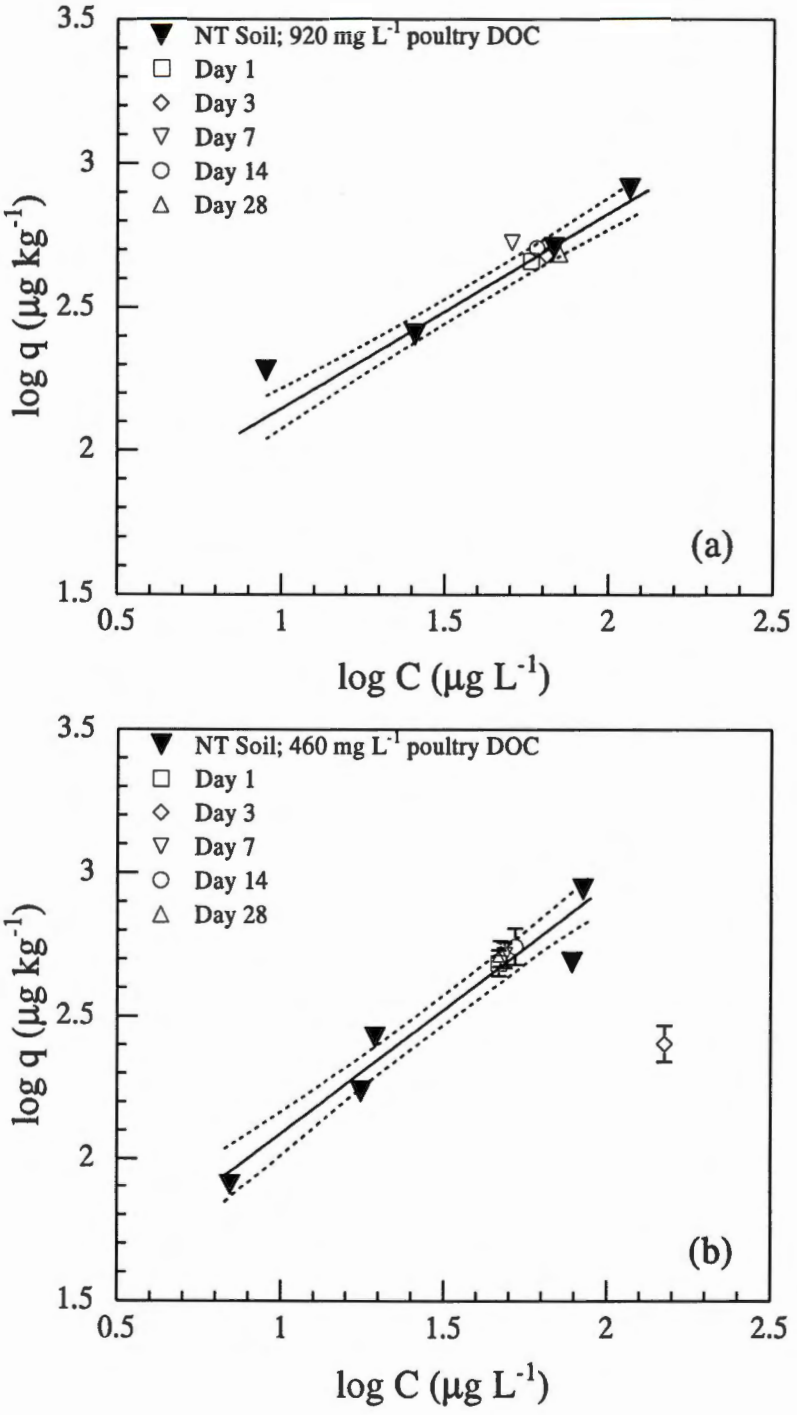


Figure 4.52. Desorption of norflurazon from no-till surface soil with (a) 1150 mg poultry DOC L^{-1} and (b) 575 mg poultry DOC L^{-1}.

