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thesis entitled
ORGANIC COMPOUND SORPTION BY
KENTUCKY BLUEGRASS (POA PRATENSIS L.)
LEAVES AND THATCH

presented by

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has been accepted towards fulfillment
of the requirements for

Masters of Science degree in Crop & Soil Sciences

Bruce Branham

Major professor

Date March 15, 1994

ORGANIC COMPOUND SORPTION BY KENTUCKY BLUEGRASS (*Poa pratensis* L.) LEAVES AND THATCH

By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTERS OF SCIENCE

Department of Crop and Soil Sciences

1994

ABSTRACT

ORGANIC COMPOUND SORPTION BY
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Soil organic matter and plant litter layers are largely responsible for the immobility of organic compounds in agronomic environments. The objective of this research was to determine organic compound sorption by turfgrass leaves and thatch based upon water solubilities (S_W) and octanol/water partition coefficients. Batch-suspension experiments for five nonionic organic compounds (phenanthrene, fenarimol, 1,2,4-trichlorobenzene, ethoprop and acetanilide) with S_W from 1 to 5405 mg L^{-1} were completed on *Poa pratensis* L. cv. Touchdown leaves and thatch. The resulting linear sorption isotherms suggest the sorption mechanism between organic compounds and leaves or thatch is consistent with a partitioning sorption mechanism. Sorption coefficients for thatch were less than those from leaves for the 4 most hydrophobic compounds, which suggests thatch is a more polar sorbent than leaves. Acetanilide was more strongly sorbed and phenanthrene was less strongly sorbed by leaves when mixed with a commercially used pesticide formulation than when it was not formulated.

To Jodi and Jason,

Do not forsake wisdom, and she will protect you;
love her, and she will watch over you. (Proverbs 4:6)

ACKNOWLEDGEMENTS

I want to wish my most sincere thanks to Dr. Bruce Branham for his unending guidance, financial assitance and friendship. The professional contributions of my committee, Dr. Stephen Boyd, Dr. Donald Penner, Dr. Paul Rieke, and Dr. Matthew Zabik were greatly appreciated. Thanks are extended to Rhone Poulenc and DowElanco for the gift of ^{14}C labeled ethoprop and fenarimol. My association with the turfgrass graduate students of Michigan State University will never be forgotten.

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INTRODUCTION

Estimates of total pesticide usage in the United States are around 500 million kg applied to 150 million ha (16% of the total land mass of the U.S.) (Pimental and Levitan, 1986). The environmental fate of pesticides is an issue of increasing concern. Due to increasing environmental awareness in the last two decades, the U.S. Environmental Protection Agency conducted a survey of drinking water wells in order to clarify the degree of contamination from pesticides (USEPA, 1990).

When cultural and other options have not been effective for the control of massive insect, disease and weed infestations, pesticide treatments are the only option for maintaining healthy crops (Potter and Braman, 1991). Unfortunately, most of the pesticide fate research has addressed more traditional forms of agriculture such as crop production and largely ignored more urban forms of agriculture. There are many dissimilarities between the turfgrass system and the crop production system. The no-tillage crop production, forage and turfgrass systems are probably the most similar. No other system has a dense monostand and thatch layer such as that which occurs in turf.

The application of pesticides to crops, which are not feeding the world, may seem unnecessary, but all one has to do is evaluate the importance of the turfgrass industry in a state such as Michigan to realize that this industry has a strong place in state economics. As of 1988 there were 2.9 $x10^6$ acres of turfgrass in Michigan (MTF, 1988). Sixty-six percent of this land area was in

lawn care/landscaping, 9% was in golf courses and 9% in highways. In that same year, lawn care operators spent $297 x 10^6, and golf courses spent $80.3 x 10^6 on turf maintenance in Michigan.

Soil organic matter and plant litter layers are largely responsible for the immobility of organic compounds in agronomic environments (Boyd et al., 1990; Chiou, 1989). The turfgrass thatch layer and grass leaves (verdure) should also act as a strong partitioning media for most pesticides.

The objectives of this research were to determine nonionic organic compound sorption (partitioning) by turfgrass leaves and thatch; secondly, to correlate water solubilities and octanol/water partition coefficients (K_{ow}) of the compounds with leaf and thatch sorption; and finally to determine the effect of surfactants in an EC formulation on nonionic organic compound sorption by leaves.

LITERATURE REVIEW

Pesticide Sorption in Soils

The following review addresses sorption of organic compounds to sorbents in agronomic systems such as conventional and no-tillage production agriculture and the relationship of this information with turfgrass systems. The term sorption can be defined as the absorption, adsorption, desorption to sorbents such as soil organic matter, or partitioning of a compound into a sorbent such as soil organic matter.

Sorption is usually determined by one of four methods (Green et al., 1980). Three of these methods were developed to leave soil columns intact and apply a flow of solution containing the solute of interest to the column. These methods help simulate the real world, but they may label nonwater soluble compounds as mobile, when sorption coefficients tell otherwise (e.g.. Hurto and Turgeon, 1979). Soil column methods have their advantages, but the batch-suspension method has become the most widely used and is accepted for pesticide registration purposes (USEPA, 1975). The batch-suspension method involves placing a solute at a known concentration in a solution (usually water), and then suspending the sorbent in the solution. The solution containing the solute and sorbent are then shaken until equilibrium is reached and the quantity sorbed is determined. The advantages of this method far outweigh the disadvantages. The batch-suspension method reaches equilibrium quickly, requires very little specialized equipment, and desorption can also be readily determined (Green et al., 1980). The disadvantages of this method are that only one data point for sorption determination can be derived from one suspension, there is poor precision at very low and high solute

concentrations, soil (sorbent) aggregate structure is not maintained, and the method tells nothing about sorption kinetics (Green et al., 1980).

Sorption is usually quantified with sorption isotherms, which relate a quantity sorbed (Q_S) to a quantity remaining in solution at equilibrium (C_e) (Singh et al., 1990). Most isotherms for sorption of organic pestcides by soil can be derived from the empirical Freundlich equation, $Q_S = KC_e^{1/n}$ (Hassett and Banwart, 1989; Weber and Miller, 1989). Where K is the sorption coefficient, and n is an empirical constant. When n=1, the isotherm is linear, and this occurs frequently for nonionic pesticides (Chiou, 1989). Weber and Miller (1989) give thorough descriptions of nonlinear isotherms and when they occur. The K value (slope) is derived from a plot of the linear isotherm (when n=1), and it is independent of the solute concentration at concentrations from 10-80% of a compound's water solubility (Chiou, 1989). The primary factor determining the magnitude of the K value is the water solubility (S_W) of the solute (Hance, 1976; Chiou, 1989; Doust and Huang, 1992). Isotherm determination is not strongly temperature dependent from 15-35°C (Chiou, 1989; Hassett and Banwart, 1989).

Wauchope et al. (1983), Singh et al. (1990), and Mingelgrin and Gerstl (1983) have cautioned against back transformations from experimentally determined log K values in the literature, which are often reported in the log form, to quantities sorbed by soils. Differences in techniques, sorbents, and experimental conditions could lead to variations as large as 75% from what would be expected. Chiou (1989) has noted how large molecular weight solutes will often behave unpredictably due to magnification of incompatibilities between the large solute and the organic sorbent, which he views as analogous to an organic solvent.

The ratio of sorbent(soil):solution in a batch-suspension experiment can also have a significant effect on K values (Grover and Hance, 1970). They observed a 5 fold increase in linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea(*N* '-(3,4-dichlorophenyl)- *N*-methoxy-*N*-methylurea), S_W = 75 mg L^{-1} (WSSA, 1989)] adsorption at a soil:solution ratio of 1:10 from that observed at 4:1. The ratio did not have as large an effect on atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)- *s*-triazine, S_W = 33 mg L^{-1} (WSSA, 1989)] sorption (Grover and Hance, 1970) or the sorption of several insecticides (Bowman and Sans, 1985a). Most batch-suspension methods are now conducted at sorbent:solution ratios of at least 1:10 (Chiou, 1989; Singh et al., 1990), and the sorbent:solution ratio must always be reported.

As noted earlier, the soil aggregate size is disrupted with the batch-suspension method, and sorption studies conducted on nondisrupted soils show how aggregate size and soil moisture at time of treatment can greatly affect sorption (Chiou, 1989; Grover and Hance, 1970; and Hance, 1976). Dispersion of soil aggregates is much greater at lower soil:solution ratios, and K values were lower for linuron and atrazine on large soil aggregates than were predicted (Grover and Hance, 1970). Another study (Hance, 1976) showed that soil aggregate size affected sorption of more polar compounds such as metribuzin [(4-amino-6-(1,1-dimethylethyl)-3-(methlythio)-1,2,4-triazin-5(4 *H*)-one), S_W = 1220 mg L^{-1} (WSSA, 1989)], but a less polar compound such as simazine [2-chloro-4,6-bis(ethylamino)- *s*-triazine, S_W = 6.2 mg L^{-1} (Wauchope et al., 1992)] showed no dependence on aggregate size. In this same study, metribuzin was not as easily removed from a soil that was wet when treated as from a soil that was dry when treated. The opposite was true for the simazine, which was not as easily removed from a soil that was dry when treated as from a soil that was wet when treated (Hance, 1976). It will be explained later how

nonionic compound sorption by hydrated soils is linear and largely dependent upon the concentration of soil organic matter (SOM), but when soils are dry or subsaturated nonlinear isotherms can be expected.

Chiou and Schmedding (1982) were one of the first to propose the theory of nonionic compound partitioning in soils rather than an adsorption/desorption mechanism, and this theory has remained largely unopposed with only a few exceptions (Mingelgrin and Gerstl, 1983). The evidence for a partitioning mechanism is as follows: 1) compounds nearly always exhibit linear sorption isotherms over a large concentration range approaching their water solubilities, 2) there are no competitive effects when two solutes are placed in the same solution (Chiou et al., 1983, and Chiou 1989), and 3) the lack of temperature dependence on isotherm determination indicates small exothermic or endothermic enthalpies are involved as would be expected for a partitioning process (Hassett and Banwart, 1989; Chiou, 1989; Wauchope et al., 1983). Wauchope et al. (1983) and Wauchope and Koskinen (1983) have given a thorough review of binding mechanisms. They feel the important measurement is the free-energy change (ΔG) associated with the transition from one state to another, such as from the aqueous state to the adsorbed state for a given solute. Both of these papers also discuss the changes in entropy and enthalpy of the solvent close to the "binding site", and how this can be used to investigate sorption. Weber and Peter (1982) hypothesized that the binding of acetanilide herbicides was probably planar H bonding and charge transfer across π bonds with SOM. Wauchope and Koskinen (1983) demonstrated through thermodynamic analysis that nonpolar herbicides behave similarly when binding to the soil surface, and the binding mechanism is non-specific.

Partitioning of organic compounds in soils is often compared with the partitioning of a solute between two immiscible solvents such as octanol and water (Chiou and Schmedding, 1982 and 1983; Chiou, 1989; Hassett and Banwart, 1989; Schwarzenbach and Westall, 1981; Gerstl and Mingelgrin, 1984). The partitioning between the two solvents determines a partition coefficient (K_{ow}) for the two solvent system, which is a constant for a given solute (OECD, 1981). The K_{ow} is a better modeling parameter than water solubility (S_w) because of large inconsistencies in reported S_w values in the literature. K_{ow} can be accurately determined for all but extremely polar compounds (Gerstl and Mingelgrin, 1984), and the lower a given compound's water solubility, the better the correlation between its high K_{ow} and soil sorption (Mingelgrin and Gerstl, 1983).

There is a linear inverse relationship between log K_{ow} and log S_w (Müller and Klein, 1992), but this relationship improves when S_w is converted to super-cooled liquid water solubility for compounds with a melting point greater than 25°C (Chiou and Schmedding, 1982; Müller and Klein, 1992; Briggs, 1981; Dell et al. 1994). Chiou and Schmedding (1982) explained the ideal linear inverse relationship would have a slope of -1, and conversion to super-cooled liquid water solubility brings the slope closer to the ideal -1. He evaluated 36 aromatic liquids and solids and correlated log K_{ow} with log S_w (super-cooled S_w) to get an r^2 of 0.994 and a slope of -0.862. The very slight solubility of water in octanol and octanol in water cannot be ignored because they have a large influence on the solubility of extremely hydrophobic compounds in each phase (Mackay, 1977; Chiou and Schmedding, 1982; Briggs, 1981).