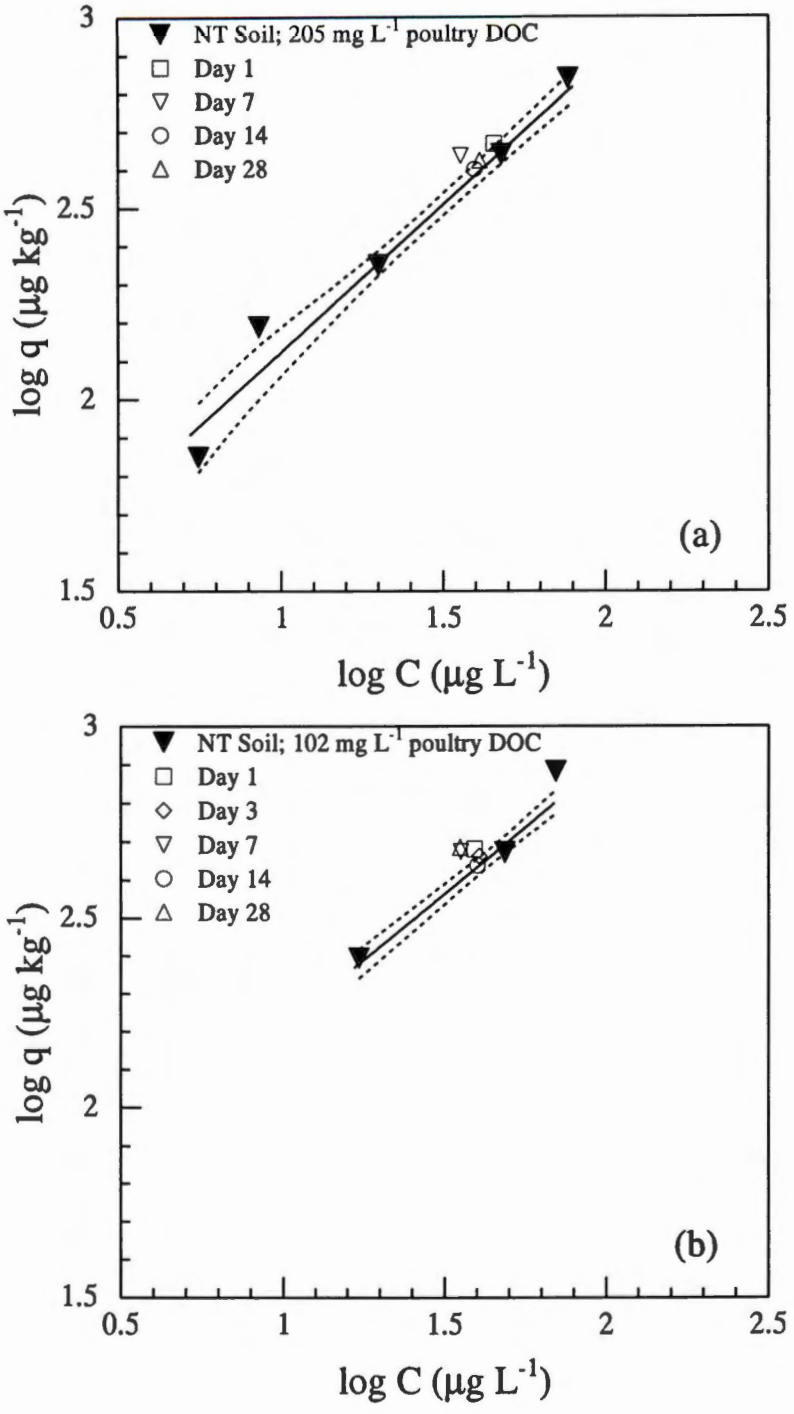


Figure 4.53. Desorption of norflurazon from no-till surface soil with (a) 255 mg poultry DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