Nearly all sorption studies draw correlations between K_{ow} values and experimentally determined K values from isotherms (Chiou, 1989). This has

proven effective on soil organic matter (Chiou, 1989), lake sediments (Means et al., 1980), plant cuticle (Kerler and Schönherr, 1988a) and even more complex lipids such as those found in fish fats (Chiou, 1985) and the organic rich linings in earthworm burrows (Stehouwer et al., 1993). Mingelgrin and Gerstl (1983) point out the limitations of using parameters such as K_{om}, K_{ow} and S_w for correlations with soil sorption. Correlations between K_{ow}, percent organic carbon and S_w parameters to sorption by subsoils has proven ineffective in at least one instance (Ainsworth et al., 1989) due to differences in the structure and type of organic carbon. Dell et al. (1994) and Veith et al. (1979) have described the strong linear relationship between K_{ow} values and retention times from reverse-phase HPLC.

The Importance of Soil Organic Matter

Soil organic matter (SOM) is the soil fraction that is of primary importance for organic compound sorption (Weed and Weber, 1974). The SOM includes polymeric humic and fulvic acids, which are usually defined by their extractablility from soils (Stevenson, 1982). There is some disagreement as to when the percent clay may become important in organic compound sorption (Hassett and Banwart, 1989; Schwarzenbach and Westall, 1981; Chiou, 1989; Chiou et al., 1983; Gerstl and Mingelgrin, 1984; Wilson et al., 1981; Wietersen et al., 1993; Weber and Peter, 1982), but water holding capacity and hydraulic conductivity are important also (Wietersen et al., 1993). In general, the percent clay becomes important when the % SOM is less then 1-2% and the percent clay is greater than 10-12%. The type and content of the clay minerals in dry soils can be important (Chiou, 1989; Ainsworth et al., 1989; Singh et al., 1990; Loux et al., 1989). Rutherford and Chiou (1992) explained how "the main effect of water in drying-wetting cycles is the suppression of adsorption by minerals

rather than partitioning into organic matter". Subsoils will show widely varying sorption characteristics due to different degrees of weathering when the percent organic matter present is minimal (Ainsworth et al., 1989).

The differences in sorption of nonionic organic compounds to different soils and between different studies are probably due to the differences in quantity and polarity of the SOM (Gerstl and Mingelgrin, 1984; Rutherford et al., 1992; Manilal and Alexander, 1991). For this reason many researchers will report partition coefficients normalized for soil organic matter (K_{om}) or organic carbon (K_{oc}) (Hassett and Banwart, 1989; Chiou, 1989). K_{om} and K_{oc} values are determined by dividing the K value from the isotherm by the fraction of soil organic matter or organic carbon. Therefore, K_{om} and K_{oc} increase linearly with increasing organic matter and organic carbon contents of soils, and the prediction of K values from K_{oc} of soil ($K = K_{oc}$ x organic carbon fraction) is best when the organic carbon content is moderate to high (Mallawatantri and Mulla, 1992). Mallawatantri and Mulla (1992) showed that every compound does not have a single K_{oc} value due to the wide variability present in the content and nature (polarity) of SOM and soil minerals. Karickhoff (1981) presented the equation $K_{oc} = 0.411\ K_{ow}$.

The affinity of some hydrophobic compounds for soil organic matter is so strong that the concentration of dissolved organic matter (DOM) in solutions can not be ignored (Chiou et al., 1986 and 1987; Kile and Chiou, 1989). Organic matter is dissolved into soil water as water infiltrates through a soil profile, and it can mobilize compounds that are normally immobile (Stahnke et al., 1991; Gschwend and Wu, 1985). Chiou et al. (1986) concluded DOM is only important for the most water insoluble organic compounds such as DDT [1,1'-(2,2,2-trichloroethylidene)bis(4-chlorobenzene) S_w = 1.2-5.5 $\mu g\ L^{-1}$ (Montgomery, 1993)], when the DOM is nonpolar, and when the concentrations

of DOM are 100x greater than the S_W of the compound of interest. An organic solute can form micelles with DOM (Kile and Chiou, 1989), and the micelles are similar to those formed in pesticide formulations (WSSA, 1982). The solubility enhancement of hydrophobic organic compounds may make the compound more mobile in the soil's aqueous phase, but the formation of micelles did not make a hydrophobic compound more easily degradable by microorganisms for Laha and Luthy (1992).

Caution must also be taken when modifying the solution (water) with solvents such as organic alcohols. Such modifications may allow an extremely hydrophobic solute such as DDT to dissolve in the solution, but this modification will change the solvent strength relative to the sorbent thereby changing the affinity of the solute for the sorbent (Hassett and Banwart, 1989; Kile and Chiou, 1989). This effect will be more pronounced on nonpolar solutes. One must also pay attention to whether micelles can be formed with the modifying solvents and the solute (Hassett and Banwart, 1989; Kile and Chiou, 1989).

Spencer et al. (1988) and Taylor and Spencer (1990) gave thorough descriptions of the factors involved in organic compound volatilization from soil. They concluded that compounds accumulate at the soil surface by convection through soil water before they evaporate. Volatilization increases as the concentration of a compound increases at the soil surface. Volatilization of compounds is usually modeled using the Henry's Law Constant (K_H), which is the equilibrium constant for a compound between vapor and a solution. Chemicals with low Henry's Law Constants have been shown to accumulate at the soil surface while water is evaporating (Spencer et al., 1988). This accumulation was shown to result in increased volatilization over time. Volatilization of compounds with low K_H is determined by the still-air boundary layer above a soil, water evaporation rate and the K_H. When a compound has

a high K_H, volatilization is largely controlled by the soil properties. Spencer et al. (1988) accurately predicted the volatilization of two very different compounds using their K_H values.

The one factor in pesticide fate research that is most variable is microbial degradation (Hance, 1988). Scribner et al. (1992) found that aged simazine residues did not desorb from a soil as readily as newly added residues. Therefore, the aged residues did not enter the aqueous phase as readily as new residues where they could be degraded. As is the case with many pesticide sorption studies (Bowman and Sans, 1985b), the desorption mechanisms were not clear, but the longer the simazine remained in the soil, the less accurate were the predictions of partitioning between soil and water. After 3-4 months only 5% of the simazine residues that were predicted to be in soil solution were actually present there. Therefore, the sorbed simazine residues remained in the soil much longer than expected (based on their half-life and partition coefficients), because the sorbed residues could not be degraded. Koskinen and Harper (1990) explain how a compound's bonding to soils can get stronger as residence times increase. Laha and Luthy (1992) showed that hydrophobic compounds could be easily mobilized in soils with surfactants, but cpompounds in micelles were fairly non degradable.

Models have been developed for predicting pesticide sorption (Green and Karikhoff, 1990) and fate (Wagenet and Rao, 1990). Green and Karikhoff (1990) presented numerous equations for predicting K_{OC} from K_{OW} and/or S_W taking the characteristics of the solute into consideration. One of the first fairly accurate models was PRZM (Pesticide Root Zone Model) (Carsel et al., 1984), but it was soon discovered that PRZM had its limitations (Wagnet and Hutson, 1986). Wagnet and Hutson (1986) devised a leaching model of their own and called it LEACHMP (Leaching Estimation and Chemistry Model-Pesticides).

They tested their model in the field on the herbicide aldicarb [2-methyl-2-(methylthio)-propionaldehyde *O*-(methylcarbamoyl)oxime, S_w = 6000 mg L^{-1} (Wauchope et al., 1992)] and the results were very promising. Jury et al. (1983, 1984a,b,c) thoroughly described the processes involved in building a model for pesticide fate in soils. They grouped chemicals into three broad classifications based on their properties, and determined the necessity for estimations and determinations of the following parameters to get an accurate picture of the most probable loss pathway: 1) Organic carbon partition coefficient (K_{OC}), 2) Saturated vapor density (K_H and/or vapor pressure), 3) water solubility (S_w), and 4) half-life ($t_{1/2}$). They tested their model on 35 organic compounds, many of which were pesticides, and most chemicals performed as expected. Jury et al. (1984c) also predicted the major loss pathway for five organic compounds, and the model accurately predicted sorption based on reported data for the five compounds. Other models such as GLEAMS (Ground water loading effects of agricultural management systems) evaluate soil-pesticide-climate interactions (Truman and Leonard, 1991). The changes in half-life while a compound is interacting with the soil causes the largest problems for predicting its fate (Truman and Leonard, 1991).

Boesten and van der Linden (1991) presented a pesticide sorption model, which coupled K_{om} values with pesticide transformations. They showed that at low transformation rates, leaching was most sensitive to K_{om}, but at high K_{om} values the predictions were most sensitive to transformation rates. Boesten and van der Linden (1991) explained that a change by a factor of 2 in the K_{om} value or transformation rate could change the prediction for leaching by as much as a factor of 10. This same study and Gold et al. (1988) showed increased pesticide leaching potential in the autumn versus the spring.

No-Tillage vs. Conventional Tillage

The crop residue (litter) layer of a no-tillage corn field has been evaluated for its ability to immobilize organic compounds (Boyd et al., 1990; Mallawatantri and Mulla, 1992). Boyd et al. (1990) found 35-60 times higher sorption of benzene (S_W = 1780 mg L^{-1}), ethylbenzene (S_W = 153 mg L^{-1})and 1,2,3-trichlorobenzene (S_W = 16.3 mg L^{-1}) to the crop residue layer than to a soil's A horizon. The high concentration of soil organic matter on low-input farms would be expected to immobilize the more hydrophobic organic compounds (Mallawatantri and Mulla, 1992). All Boyd et al. (1990) isotherms, including binary-solute isotherms, were linear. The high K values for the carbon rich layers were found to be caused by degrading plant cuticular waxes in the plant residues, and K values for isolated plant cuticle were 5-15 times higher than those of the crop residue layer. When K values were converted to K_{OC}, taking the percent organic carbon of each sorbent into consideration, the sorbents were indistinguishable. Dell et al. (1994) found similar K_{OC} values for fungicides on turfgrass thatch and the underlying soil. Boyd et al. (1990) hypothesized that it may not be necessary to distinguish between crop residue carbon and SOM carbon for the purpose of predicting K values.

In another study on a no-tillage wheat field, the wheat stubble reduced the quantity of metolachlor [2 - chloro - *N* - (2-ethyl-6-methylphenyl) -*N* - (2-methoxy -1-methylethyl)acetamide, S_W = 530 mg L^{-1} (WSSA, 1989)], alachlor [(2-chloro-*N*-(2,6-diethylphenyl)- *N*-(methoxymethyl)acetamide, S_W = 242 mg L^{-1} (WSSA, 1989)], and acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide, S_W = 223 mg L^{-1} (WSSA, 1989)] reaching the soil by 50-90% (Petersen et al., 1988). Sixty percent of an application of atrazine was intercepted by the wheat stubble of a no-tillage field (Ghadiri et al., 1984). After the first few rainfalls (50 mm in 3 weeks) only 20% of the original application

was still in the wheat stubble. Ghadiri et al. (1984) recovered 89% of the initial application from either stubble or underlying soil at 3 weeks after treatment.

The infiltration rates for no-till systems have proven to be higher than the infiltration rates of conventional tillage systems, and this is probably the result of an increase in the number of macropores or macrochannels (Hall et al., 1991; Andreini and Steenhuis, 1990; and Dick et al., 1989). Hall et al. (1991) had more leaching of atrazine and simazine occurring in a no-tillage system than in the conventional tillage system, especially following the first irrigation. They also evaluated cyanazine {2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino] - 2-methylpropanenitrile, S_W = 171 mg L^{-1} (WSSA, 1989)} and metolachlor, but neither of these herbicides leached as readily in either no-tillage or conventional tillage fields. Therefore, the carbon rich plant layer has a strong affinity for the more hydrophobic pesticides, but the abundance of macropores may override the ability of the nonpolar tissues to immobilize organic compounds.

These no-tillage agronomic systems also lessen the movement of organic compounds by runoff (Hall et al., 1991; Andreini and Steenhuis, 1990; and Dick et al., 1989), but Kentucky bluegrass sod has proven to be the most effective method of limiting runoff in at least one instance (Krenitsky and Carroll, 1993).

The Nature of Turfgrass Thatch

Recent research in Cape Cod, MA has shown that pesticide applications on golf courses do not contribute to ground water contamination (Cohen et al., 1990). The primary reason pesticides are immobilized in the turfgrass root zone is the thatch layer (Dell et al. 1994). Thatch was defined by Beard (1973) as "a tightly intermingled layer of dead and living stems and roots that

develop(s) between the zone of green vegetation and the soil surface" of turf. The layer contains "sclerified vascular strands of stems and leaf sheaths, intact fibrous roots, nodes and crown tissue" (Hurto et al., 1980). Turgeon et al. (1975) showed that the abundance of thatch in a turf caused increases in disease incidence, wilting tendency, and reduced shoot and root growth. Because thatch has a high lignin (carbon) content (Ledeboer and Skogley, 1967), one might think infiltration rates through the thatch will be minimal, but that was not the case as Taylor and Blake (1982) showed that once a thatch was wet (2 cm water applied) the infiltration rate through the thatch layer equaled that of the underlying soil. Since thatch is an organic rich sorbent, one would expect significant pesticide sorption in the thatch layer relative to the underlying soil (Dell et al., 1994; Ledeboer and Skogley, 1967). Thatch does have a large quantity of macropores (higher porosity) and low bulk density relative to soils (Hurto et al., 1980; Dell et al., 1994). Hurto et al. (1980) demonstrated the presence of a discontinuity at the thatch-soil interface that slowed the unsaturated water flow between thatch and soil.

Sears and Chapman (1979) demonstrated the persistence of insecticides when they found 60% of a chlordane treatment was still present in an annual bluegrass fairway's thatch 56 days after treatment (DAT). They attributed this to lower populations of microorganisms and to high moisture contents in the thatch layer. When acetanilide herbicides were applied to the wheat stubble of a no-tillage field, Petersen et al. (1988) found that cooler temperature under the wheat stubble increased the herbicides persistence. They also found that acetanilide herbicides were not as easily removed (desorbed) from wheat stubble that was wet when treated as it was from wheat stubble that was dry when treated.

Thatch is a great environment for microbial activity (Balogh and Anderson, 1992, p. 278), but the population of microorganisms might be drastically altered by successive applications of pesticides (Felsot, 1989). Diazinon [*o,o*-diethyl-*o* -(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothiote, S_W = 60 mg L^{-1} (Wauchope et al., 1992)] has been shown to degrade very readily in irrigated turf where there is a thatch layer present (Branham and Wehner, 1985). Hurto et al. (1979) first observed that degradation of benefin [*N*-butyl-*N*-ethyl-α,α,α-trifluoro-2,6-dinitro-*p*-toluidine, S_W = 0.1 mg L^{-1} (Wauchope et al., 1992)] and DCPA [dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate, S_W = 0.5 mg L^{-1} (Wauchope et al., 1992)] in a thatch was much greater than in a soil under identical conditions. Turgeon et al. (1975) observed that treatments of bandane (polychlorodicyclopentadiene) and calcium arsenate (S_W = 130 mg L^{-1}) were immobilized by thatch layers, and this was correlated with a lack of earthworms and earthworm burrows. The bandane and calcium arsenate caused an accumulation of thatch (Turgeon et al., 1975).

Thatch decomposition and turfgrass growing conditions can be improved by cultivation methods, which incorporate soil into the thatch layer (Hurto et al., 1980; Danneberger and Turgeon, 1986). Soil incorporation into thatch layers is also accomplished by earthworms that use the plant tissues as a food source (Randell et al., 1972). Randell et al. (1972) showed that applications of dieldrin [3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth [2,3-*b*]oxirene, S_W = 0.14 mg L^{-1} (Montgomery, 1993)] and chlordane [α-1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan, S_W = 51 μg L^{-1} (Montogomery, 1993)] resulted in thatch accumulations, by decreasing the number of earthworm burrows near the surface. Cohen et al. (1990) found chlordane in the ground water of Cape Cod indicating it may be mobile, but

they strongly implied that the chlordane came from improperly installed monitoring wells.

Potter et al. (1990) proved unequivocally that treatments of benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate S_W = 2.0 mg L^{-1} (Wauchope et al., 1992)], ethoprop [*o*-ethyl-*s*,*s*-di-*n*-propylphosphorodithioate, S_W = 750 mg L^{-1} (Wauchope et al., 1992)], carbaryl [1-naphthyl-*N*-methylcarbamate, S_W = 120 mg L^{-1} (Wauchope et al., 1992)] and bendiocarb [2,2-dimethyl-1,3-benzodioxol-4-yl methyl carbamate, S_W = 40 mg L^{-1} (Wauchope et al., 1992)] at label rates reduced earthworm populations by 60-99% for 20 weeks. This decrease in the earthworm population was correlated with a decrease in thatch decomposition. They also observed a decrease in the population of ants after treating with diazinon, isazofos [*o*-5-chloro-1-isopropyl--1*H*-1,2,4-triazol-3-yl *o*,*o*-diethylphosphorothioate, S_W = 69 mg L^{-1} (Wauchope et al., 1992)] and chlorpyrifos [*o*,*o*-diethyl *o*-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, S_W = 0.4 mg L^{-1} (Wauchope et al., 1992)]. Potter et al. (1990) observed no decreases in the population of earthworms following herbicide applications. Even nitrogen fertilization (NH_4NO_3) greater than 5 g N m^{-2} yr^{-1}, which lowered soil/thatch pH, has caused a decrease in the biomass of earthworms present, thereby increasing thatch accumulation (Potter et al., 1985). Smiley and Fowler (1986) hypothesized that successive fungicide applications increased the rate of tissue production rather than decreasing the rate of thatch decomposition thereby causing thatch accumulation, but Potter et al. (1990) showed that the thatch decomposition rate was the dominant factor.

Pesticides Fate in Turf

Balogh and Anderson (1992) presented a thorough list of commonly used turfgrass pesticides with their water solubilities, K_{OW}, and K_{OC} values (p.

268). They also list half-lives (p. 275) and Henry's Law constants (p. 253) for these pesticides.

Several researchers have evaluated the use of enclosed chambers to model the fate of pesticides (Branham et al., 1985; Nash and Beall, 1980). In both of these studies, it was found that the thatch layer and/or the top 2 cm of soil immobilized the pesticides evaluated, and then they were readily degraded or metabolized. Because these were enclosed chambers, and CO_2 evolution could be quantified, these experiments provided a means for obtaining a mass balance of the pesticide applied. Unfortunately, the environment within a chamber does not represent the "real world" due to higher temperatures, lack of air movement and the filtering out of wavelengths of light. Intact monolith lysimeters are probably the most realistic method of determining pesticide mobility (Miltner et al., 1990).

The earliest pesticide fate studies on turf determined the lengths of time required between time of treatment and when reentry to the lawn or golf course was safe (Goh et al., 1986a,b; Kuhr and Tashiro, 1978; Sears and Chapman, 1979). These studies all evaluated insecticides, which are usually the most toxic (with the exception of nematicides) of all pesticides used in turfgrass. In all of these studies, very little downward movement of the insecticides below the thatch was ever detected. . Removable chlorpyrifos (S_W = 0.4 mg L^{-1}) residues dropped below the estimated safe level of 0.5 μg cm^{-2} immediately if watered in and within 2-6 hours if not watered in (Goh et al., 1986a,b). Kuhr and Tashiro (1978) found only 10 ppm chlorpyrifos remaining on Kentucky bluegrass leaves 3 weeks after treatment (WAT) regardless of the formulation applied (EC or G). Kuhr and Tashiro (1978) also found posttreatment irrigation was largely ineffective for removal of chlorpyrifos and diazinon (S_W = 60 mg L^{-1}) from a turf canopy. Dichlorvos [phosphoric acid 2,2-dichloroethenyl dimethyl ester, S_W =

16 g L^{-1} (Montgomery, 1993)] levels on leaves were not reduced below safe levels (0.06 μg cm^{-2}) with 1.2 cm posttreatment irrigation (Goh et al., 1986a,b). When irrigated, the dichlorvos did not dissipate below safe levels until 2 hours after treatment (HAT), and was not detectable by 23 HAT (Goh et al., 1986b). When not watered in, dichlorvos required 14 hours before it dropped below safe levels (Goh et al., 1986a). Reducing the spray volume to half the recommended rate had no effect on chlorpyrifos and dichlorvos fate (Goh et al., 1986a).

There is evidence that hydrophobic organic compounds will permeate into the plant cuticle when they are immobilized (Willis et al., 1992a and 1994). Willis et al.(1994) showed that permethrin [(3-phenoxyphenyl)-methyl(1 *R,S*)-*cis,trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-propanecarboxylate, S_W = 0.006 mg L^{-1}] and sulprofos [*O*-ethyl *O*-(4-methylthiophenyl)- *S*-propyl phosphorodithioate, S_W = 0.31 mg L^{-1}] were immobilized by cotton leaves. These compounds were more tightly sorbed the longer they were allowed to remain on leaves before posttreatment irrigation (51 mm h^{-1} for 60 min) was applied.

Dell et al. (1994) determined sorption isotherms on *Poa pratensis* L. thatch and the underlying soil for the fungicides triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl 1-1-(1*H* -1,2,4-triazol-1-*g*-1), S_W = 260 mg L^{-1}], vinclozolin [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione, S_W = 1000 mg L^{-1}], chloroneb [1,4-dichloro-2,5-dimethoxybenzone, S_W = 8.0 mg L^{-1}). The K values for thatch were nearly ten times the K values for the underlying soil for each compound. The isotherms for vinclozolin on thatch and triadimefon on soil were not linear (unlike the other compound/sorbent combinations) due to the ionic nature of the compounds and sorbents. Dell et al. (1994) also estimated sorption coefficients for numerous other turfgrass

fungicides from K_{ow} values (Karickhoff, 1981), but predictions were poorly correlated with experimentally determined values. Sears and Chapman (1979) found diazinon and isazofos were nondetectable in an annual bluegrass fairway's thatch 14 DAT, but Niemczyk and Krueger (1987) had high levels of isazofos remaining in the thatch at 8 WAT. The lack of mobility for diazinon applied to turf has already been established (Branham and Wehner, 1985).

Niemczyk and Krueger (1987) determined posttreatment irrigation was effective for removing isazofos from the turf canopy, and ineffective for moving the insecticide below the thatch (96-99% of the application could be recovered from the thatch). Niemczyk (1987) found the same to be true for isofenphos [1-methylethyl-2-[[ethoxy[(1-methylethyl)-amino]phosphinothioyl]oxy]benzoate, S_w = 24 mg L^{-1} (Wauchope et al., 1992)] where 92-99% of the original treatment could be recovered from the thatch following posttreatment irrigation. This study was also important in showing that posttreatment irrigation did not make the immobilized compound more effective for control of *Popillia japonica*. Therefore, grub control that does occur from these immobilized insecticides must be due to the grubs coming up to feed on the treated thatch (Niemczyk, 1987), and/or very small amounts of the insecticide could be toxic. Branham and Miltner (1993) observed no isazofos residues in leachate from intact monolith lysimeters in turf, and this was also the case for chlorothalonil [tetrachloroisophtalonitrile, S_w = 0.6 mg L^{-1} (Wauchope et al., 1992)] and fenarimol [α-(2-chlorophenyl)-α-(4-chlorophenyl)-5-pyrimidi-nemethanol, S_w = 14 mg L^{-1} (Wauchope et al., 1992)].

Since turfgrass leaves and thatch layers are usually effective for immobilizing insecticides, the highly water insoluble preemergence herbicides must also be immobilized by these sorbents. Stahnke et al. (1991) found nearly all of a pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine,

S_W = 0.275 mg L^{-1} (Wauchope et al., 1992)] treatment could be recovered from *Poa pratensis* L. 'Touchdown' leaves (95%) or thatch (5%). It took 42 days for the amount of pendimethalin on leaves to drop below that in the thatch and 168 days before no pendimethalin was recovered from the leaves. A *Poa pratensis* L. 'Baron' turf, which had a less dense canopy than 'Touchdown', had more pendimethalin in the thatch relative to the leaves. Stahnke et al. (1991) never found any pendimethalin residue below 30 cm on either turf, and had a 3 μg L^{-1} pulse of the compound attached to soil colloids in collected leachate following heavy rainfalls 6-14 DAT and 95 DAT. Krause and Niemczyk (1989) found 77-100% of pendimethalin, bensulide [*s*-(*O*,*O*-diisopropyl)phosphorodithioate ester, S_W = 5.6 mg L^{-1} (Wauchope et al., 1992)], and oxadiazon [3-[2,4-dichloro-5-(1-methylethoxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2(3 *H)* -one, S_W = 0.7 mg L^{-1} (Wauchope et al., 1992)] applications in the thatch layer after treatment. When thatch was not present, 82.5-99.6% of these same applications was found in the top 2.5 cm root zone of the turf.