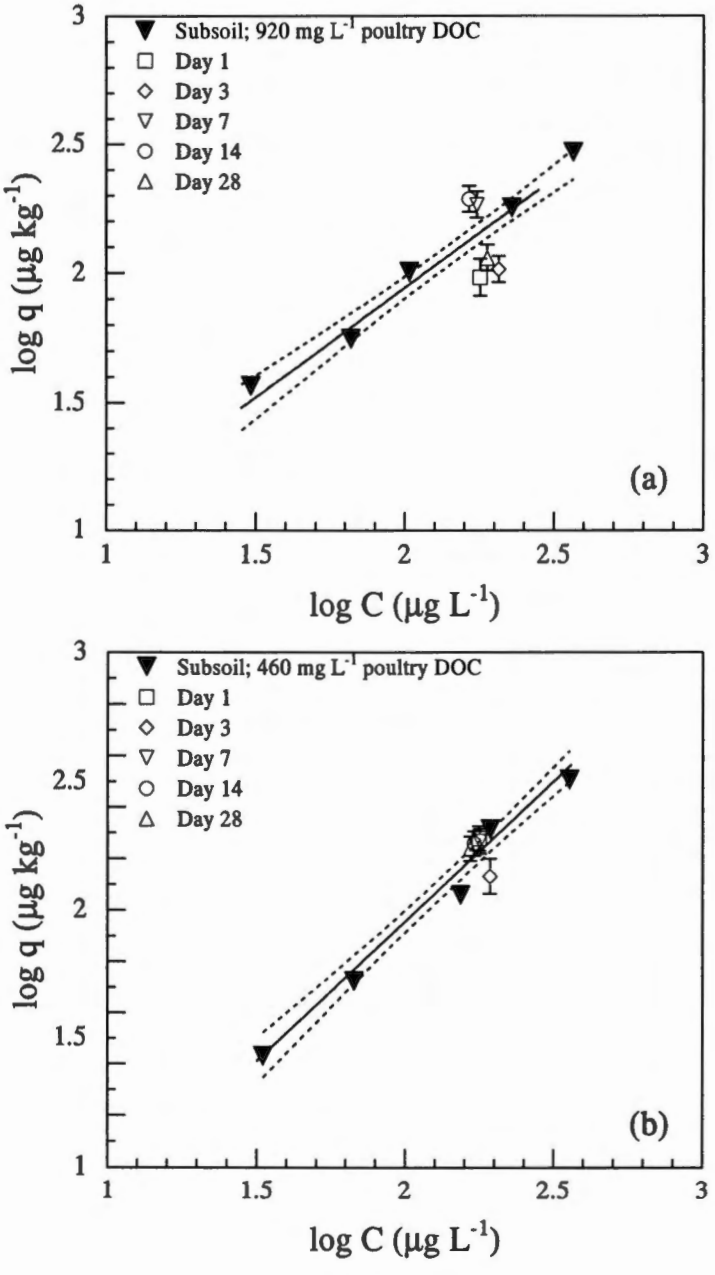


Figure 4.54. Desorption of norflurazon from subsoil with (a)1150 mg poultry DOC L^{-1} and (b) 575 mg poultry DOC L^{-1}.

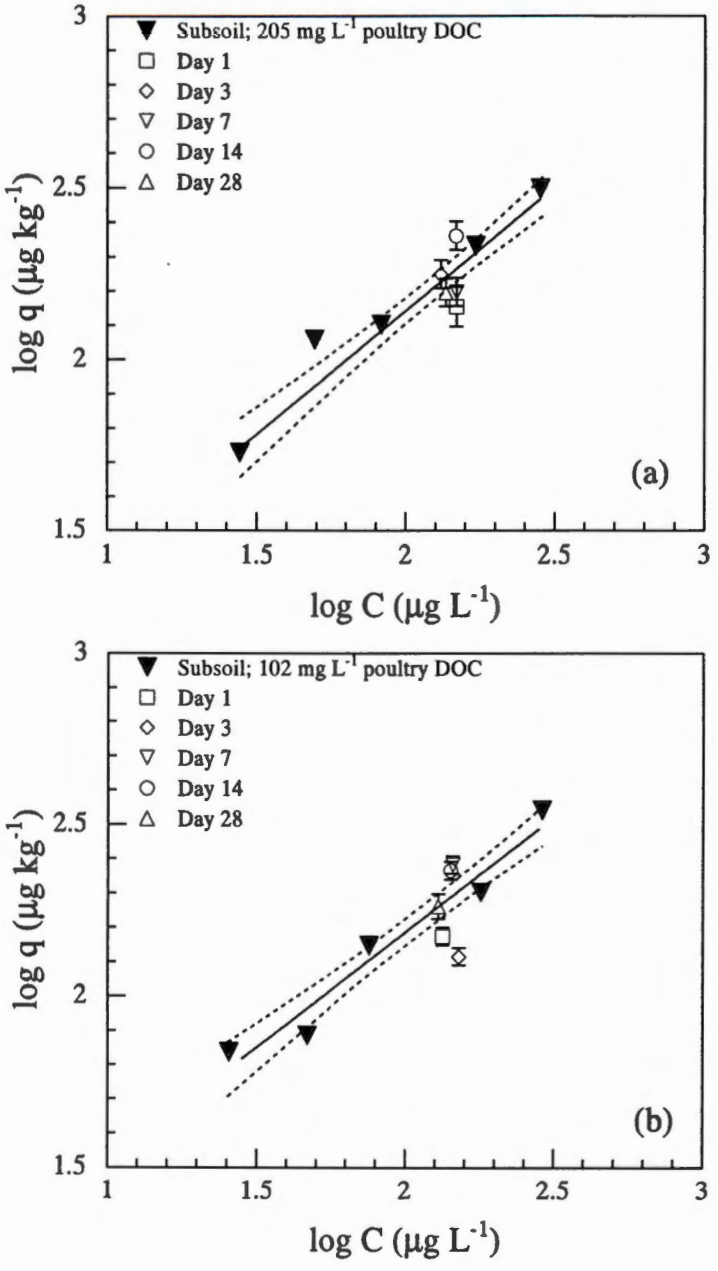


Figure 4.55. Desorption of norflurazon from subsoil with (a) 255 mg poultry DOC L^{-1} and (b) 130 mg poultry DOC L^{-1}.