Other studies show only minimal leaching (<24 μg L^{-1}) of 2,4-D [2,4-dichlorophenoxyacetic acid, S_W = 900 mg L^{-1} (Wauchope et al., 1992)] and dicamba [amine and sodium salts of 2-methoxy-3,6-dichlorobenzoic acid, S_W = 400 g L^{-1} (Wauchope et al., 1992)] (Branham and Miltner, 1993; and Gold et al. 1988), but posttreatment irrigation has proven effective for removal of 2,4-D from leaves (Thompson et al., 1984). Gold et al. (1988) never observed more than 100 μg L^{-1} of either 2,4-D or dicamba in leachate even though suction was applied and the turf was overwatered. In fact, 2,4-D can be very tightly held by *Poa pratensis* L. leaves so that even with vigorous wiping less than 10% of an application will be removed (Thompson et al., 1984).

Hurto and Turgeon (1979) observed better weed control for many preemergent herbicides when a *Poa pratensis* L. thatch was present, but

greater mobility of most herbicides through a turf with a thatch was observed than through a turf with no thatch present. This does not seem consistent with what would be expected with water insoluble (hydrophobic) compounds. In batch-sorption experiments Hurto and Turgeon (1979) found more sorption of benefin, bensulide and DCPA to thatch than to soil. They concluded injury to the *Poa pratensis* L. only occurred when a thatch was present, and the herbicides were moving through the thatch to injure the roots below. It may be that the density of the thatch was small enough to allow bulk flow of the herbicides through the thatch before they could reach equilibrium, or there may have been many roots in the thatch. Roots have been shown to prefer growing in thatch rather then growing into underlying soils (Hurto et al., 1980).

The Pesticide Formulation's Effect on Pesticide Fate

Preemergence herbicides, the most water insoluble pesticides used in turfgrass, would be considered immobile based on their water solubilities and one might expect them to be completely immobilized by hydrophobic waxes on leaves. Recommendations call for turf managers to water these compounds in, and this should only prove effective if the water solubility of the compounds are greatly increased by the formulation.

Numerous studies conducted on cotton have demonstrated the removal of pesticide residues from leaves decreases with time, but usually greater than 50% of the mass balance of residue on the leaves could be removed with as little as 7 mm rainfall (McDowell et al., 1985) when irrigated within 24 h after treatment (Pick et al., 1984; Smith et al., 1987; Southwick et al., 1983; and Willis et al., 1991, 1992b, 1994). The type of formulation (emulsifiable concentrate (EC), wettable powder (WP) or vegetable and mineral oils) had little to no effect on the retention of pesticide residues on leaf surfaces when applications were

followed with rainfall (Baker and Shiers, 1989; Smith et al., 1987; and Willis et al., 1991), but Pick et al. (1984) observed slightly better retention with an EC formulation than with a WP. Compounds applied as emulsifiable concentrates or wettable powders permeate plant cuticles readily, and are difficult to desorb (Baker et al., 1983). All of the pesticides in these formulation studies were easily removed from leaves by rainfall occurring within 24 h after the time of treatment even though the active ingredients were water insoluble.

Bryson (1987) found 10 herbicides were made much less efficacious for johnsongrass control with posttreatment irrigation, regardless of the water solubility of the herbicide and the time interval between treatment and the onset of rainfall (0-240 min.). Southwick et al. (1983) observed better leaf penetration for formulations in water tank-mixes than with formulations in oil. Also, the use of ultra-low-volume application techniques has been proven ineffective for improving pesticide retention to cotton leaves (Southwick et al., 1983; and Willis et al., 1992b). Therefore, pesticides in formulations are not as tightly bound to leaves as might be expected based on their hydrophobicity. The effect of the surfactants, solvents and emulsifiers in formulations appears to be particularly important in determining the sorption/washoff from leaves and may result in a deeper initial penetration of the pesticide/formulation complex than would be expected from the active ingredient's properties.

The Importance of Plant Cuticle

The cuticular membrane (CM) of plants covers all above ground portions of a plant, and the specific nature of the cuticular membrane is different for every species (Holloway, 1982). The membrane is formed as a layer of wax, and the wax particles are oriented perpendicular to a leaf surface (Baker, 1982). The waxes within a cutin matrix "consist of a variety of long-chain even-

numbered (C_{22}-C_{24}) primary alcohols, acetates, aldehydes and fatty acids, and their hydroxy- and oxyderivatives, and odd-carbon-numbered (C_{17}-C_{35}) hydrocarbons, secondary alcohols, ketones, ketols, and beta-diketols" (Baker, 1982). The primary function of this membrane is protection of internal leaf organs, and the prevention from leaf dehydration. Therefore, above ground portions of plants are relatively impermeable to water and constructed of water-insoluble compounds. The relative thickness and morphological characteristics of the cuticle are also dependent upon the stage of development of the plant, and the climactic conditions under which it is being grown (Baker, 1982). Immature leaves have been shown to have twice as much wax as more mature leaves (Baker et al., 1983). Kerler and Schönherr (1988a) estimate 0.1 m^3 of cuticle in 1 ha of grass with a 1 μm thick cuticle and a leaf area index of 0.5. This represents a large abundance of cuticle in a turf, and it may be expected that hydrophobic compounds will readily sorb to this hydrophobic sorbent.

Work conducted by Kerler and Schönherr (1988b) showed that permeance coefficients for compounds applied to isolated cuticular membranes (CM) with log K_{ow} values from 2 to 7.9 could be estimated to within an order of magnitude of values determined experimentally. More importantly, the precision of the predictions was best when "the molar volumes of the test compounds were also taken into consideration by relating the log P (permeance coefficient) to log K_{cm} / molar volume", where K_{cm} = the partition coefficient between CM and water. The permeance coefficient can be determined from the slope of a plot of quantity diffused vs. time. Kerler and Schönherr (1988b) showed that with increasing K_{ow}, increasing permeance was observed, as would be expected based on partitioning theory. They presented an equation for predicting permeance coefficients (r^2 = 0.98) without experimentation.

Kerler and Schönherr (1988b) explained that compounds with low polarities will tend to dissolve in soluble cuticular lipids, which are also relatively nonpolar. If this is the case, then as the polarity of a given solute decreases (water solubility decreases), the differences in permeance between species should decrease.

Kerler and Schönherr (1988a) explained that the similarities in the chemical properties of octanol and cutin arise from the fact that they both have an 8:1 ratio of nonpolar to polar groups. Prediction of partitioning in cuticles will only improve when our knowledge of the chemical nature of cuticle improves (Kerler and Schönherr, 1988a). More data is needed comparing the nonpolar solvents and naturally occurring nonpolar organic compounds such as cutin or humus. The nature of the soluble cuticular lipids and non-lipid compartments within a cuticular membrane (CM) will also lead to better understanding of partitioning and diffusion processes for CM's. But Kerler and Schönherr (1988a) noted that sorption differences between species were smaller than differences between predicted and experimentally determined K_{cm}.

Schreiber and Schönherr (1992) considered the uptake of organic compounds by intact needles from five coniferous tree species. They observed consistent biphasic uptake of all compounds tested, the first phase of which was attributed to sorption to cuticular surfaces and was complete in 30 minutes. The second phase was attributed to uptake into the needle and was much slower to reach equilibrium. The isotherms for all five species tested had the same shape and were non-linear. Rates of sorption of a given species and a given compound differed considerably among individual needles tested. The differences between the sorption of the organic compounds tested for a given species are attributed to the S_w of the compounds. Schreiber and Schönherr (1992) found only 81-98% of a given compound could be desorbed, because it

was trapped within the CM. Therefore, the compounds apparently diffused through the CM or were compartmentalized.

Boyd et al. (1990) evaluated sorption of non-ionic organic compounds by isolated plant cuticle, corn residues (in a no-tillage field), the soil/residue layer immediately underlying the corn residue, and the A horizon of the soil. By evaluating sorption coefficients for all of the above sorbents, Boyd et al. (1990) was able to speculate on the important role of cuticular sorption of organic compounds once the cuticle becomes part of the leaf litter. The observed uptake of the organic compounds by cuticle were 5 to 15 times higher than for the corn residue layer. This is consistent with a hypothesis that claims cuticle is a major partition medium. As expected, sorption was inversely related to water solubility. K_{om} values were similar for all four sorbents tested, and they closely resembled the K_{ow} values. Boyd et al. (1990) also evaluated binary-solute uptake but observed no competitive effects between solutes. This is consistent with a partitioning sorption mechanism, and as noted earlier (Kerler and Schönherr, 1988a) the organic solvent octanol appears to be analogous to the CM when considering sorptive capabilities. Future research should consider the effects of further plant decomposition on plant cuticle sorption. Since the organic compounds Boyd et al. (1990) evaluated did not differ between organic binding sites on different sorbents (similar K_{om} values), we may be able to conclude that cuticular sorption of organic compounds is nearly identical to sorption by humic materials in the soil.

MATERIALS AND METHODS

Sorbents

Leaves and thatch were collected from an 8-year old 'Touchdown' *Poa pratensis* L. turf. The turf was grown over a Marlette sandy loam soil (fine-loamy, mixed, mesic Glossoboric Hapludalfs), received 195 kg N ha^{-1} yr^{-1}, and at least 2.5 cm irrigation or rain per week. The 5.1 cm of leaf tissue (verdure) was removed in late August and stored at -9° C. Thatch and soil were also collected with a 15-cm diameter golf green cup cutter to at least 7 cm deep. The thatch-soil boundary (4 cm deep) was identified by the lowest depth at which rhizomes could be seen. The thatch was separated from the soil (4 cm deep). Thatch plugs were floated in distilled/deionized H_2O and gently agitated to remove as much soil as possible. The thatch was allowed to dry at 21° C for 96 h and was stored at -9° C. Table 1 shows the pertinent thatch characteristics (% organic carbon, % organic matter, moisture, particle size, pH, CEC, and bulk density) before and after washing. Stored thatch and leaf samples were oven-dried (70° C for 48h) to determine percent moisture. The fresh weight was corrected for percent moisture to determine dry weights for isotherm calculations.

The washed thatch was not ground because grinding could release colloidal material into solution and create more surface area with additional sorption sites. Initial experiments showed that grinding of thatch and removal of soil did not alter acetanilide sorption (Appendix A). Sorbents evaluated in the initial experiment were thatch ground to 2 mm and unground thatch.

Table 1 - Characteristics of thatch and underlying soil

Characteristic *	Underlying Soil	Thatch	
		Unwashed	Washed
% OM**	---	82.5 ± 6.7	82.1 ± 4.0
% OC**	2.7 ± 0.4	38.6 ± 3.9	39.8 ± 0.9
% Moisture by Wt.***	5.5 ± 0.5	7 ± 2	79 ± 2
Bulk density (g cc^{-1})	1.74 ± 0.02	0.38 ± 0.04	---
CEC	7	---	---
% Clay	16	---	---
% Silt	15	---	---
% Sand	69	---	---
pH	7.5	7.5	7.5

* Determined Michigan State University Soil Testing Laboratory.
** Percent OM and OC of leaves was 76.3 ± 1.0 and 37.8 +/- 2.8, respectively.
*** Determined by drying at 70° C for 48 h.

Model Organic Compounds

The nonionic organic compounds (MOC's) chosen were acetanilide, ethoprop (*o*-ethyl *s,s*-dipropyl phosphorodithioate), 1,2,4-trichlorobenzene, fenarimol [α-(2-chlorophenyl)-α-(4-chlorophenyl)-5-pyrimidinemethanol], and phenanthrene. The water solubilities of these compounds are 5405, 750, 49, 14 and 1 mg L^{-1}, respectively. Table 2 shows water solubilites (S_W), octanol/water partition coefficients (K_{OW}), molecular weight, melting and boiling points of MOC's used. The purity of all MOC's was verified by thin-layer chromatography (Appendix B) (Touchstone and Dobbins, 1983). All radio-labeled compounds were stored at -9° C while non-labeled compounds were stored at 21° C. The K_{OW} for acetanilide was determined experimentally (OECD, 1981). The K_{OW} values for all other compounds were retrieved from the literature (Table 2). These compounds were also chosen for their chemical stability to minimize degradation losses during sorption measurements and to give a range of S_W. The structure of all five compounds were compiled into Appendix F.

Table 2 - Properties of nonionic organic compounds

MOC	S_w (mg L^{-1})	log S_w* (mol L^{-1})	log K_{ow}	Mol. Wt.	Mt. Pt. (C)	Bl. Pt (C)
acetanilide	5405**	(-1.19)	1.74***	135.2	114	304
ethoprop	750‡	-2.51	3.59§	242.3	20	88
1,2,4-TCB	49†	-3.57	4.02†	181.5	17	213
fenarimol	14‡	(-3.12)	3.40‡	331.2	115	NA
phenanthrene	1†	(-4.48)	4.57†	178.2	100	340

* Numbers in parenthesis represent super-cooled liquid water solubilities for compounds that are solids at 25° C (Chiou and Schmedding, 1982).
** Windholz et al., (1983).
***Determined by standard method from OECD (1981).
† Chiou (1989)
‡ USEPA (1992)
§ Rhone Poulenc Technical Bulletin for Ethoprop - *CHIPCO® MOCAP®* Brand 10G Pesticide.

Isotherm Determinations

Batch-suspension experiments were conducted to determine sorption isotherms. The initial concentration (C_i) of all compounds ranged from 10-80% of the compound's water solubility. The C_i included both ^{14}C-labeled and non-labeled MOC. The range of C_i values evaluated, purity and specific activity for each MOC are listed in Table 3. The low C_i's of hydrophobic compounds (phenanthrene, fenarimol, and 1,2,4-trichlorobenzene) were verified by HPLC. Three grams of leaves or 12.0 g of thatch were placed in a 30 ml Corex (Baxter Sci.) centrifuge tube. Twenty-six ml of solution containing the MOC were dispensed into leaf tubes and 18 ml into thatch tubes. The sorbent:solution ratios were 1.2/10 and 6.7/10 for leaves and thatch, respectively. Head space in tubes was minimized to lessen volatilization. Three tubes (replications) for each C_i were equilibrated simultaneously. The tubes were covered with foil and Teflon-lined screw-caps, and placed in a horizontal position on a rotary platform shaker. They were shaken at 120 rpm for 24 h in the dark. The

temperature was maintained at 25° C in order to maintain the predetermined water solubility of each solute.

Table 3 - Compound purity, specific activity, and concentration range evaluated as C_i

MOC	Purity * (%)	^{14}C Spe. Act. (Bq mmol $^{-1}$)	% Sw Range Evaluated as C_i
acetanilide	97	2.2×10^9	10 - 80
ethoprop	96.2	1.8×10^8	10 - 80
1,2,4-TCB	99	2×10^6	7 - 62
fenarimol	97	2.5×10^8	12 - 83
phenanthrene	99	3.1×10^8	10-80

* Reported by Sigma Chemical Co., verified by thin-layer chromatography or HPLC (Appendix B)

The initial MOC concentrations were verified by collecting 1 ml subsamples as solutions were dispensed into the tubes. After the 24 h equilibration time, the thatch tubes were centrifuged at 9264 g for 20 min. Centrifugation was not necessary for tubes containing leaves. Three 1-ml aliquots of the supernatant were removed from each tube, and the mean equilibrium concentration (C_e) was determined. Initial concentrations (C_i) and C_e were quantified by liquid scintillation counting for 10 minutes on a liquid scintillation counter (Packard Tri-Carb Model 1500) with 20 ml aqueous (Safety Solve) counting cocktail (Research Prod. Int. Corp., Mt. Prospect, IL.) in each vial to determine disintegrations per minute (DPM). Quenched standards (Dupont) were used to derive a quench curve, which related the degree of quenching to a tSIE (Transformed Spectral Index of the External Standard Spectrum) value derived from the Compton spectrum induced in the sample by the external standard source (^{133}Ba).

The quantity sorbed (Q_S) in mg kg^{-1} was determined by $Q_S = [(C_i - C_e)V_S] / M_S$, where C_i and C_e are the initial and equilibrium supernatant concentrations (mg ml^{-1}); V_S is the volume of solution added to each tube (ml); and M_S equals the mass of sorbent (kg). All isotherms were determined twice to verify reproducibility of results. This method gave 24 points for the regression (isotherm) plot.

Volatile organic compounds (ethoprop and 1,2,4-trichlorobenzene) and fenarimol, which can photodecompose under artificial light, were added to tubes containing no sorbent. These tubes were treated identically as tubes used in earlier batch-suspension experiments to determine losses during equilibration. Equilibration concentrations (C_e) were corrected for losses before Q_S was calculated.

Preliminary experiments showed equilibrium for acetanilide and phenanthrene was reached in 4 h (Appendix C). The most widely used equilibration time in published isotherm studies is 24 h, and because there was no further sorption between 4 and 24 h in our experiments, we chose a 24 h equilibration period.

Another experiment was conducted to determine if microbial decomposition of acetanilide occured in the 24-h equilibration period. Decomposition would lead to changes in structure that would change sorptive characteristics. Microbial activity can be retarded in batch-suspension solutions by the addition of sodium azide (Wahid et al., 1980). This addition stops microbial degradation without drastically changing the solvent characteristics. There was no significant degradation of acetanilide in this experiment (Appendix D).

The change in supernatant pH was determined after the 24-h equilibration period for leaves and thatch in distilled/deionized H_2O. Solution

pH decreased from 7.48 ± 0.48 to 5.20 ± 0.94 during equilibration with leaves and from 7.68 ± 0.39 to 7.28 ± 0.09 for thatch (Appendix E), which suggests it may be necessary to buffer the solutions in batch-suspension experiments with these sorbents. Buffering was not necessary for the MOC's evaluated here since they are non-ionizable.

Solubility enhancement (S_w^*) can be estimated by a compound's partition coefficient for dissolved organic carbon (K_{DOC}) and the concentrations of dissolved organic carbon (DOC) with the equation $S_w^* = S_w (1 + K_{DOC})$ (Chiou and Schmedding, 1982). Based on this equation, phenanthrene was the only compound evaluated that may experience water solubility enhancement at the relatively large [DOC] present in the supernatant solutions (300 mg L^{-1} for thatch and 450 mg L^{-1} for leaves). Phenanthrene's S_w would be increased to 1.1 mg L^{-1} (a 10% increase), and this would not drastically change the isotherm for the compound. This correction is often necessary for extremely hydrophobic compounds such as DDT (Sw = 1.2-5.5 μg L^{-1}).

The sorption coefficients (K) for each compound on thatch and leaves were determined by plotting Q_s and C_e and finding the slope of the regression line. The K values were then plotted versus other easily determined parameters (K_{ow}, S_w, K_{oc}, K_{om}) to evaluate all relationships that may exist. The K values for all compounds can be converted to K_{oc} and K_{om} values using the relationship of K_{oc} = K / (organic carbon fraction) or K_{om} = K / (organic matter fraction). The percent organic carbon (OC) was 37.8 ± 2.8% for leaves and 39.8 ± 0.9% for thatch, while the percent organic matter (OM) was 76.3 ± 1.0 for leaves and 82.1 ± 4.0 for thatch.

Formulated Compound Isotherms

Initial phenanthrene and acetanilide solutions were spiked with 0.5% v/v *Primo®* (Ciba Geigy) formulation (emulsifiable concentrate) blank to determine how the presence of a formulation may affect isotherms. Formulation information is usually proprietary, but Ciba Geigy disclosed the following constituents: primarily aromatic petroleum hydrocarbons (C-11 and C-12), less then 8% light mineral oil, and less then 10% anionic and nonionic emulsifiers. Phenanthrene and acetanilide solutions of approximately 10, 40, 60 and 80% of S_W were made, and leaf isotherms were determined as before. All samples were left in the dark for 1 h before liquid scintillation counting was conducted, because the *Primo ®* formulation caused counting cocktail to fluoresce in the presence of artificial light.

RESULTS

Batch-Suspension Isotherms

All 5 nonionic organic compounds (acetanilide, ethoprop. 1,2,4-trichlorobenzene, fenarimol, and phenanthrene) had linear ($r^2 > 0.922$) sorption isotherms for the concentration ranges tested (Figures 1-5). Values of K are the slope of the sorption isotherm plotted as a regression line through the data points for quantity sorbed (Q_S) and the equilibrium concentration (C_e). All compounds, with the exception of phenanthrene, had y-intercept values far from the ideal of zero. All figures and graphs are compiled at the end of the results section.

The results of the isotherm determinations are summarized below and in Table 4. Acetanilide (S_W = 5405 mg L^{-1}) had a K value for *Poa pratensis* L. leaves of 3.53 ± 0.42, while the thatch K value was 6.32 ± 0.28. The regression equations for acetanilide on *Poa pratensis* L. were $Q_S = 3.53\ C_e + 325$ (r^2 = 0.939) for leaves and $Q_S = 6.32\ C_e + 252$ (r^2 = 0.991) for thatch (Figure 1). Ethoprop (S_W = 750 mg L^{-1}) had a K value for *Poa pratensis* L. leaves of 32.4 ± 2.40, while the thatch K value was 16.2 ± 0.69. The regression equation for ethoprop on *Poa pratensis* L. leaves was $Q_S = 32.4\ C_e - 134$ (r^2 = 0.971) and the equation for thatch was $Q_S = 16.2\ C_e - 38.5$ (r^2 = 0.943) (Figure 2). The K values for 1,2,4-trichlorobenzene (S_W = 49 mg L^{-1}) were 167 ± 7.29 for leaves and 19.2 ± 1.13 for thatch. The regression equations used to determine these K values were $Q_S = 167\ C_e - 84$ (r^2 = 0.990) for leaves and $Q_S = 19.2\ C_e + 0.32$ (r^2 = 0.982) for thatch (Figure 3). Fenarimol (S_W = 14 mg L^{-1}) had a leaf K

value of 155 ± 13.3, while the K value for thatch was 86.5 ± 6.92. The regression equations for the isotherms were $Q_S = 155\ C_e + 9.69$ ($r^2 = 0.962$) for leaves and $Q_S = 86.5\ C_e + 3.41$ ($r^2 = 0.922$) for thatch (Figure 4). The least water soluble compound evaluated, phenanthrene ($S_W = 1$ mg L^{-1}), had very high K values for leaves (2520 ± 307) and thatch (793 ± 80.4). The regression equations for the isotherms were $Q_S = 2520\ C_e + 0.98$ ($r^2 = 0.929$) for leaves and $Q_S = 793\ C_e + 0.075$ ($r^2 = 0.952$) for thatch (Figure 5).

Table 4. Sorption coefficients, y-int., and r^2 values for nonionic organic compounds on leaves and thatch.

Compound	Leaves			Thatch		
	K	y-int.	r^2	K	y-int.	r^2
acetanilide	3.53 ± 0.42	325 ± 1070	0.939	6.32 ± 0.28	252 ± 396	0.991
ethoprop	32.4 ± 2.40	-134 ± 462	0.971	16.2 ± 0.69	-38.5 ± 140	0.943
1,2,4-tcb	167 ± 7.29	-84 ± 21	0.990	19.2 ± 1.13	0.32 ± 2.6	0.982
fenarimol	155 ± 13.3	9.69 ± 16	0.962	86.5 ± 6.92	3.41 ± 5.3	0.922
phenanthrene	2520 ± 307	0.075 ± 0.37	0.929	793 ± 80.4	0.98 ± 1.7	0.952

The K values for all compounds were converted to K_{OC} and K_{OM} values using the relationship of K_{OC} = K / (organic carbon fraction) or K_{OM} = K / (organic matter fraction) (Figure 6, Table 5). The percent organic carbon (OC) was 37.8 ± 2.8% for leaves and 39.8 ± 0.9% for thatch, while the percent organic matter (OM) was 76.3 ± 1.0 for leaves and 82.1 ± 4.0 for thatch. The K_{OC}, K_{OM} and K values for sorption of all compounds by leaves were always greater than the corresponding K values for thatch other than the most water soluble compound evaluated, acetanilide. Therefore, the *Poa pratensis* L.

leaves appear to be a less polar (more hydrophobic) sorbent than *Poa pratensis* L. thatch. The K values were always greater for less water soluble compounds for both sorbents with only one exception. The K_{leaves} value for fenarimol was lower than the K_{leaves} value for 1,2,4-trichlorobenzene.

The K_{OC} values for leaves and thatch were compared with empirical estimates of K_{OC} compiled by Green and Karickhoff (1990) (Table 6). The equation: log K_{OC} = -0.68 log S_W (μg ml-1) + 4.273 originally from Hassett et al. (1980) provided the closest estimate for the five compounds, but Green and Karickhoff (1990) have shown that different empirical equations fit different families of organic compounds.