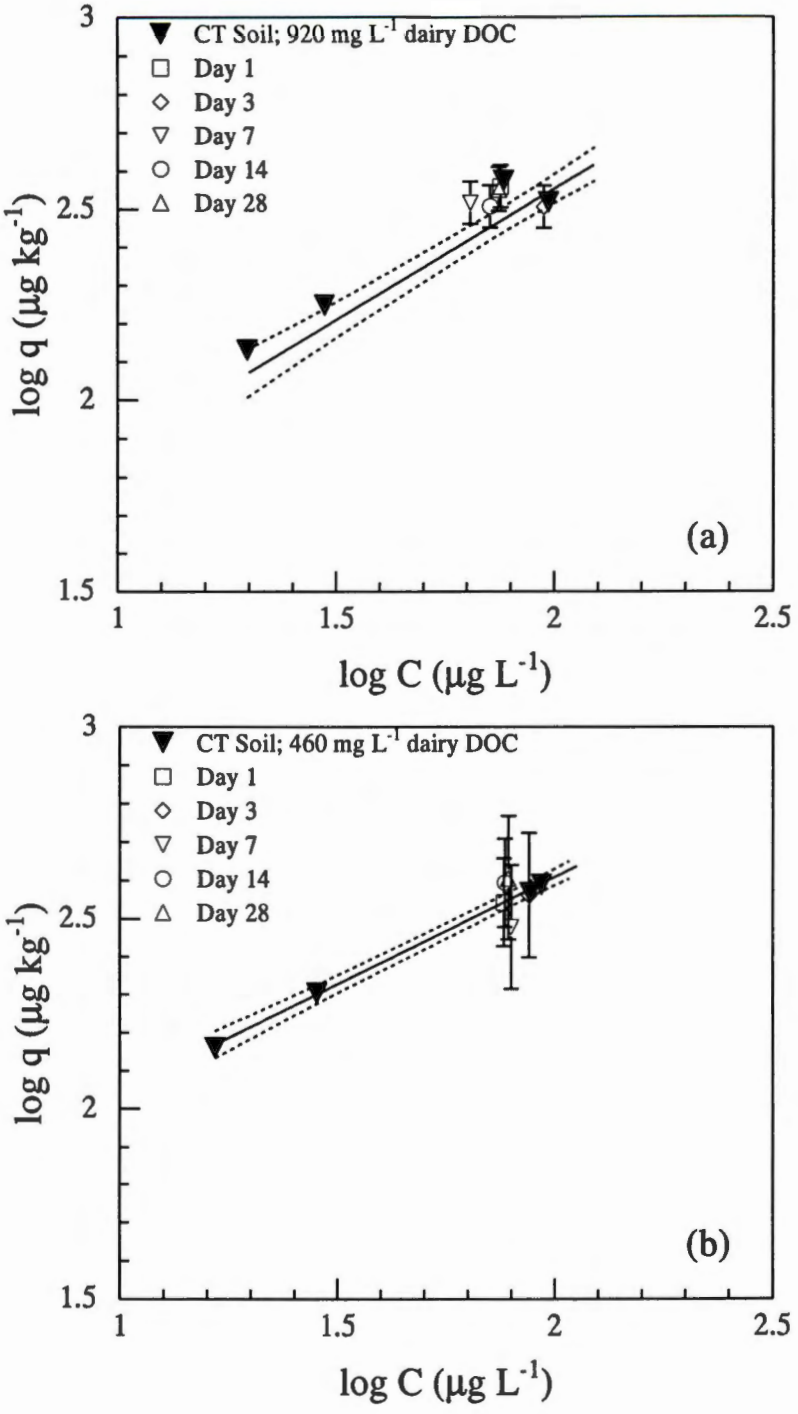


Figure 4.56. Desorption of norflurazon from conventional tillage surface soil with (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