Sw and Kow Correlations

When the S_W of compounds was converted to super-cooled liquid S_W, with the melting point correction (Chiou and Schmedding, 1982), the relationship between log K_{OW} and log S_W was greatly improved (Figure 7). The super-cooled liquid water solubility was derived from the equation log S_W = (log K_{OW} - 0.710) / -0.862 derived by Chiou and Schmedding (1982) for 36 aromatic liquids and solids that had their S_W converted to super-cooled liquid S_W (r^2 = 0.994). This correction of S_W was only conducted for compounds that are solids at 25° C, and it is a way of correcting for the energy needed to dissolve a solute in a solution. With the conversion to super-cooled liquid S_W (mol L^{-1}), log S_W = -0.828 log K_{OW} + 1.00 (r^2 = 0.916), but when the S_W (mol L^{-1}) was not converted, log S_W = -0.590 log K_{OW} + 1.45 (r^2 = 0.705) and there was no longer a linear relationship (P=0.075). The super-cooled liquid log S_W was plotted versus the experimentally determined K values for both *Poa pratensis* L. leaves and thatch (Figure 8). The regression equations were log K_{leaves} = -0.842 log S_W - 0.529 (r^2 = 0.974) and log K_{thatch} = -0.567 log S_W - 0.0586 (r^2 = 0.719).

The lower r^2 for thatch is an indication that thatch is a less homogeneous sorbent (more variety of polar and nonpolar functional groups) than leaves. The relationship between log K_{thatch} and log S_w would have been significant ($r^2 = 0.934$) if 1,2,4-trichlorobenzene did not have such a low K_{thatch} value.

The relationship between log K_{ow} and the experimentally determined K values for leaves and thatch were log $K_{leaves} = 0.906 \log K_{ow} - 1.17$ ($r^2 = 0.846$) and log $K_{thatch} = 0.567 \log K_{ow} - 0.339$ ($r^2 = 0.540$) (Figure 9). The relationship between log K_{thatch} and S_w or K_{ow} was not linear ($P>0.05$).

Formulated Compounds

When the least water soluble compound evaluated, phenanthrene, was formulated in a tank mix with 0.5% v/v *Primo®* blank, the K_{leaves} value was drastically reduced from 2520 ± 307 to 59.8 ± 13.8 (Figure 10). The regression equation for this formulated isotherm was $Q_s = 59.8\ C_e + 4.18$. The formulated phenanthrene isotherm also had a lower r^2 (0.793) than the nonformulated isotherm ($r^2 = 0.929$). Acetanilide produced a higher K_{leaves} value (6.58 ± 0.97) when formulated in a tank mix with 0.5% v/v *Primo®* blank than when it was not formulated (3.53 ± 0.42) (Figure 11). The variability for the formulated acetanilide isotherm was only slightly increased ($r^2 = 0.899$) over that of the nonformulated isotherm ($r^2 = 0.939$). The regression equation for the formulated acetanilide isotherm was $Q_s = 6.58\ C_e + 4390$.

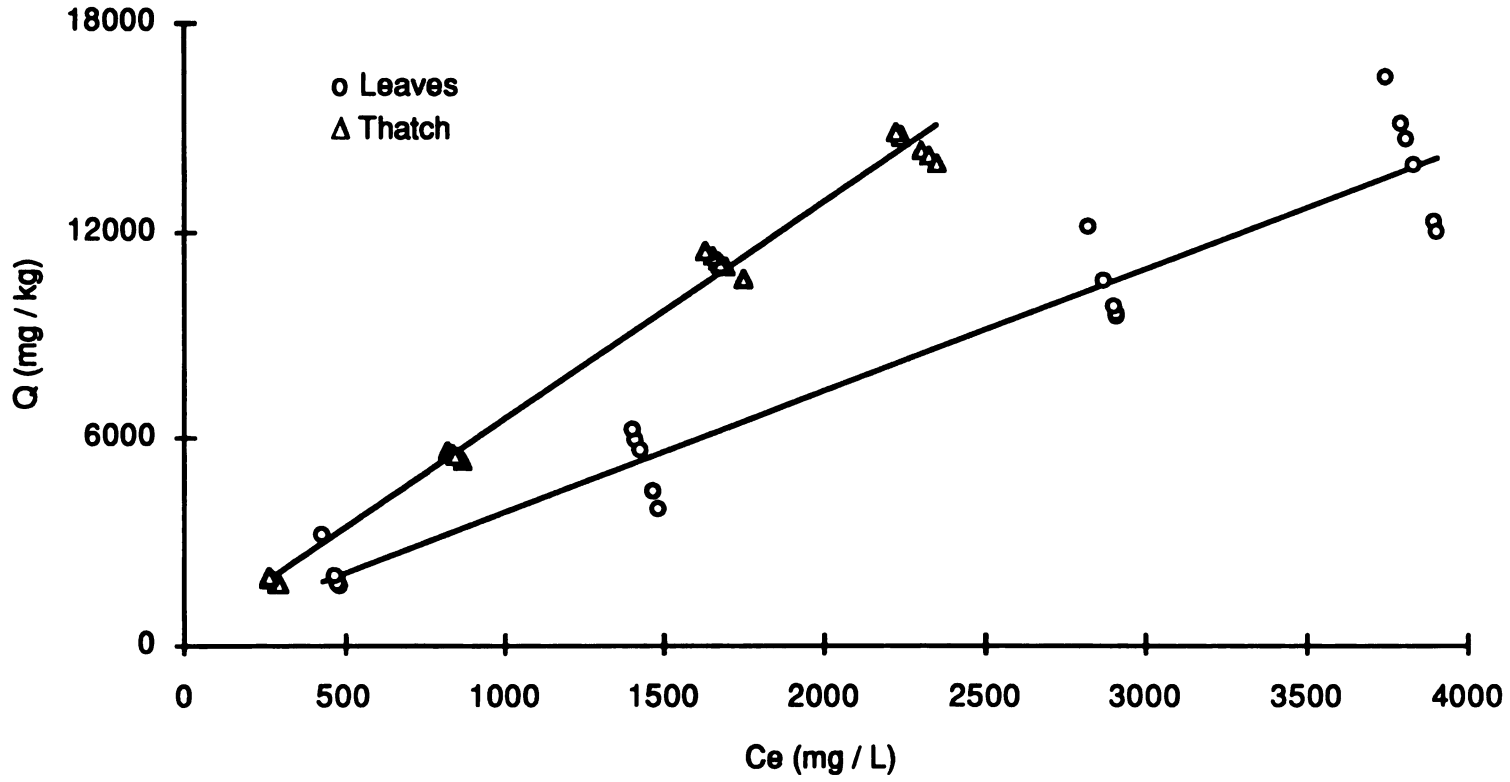


Figure 1. Isotherms for acetanilide on *Poa pratensis* L. leaves and thatch. The quantity sorbed by leaves = 3.53 C_e + 325 (r^2 = 0.939). The quantity sorbed by thatch = 6.32 C_e + 252 (r^2 = 0.991). The K value for leaves was 3.53 ± 0.42 while the K value for thatch was 6.32 ± 0.28.

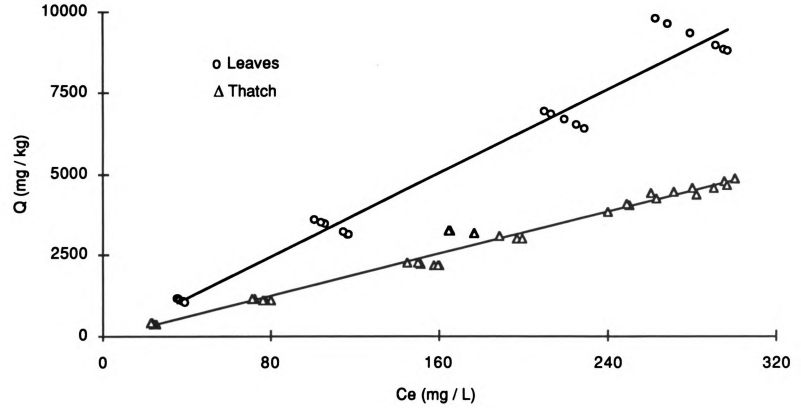


Figure 2. Isotherms for ethoprop on *Poa pratensis* L. leaves and thatch. The quanitiy sorbed by leaves = 32.4 C_e - 134 (r^2 = 0.971). The quantity sorbed by thatch = 16.2 C_e - 38.5 (r^2 = 0.943). The K value for leaves was 32.4 ± 2.40 while the K value for thatch was 16.2 ± 0.69.

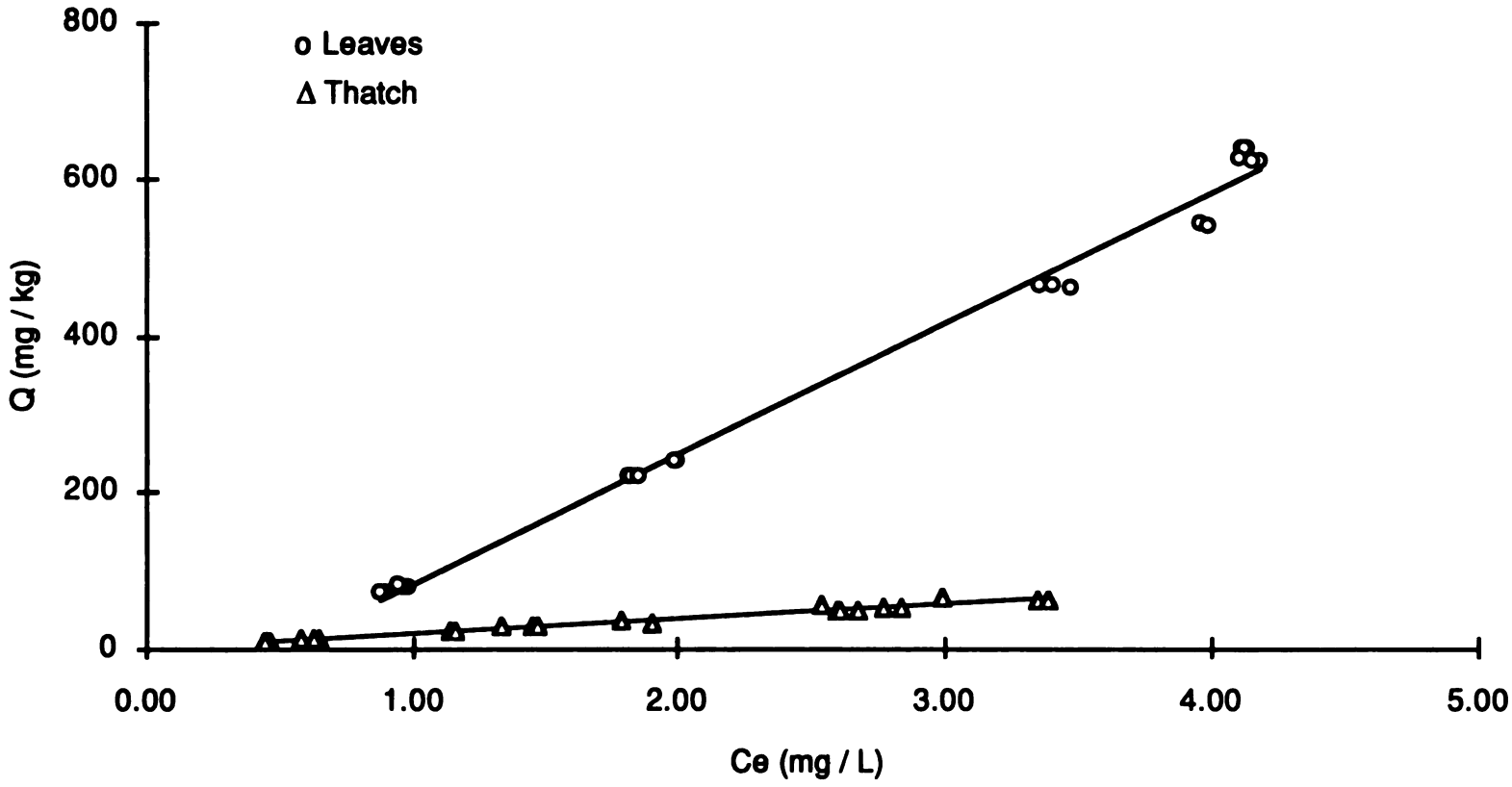


Figure 3. Isotherms for 1,2,4-trichlorobenzene on *Poa pratensis* L. leaves and thatch. The quantity sorbed by leaves = 167 C_e - 84 (r^2 = 0.990). The quantity sorbed by thatch = 19.2 C_e + 0.32 (r^2 = 0.982). The K value for leaves was 167 ± 7.29 while the K value for thatch was 19.2 ± 1.13.