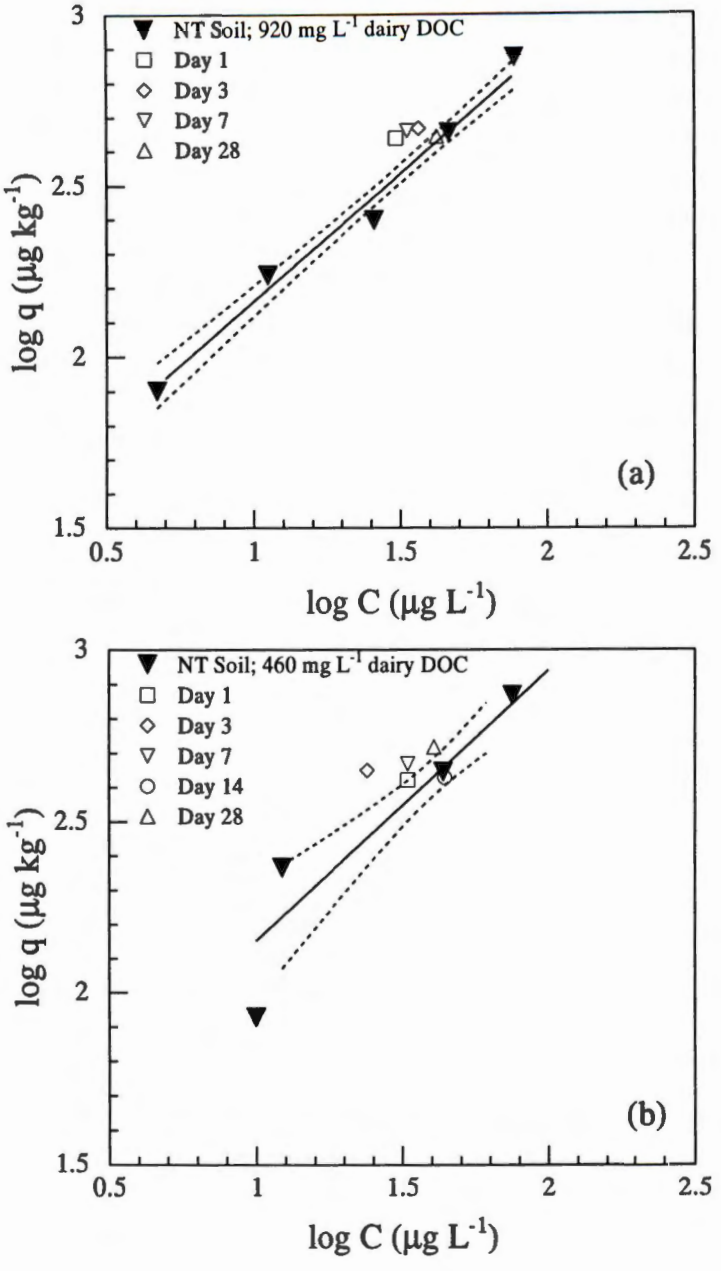


Figure 4.57. Desorption of norflurazon from no-till surface soil with (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

reversibility was achieved after 14 and 28 days of equilibration. Figure 4.58 shows hysteresis with 3 and 7 days of equilibration in the 575 mg dairy DOC L^{-1} desorption system (Figure 4.57). Overall, NORF desorption from NT surface soil increased with desorption equilibration time. Sorption of NORF by SUB soil was reversible with 1150 mg dairy DOC in the desorption system (Figure 4.58). Norflurazon sorption was generally reversible with 575 mg dairy DOC L^{-1} in the desorption system (Figure 4.58).

No-till Dissolved Organic Carbon:

Norflurazon desorption hysteresis is evident with 95 and 47 mg NT DOC L^{-1} in the SUB soil desorption systems (Figure 4.59). Statistical separation of the desorption data indicates that desorption is significantly less after 7, 14, and 28 days than in the first 3 days of equilibration (Table 4.8). Thus, desorption is inversely correlated with desorption equilibration time. Figure 4.59 shows desorption hysteresis after 7, 14, and 28 days of equilibration in the 47 mg NT DOC L^{-1} system. Thus, NORF desorption decreases with time and displays hysteresis after 7 days in NT DOC systems.

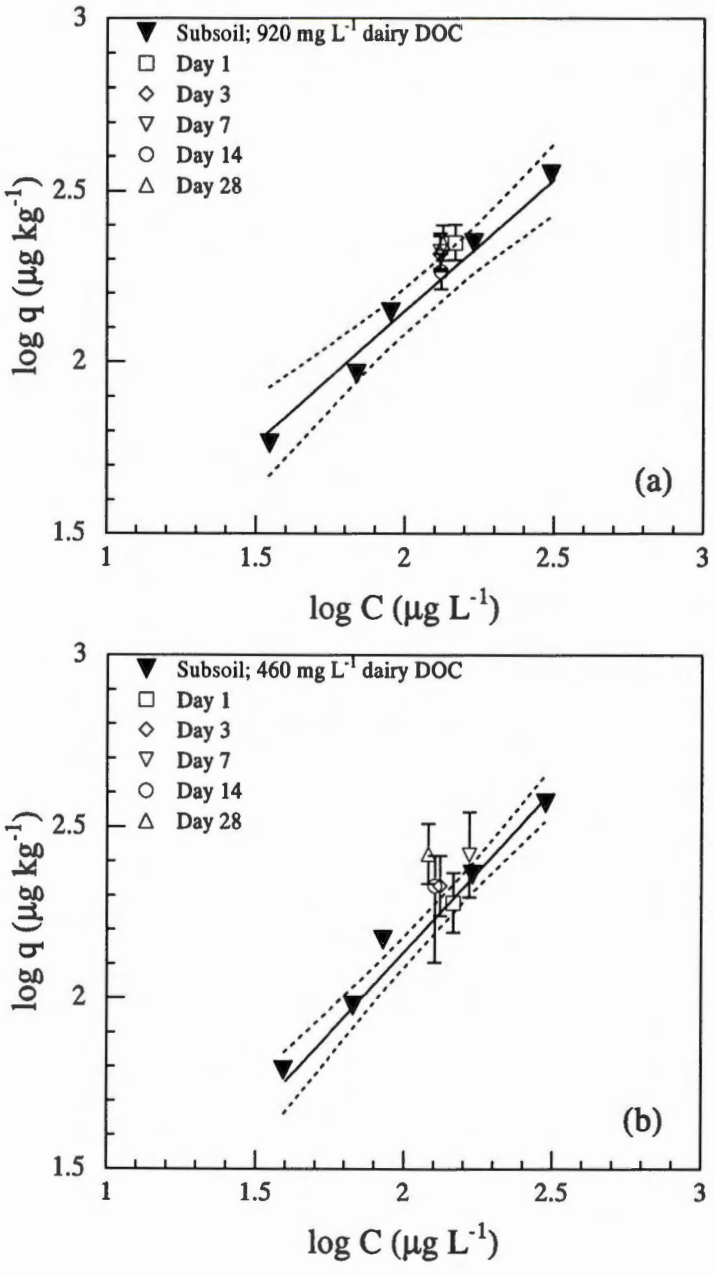


Figure 4.58. Desorption of norflurazon from subsoil with (a) 1150 mg dairy DOC L^{-1} and (b) 575 mg dairy DOC L^{-1}.

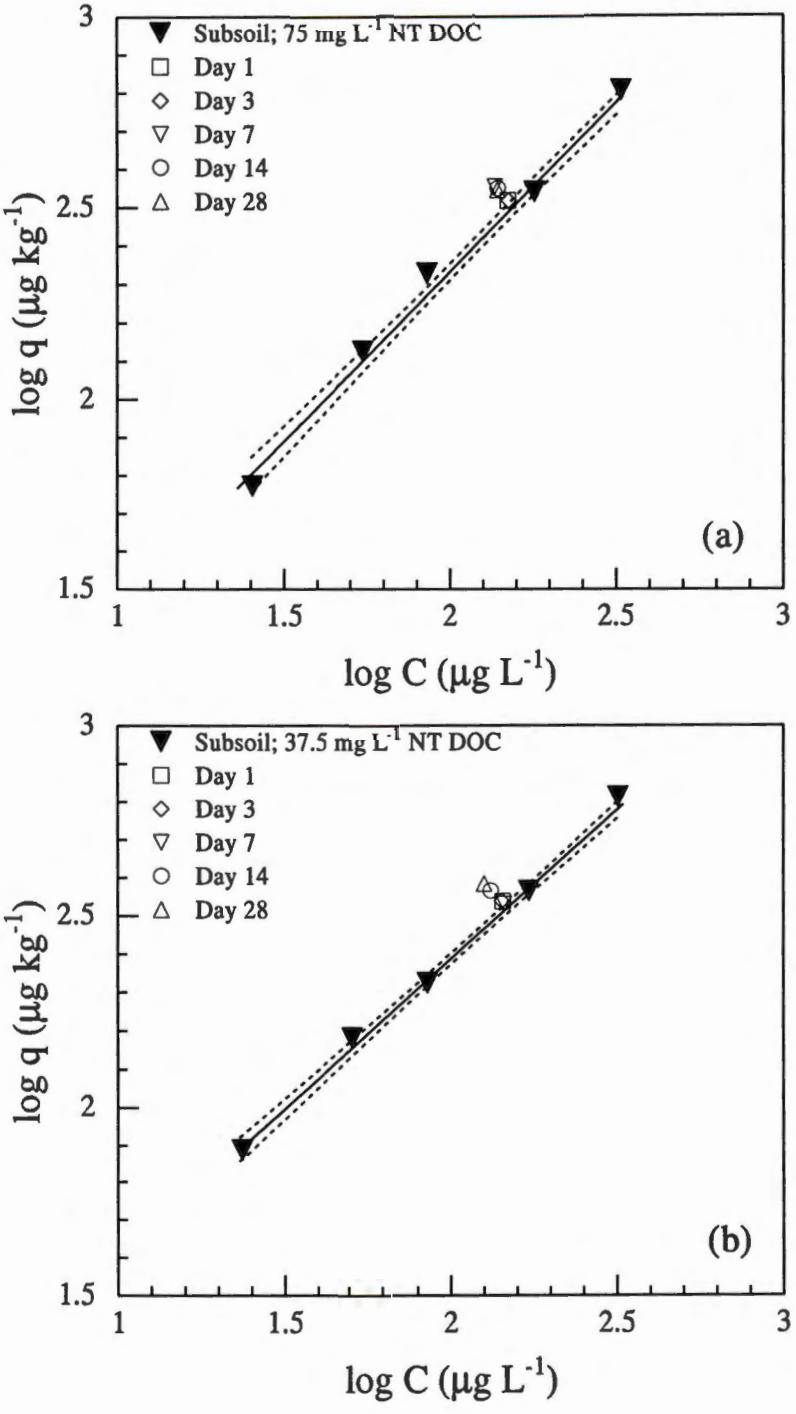


Figure 4.59. Desorption of norflurazon from subsoil with (a) 95 mg no-till DOC L^{-1} and (b) 47 mg no-till DOC L^{-1}.