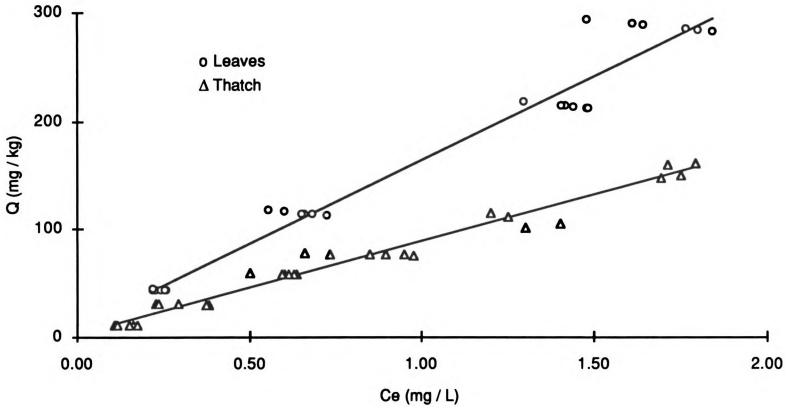


Figure 4. Isotherms for fenarimol on *Poa pratensis* L. leaves and thatch. The quantity sorbed by leaves = 155 C_e + 9.69 (r^2 = 0.962). The quantity sorbed by thatch = 86.5 C_e + 3.41 (r^2 = 0.922). The K value for leaves was 155 ± 13.3 while the K value for thatch was 86.5 ± 6.92.

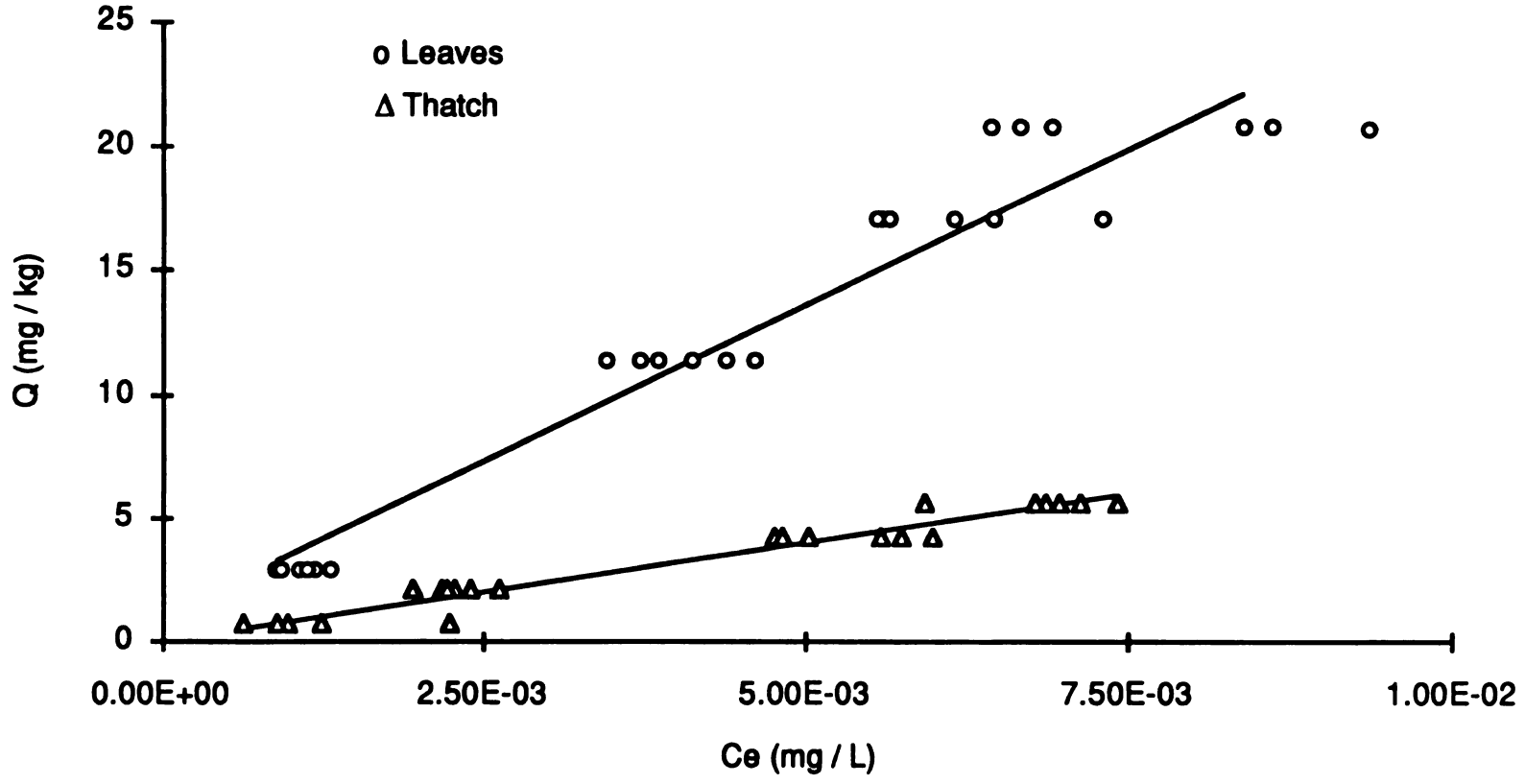


Figure 5. Isotherms for phenanthrene on *Poa pratensis* L. leaves and thatch. The quantity sorbed by leaves = 2520 C_e + 0.98 (r^2 = 0.929). The quantity sorbed by thatch = 793 C_e + 0.075 (r^2 = 0.952). The K value for leaves was 2520 ± 307 while the K value for thatch was 793 ± 80.4.

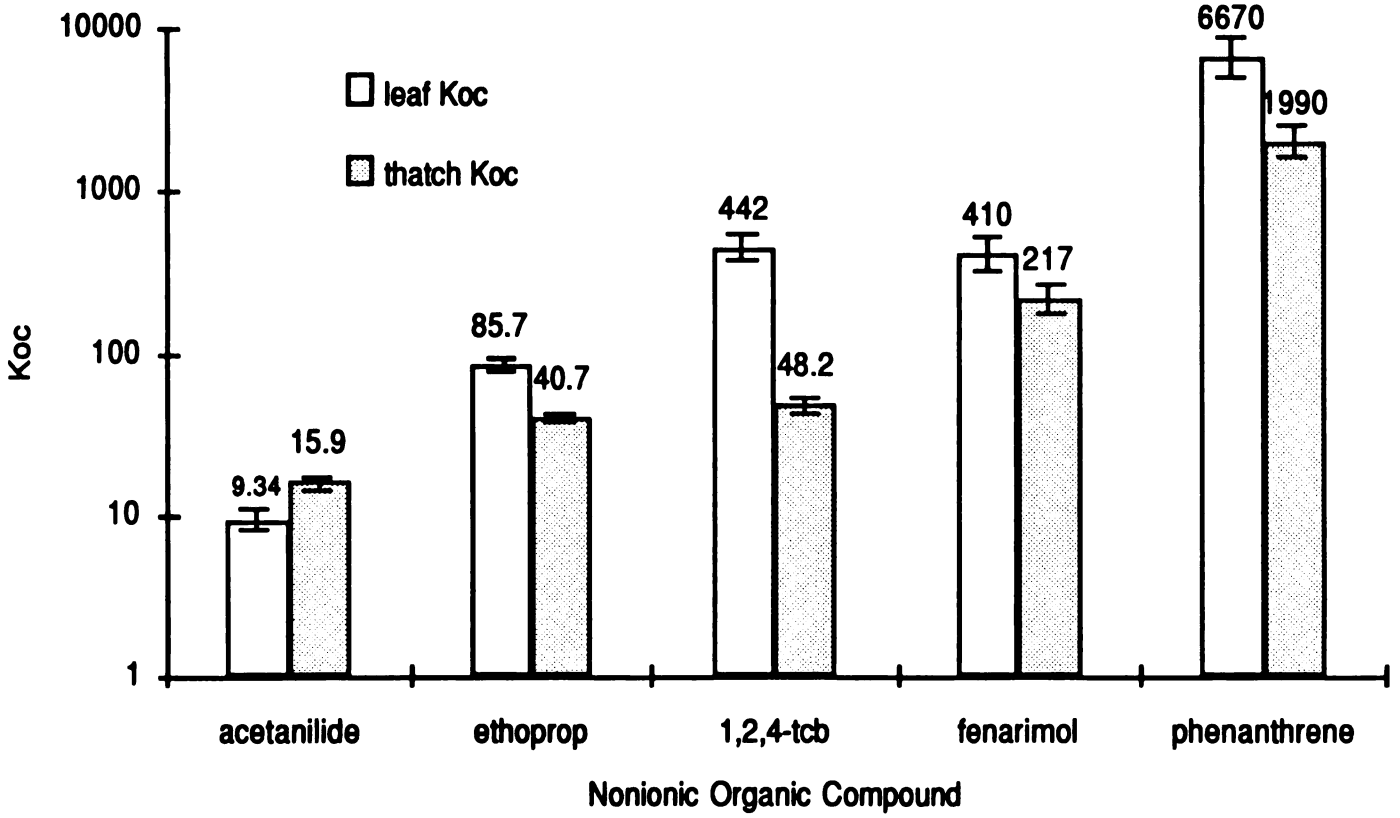


Figure 6. K_{OC} values for nonionic organic compounds on *Poa pratensis* L. leaves and thatch. The leaves were 37.8 ± 2.8% organic carbon, and the thatch was 39.8 ± 0.9% organic carbon. Derived from Koc = K / organic carbon fraction.

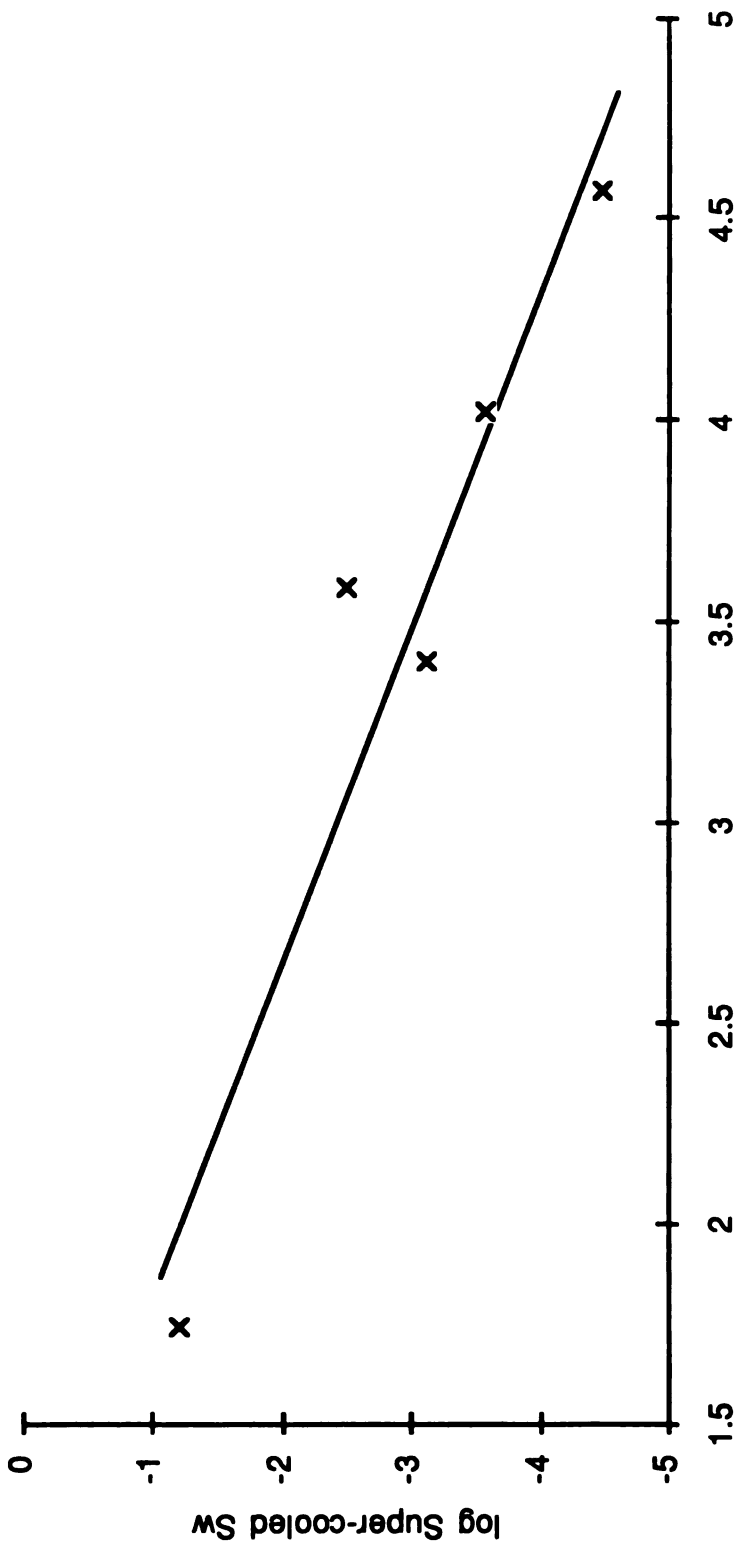


Figure 7. Relationship between Kow and super-cooled liquid S_W (mol L^{-1}) (r^2 = 0.916). Compounds that are solids at 25° C had their S_W converted to super-cooled liquid S_W (Chiou et al., 1982). If this conversion is not completed r^2 = 0.705.