CHAPTER V

SUMMARY AND CONCLUSIONS

Fluometuron (FLMT) and norflurazon (NORF) are preemergence herbicides applied to cotton in the southeastern U.S. Residual levels of both herbicides have been detected in soils long after application, potentially posing risks to subsequent crops and groundwater resources. Sorption of trace organic compounds in the soil environment is an important mechanism influencing their fate and behavior. The sorption of trace organic compounds by soil organic matter (SOM) is commonly cited as the dominant mechanism by which herbicides are removed from the aqueous phase. Both batch sorption and field studies have shown that SOM content is positively correlated with the soil retention of the FLMT and NORF. Dissolved organic carbon (DOC) may also influence the fate and behavior of trace organic compounds in the soil environment. Although the effect of DOC is not as well defined as the solid SOM, DOC concentrations greater than 100 mg L^{-1} have been shown to reduce the sorption of some trace organic compounds in soil systems.

The objectives of this study were to 1) determine the effect of tillage, (SOM content) on the sorption and desorption of FLMT and NORF, 2) determine the effect of DOC source (poultry litter, dairy manure, and NT surface soil) and concentration on the sorption of FLMT and NORF by the soils 3) examine the effect of NT DOC on subsoil sorption of FLMT and NORF.

Agricultural tillage methods greatly impact soil properties, including SOM concentration and distribution. No-till methods (NT) conserve surface mulch and natural

vegetation with minimal disturbance of soil structure during planting. Conventional tillage (CT) methods destroy soil macroporosity and native vegetative root structures and incorporate surface mulch into the plow zone. No-till soils typically have greater SOM content and greater macroporosity while CT soils have less SOM and little macroporosity.

The increased SOM content and surface mulch of NT systems enhanced the sorption of FLMT and NORF. The retention of FLMT and NORF by Lexington silt loam decreases in the follkowing order: no-till > conventional-till > sub soil. Herbicide sorption conformed to the L-curve and C-curve isotherms, with the C-curve being more representative of sorption by the high-organic carbon, NT surface soil. Current literature minimizes the importance of trace organic coupound sorption by clay fractions of soil matrices. However, significant sorption of both FLMT and NORF have been shown in pure mineral systems. Thus, SOM coupled with clay and amorphous minerals in the soil matrix are responsible for sorption of FLMT and NORF.

Dissolved organic carbon may alter the fate and transport of trace organic compounds in the soil environment. Water solubility enhancement of many nonionic pesticides has been noted in the presence of dissolved humic and fulvic acids. The aggregate enhancing properties of DOC may coat soil surfaces and alter the adsorptive capacity of the soil matrix. Competition for soil sorption sites between herbicides and DOC molecules may also effect sorption. Characterization of the relative size and functionality of DOC may elucidate the mechanisms that influence herbicide retention.

Sorption of FLMT and NORF were generally reduced with DOC in the sorption equilibration solution, regardless of source or concentration. The greatest reduction in FLMT and NORF sorption occurred with poultry DOC in the sorption solution. Dairy DOC ranked second in decreasing the amount of herbicide adsorbed by the Lexington silt loam, followed by NT DOC. Spectroscopic E_4/E_6 ratios and gel chromatographic analysis of the DOC source molecules was performed to characterize the DOC. The poultry, dairy, and NT DOC were characterized as having predominately fulvic acid - like character solutions by the E_4/E_6 ratio. Gel permeation chromatography revealed that poultry DOC had the greatest distribution of large DOC molecules, while dairy DOC had a significant distribution of both smaller and larger molecules. No-till DOC was composed of a single size distribution of molecules that were close in size to FLMT and NORF. Thus, the NT DOC was assumed to contain primarily small DOC molecules. The spectroscopic characterization of the DOC molecules coupled with the sorption results suggests that the large DOC molecules reduced the sorption of the herbicides.

The concentration of DOC in the sorption systems also influenced the sorption of FLMT and NORF. In general, sorption decreased with increasing DOC concentration for all DOC sources. Recent literature suggests that DOC concentrations below 100 mg DOC L^{-1} do not effect the sorption of trace organic compounds. However, this study shows that DOC concentrations as low as 75 and to a lesser extent, 37.5 mg L^{-1} result in reduced sorption of the herbicides.

The aqueous association of herbicide with DOC can be quantified by the K_{DOC}. Solid SOM is known to be at least twice as effective a sorbent for trace organic

compounds compared to soluble DOC. Therefore, SOM should exert a much larger influence on the sorption of FLMT and NORF in these soils. The organic carbon normalized distribution coefficients (K_{OC} values) indicate the contribution of SOM to orgnaic compound sorption. Computed K_{DOC} values greatly exceeded the K_{OC} values calculated in this study. Thus, DOC complexation of the herbicides in solution is improbable in these systems. A different mechanism of DOC influence is at work in these systems. Perhaps competition between the herbicide and DOC for limited sorption sites is at work in these systems. Conversely, DOC may coat the soil surfaces and present a hydrophobic surface that forces the herbicides to remain in aqueous solution.

Desorption hysteresis is noted extensively in trace organic compound sorption studies. Hysteresis may be an artifact of scientific methodology or a real phenomenon in the sorption of herbicides by soils. The biphasic nature of sorption and desorption reactions, especially in soils with significant SOM content, may influence the fate and behavior of trace organic compounds. Slow and continuing sorption of herbicides months after application has been shown in many field and laboratory studies. This kinetic effect may be due to the slow diffusion of solutes into organic and soil ped matrices. Moreover, the slowly sorbed fraction of pesticides requires significant time for desorption to take place. Therefore, it is important to examine the kinetics of desorption when considering the fate and transport of herbicides.

Desorption of FLMT and NORF from Lexington silt loam exhibited extensive hysteresis in all soil systems. Hysteresis was greater with NORF, compared to FLMT. No effect of SOM content on desorption hystersis was evident with these systems.

Desorption of FLMT and NORF from the Lexington silt loam samples was enhanced with the addition of DOC to the soil systems. Poultry DOC enhanced desorption the greatest followed by dairy and NT DOC, respectively. The DOC desorption systems appeared to exhibit reversible herbicide sorption when compared with the no-DOC system. However, the addition of DOC at the desorption step changed the chemistry of the system. Thus, desorption should revert to a DOC sorption isotherm. Some poultry DOC isotherms showed reversible herbicide sorption. In general, desorption was incomplete in these desorption systems.

A threshold concentration exists where DOC no longer influences herbicide sorptiion equilibria. Neither 20 nor 10 mg DOC L^{-1} facilitated reversible sorption for either herbicide. In systems with DOC concentrations greater than 20 mg L^{-1}, desorption reversibility was approached with equilibration time. However, in systems with 10 mg DOC L^{-1}, herbicide desorption hysteresis increased with equilibration time. Thus, a threshold where DOC (regardless of source) influences the sorption and desorption of herbicides, exists between 20 and 10 mg DOC L^{-1}.

Desorption of FLMT and NORF sorbed in the presence of DOC occurred at a much faster rate than the systems DOC absent. Poultry DOC both decreased sorption the greatest and enhanced desorption the most, followed by dairy and then NT DOC. The desorption of FLMT and NORF from SUB soil with 1150 mg poultry DOC L^{-1} in the desorption solution resulted in less herbicide sorption than at the onset of the desorption process, where there was only 920 mg poultry DOC L^{-1} in the sorption system. Perhaps, the desorption of herbicides in the presence of 1150 mg poultry DOC L^{-1} followed an

sorption isotherm consistent with the presence of 1150 mg poultry DOC L^{-1} in the sorption solution. The SUB soil isotherms indicate the effectiveness of the poultry DOC to suppress sorption of herbicides in these soil systems. Dairy DOC facilitated the desorption of FLMT and NORF adsorbed in the presence of lesser concentrations of dairy DOC. Similarly, NT DOC resulted in less sorption of FLMT and NORF, and greater desorption of the herbicides. Sorption of FLMT was reversible with both 95 and 47 mg NT DOC L^{-1} in the desorption solution. However, NORF desorption decreased with desorption time in the NT desorption systems. Norflurazon was reversible within 3 days of desorption equilibration. However, desorption with greater than 3 days of equilibration exhibited increased hysteresis. The NT DOC systems also ilustrate the effect of tillage on sorption processes deep within the soil profile. Tillage effects are not merely limited to the soil surface. Increased DOC content and volume of water reaching the subsoil in no-till systems could reduce the sorption of applied pesticides. Moreover, the mobility of these pesticides will be enhanced by the NT DOC in solution. Groundwater and sub surface soil water may contain and transport increased levels of pesticides in no-tillage vs. conventional tillage systems.

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VITA

Jennifer S. Dore was raised in Huntingdon, Pennsylvaina, by her loving parents, Michael and Judith Dore. She and her younger brother attended the public schools in Huntingdon County. After graduating from Huntingdon Area High School in 1990, Jennifer attended Susquehanna University. She graduated in May 1994 with a BS in Environmental Science, specializing in groundwater hydrology. She held an associate internship position with Oak Ridge Associated Universities at the Hazardous Waste Remediation Program through Lockheed Martin in Oak Ridge, Tennessee, until she enrolled at The University of Tennessee in August 1994. With the conclusion of this thesis, she will graduate with a Masters of Science, specializing in soil chemistry in December of 1996.

Currently, she is pursuing a career in soil and groundwater hydrology, specializing in the characterization and remediation of contaminated soil and groundwater.

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