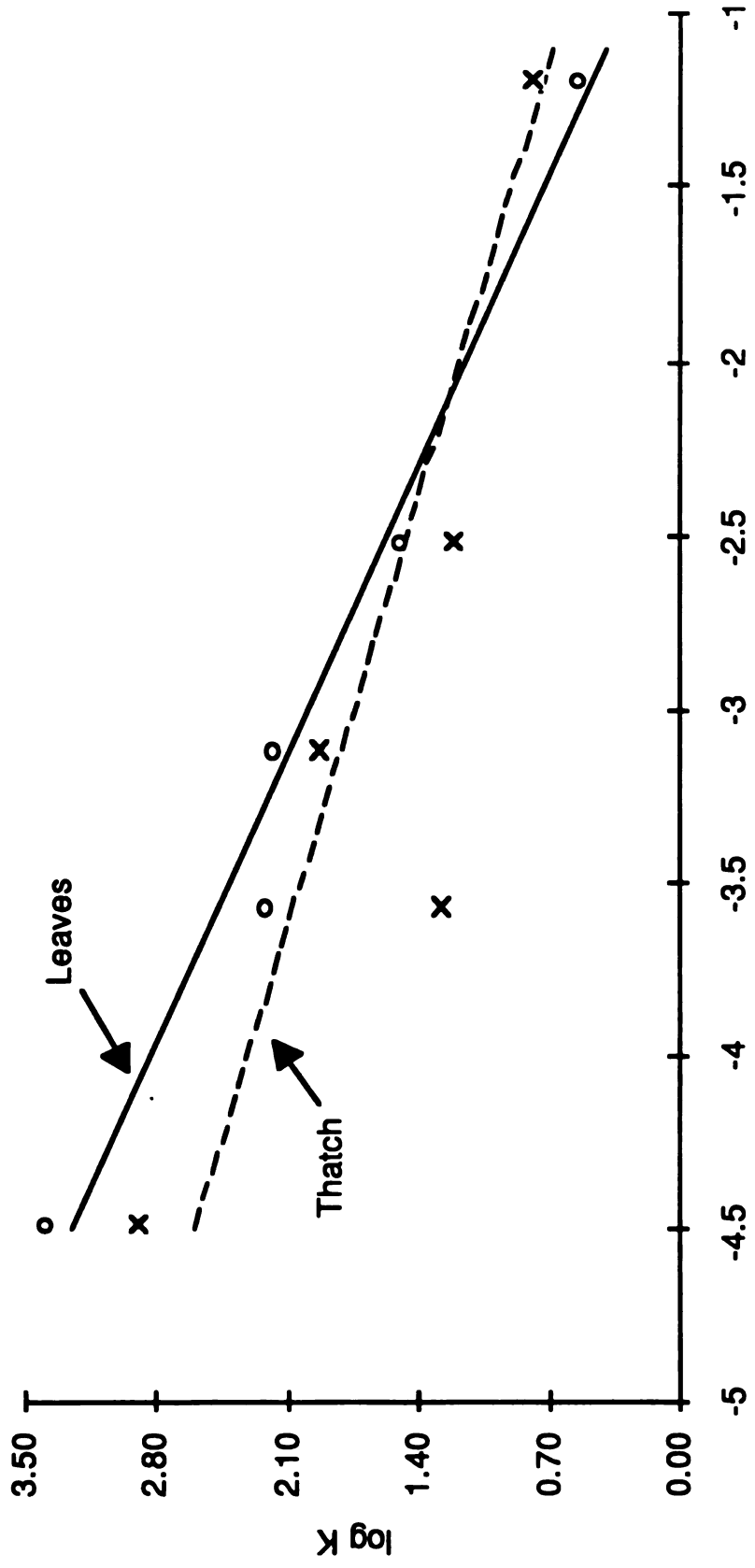


Figure 8. Relationship between S_w and experimentally determined K values for *Poa pratensis* L. leaves and thatch. The regression equation for leaves is: log K_{leaves} = -0.842 log S_w - 0.529 (r^2 = 0.974). The regression equation for thatch is: log K_{thatch} = -0.567 log S_w - 0.0586 (r^2 = 0.719).

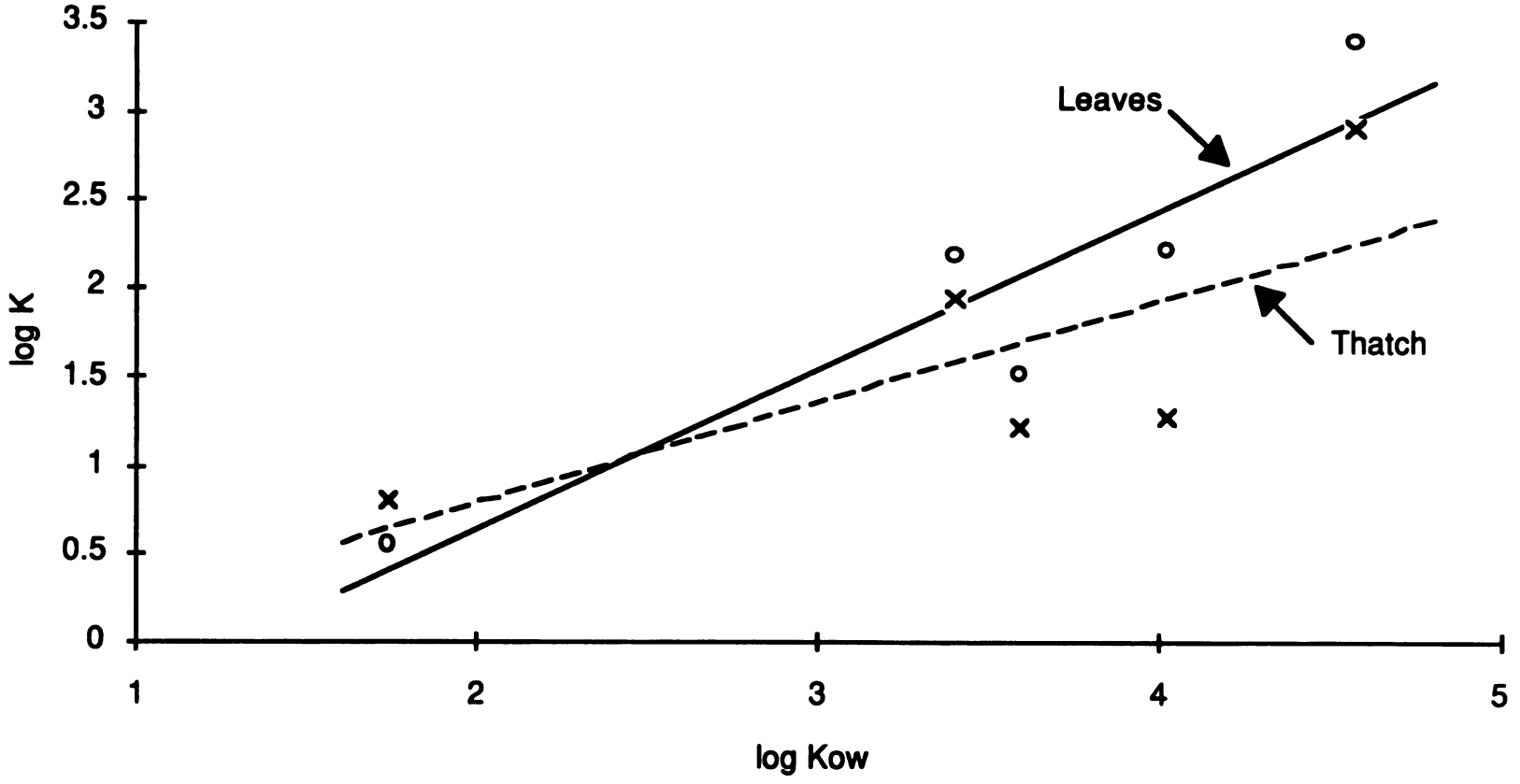


Figure 9. Relationship between K_{ow} and experimentally determined K values for *Poa pratensis* L. leaves and thatch. The regression equation for leaves is: log K_{leaves} = 0.906 log K_{ow} - 1.17 (r^2 = 0.846). The regression equation for thatch is: log K_{thatch} = 0.567 log K_{ow} - 0.339 (r^2 = 0.540).

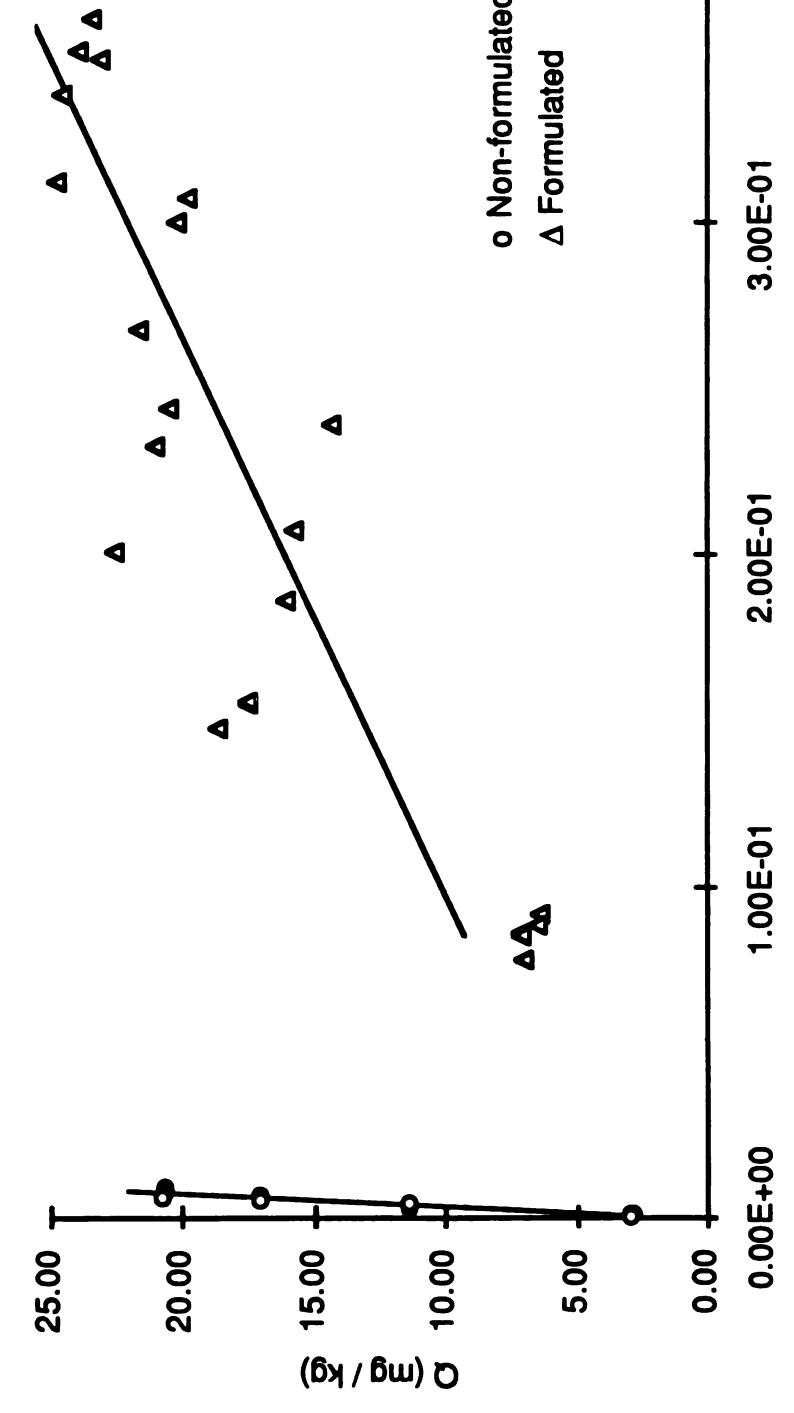


Figure 10. Phenanthrene formulated with *Primo®* blank. Sorption of formulated phenanthrene by *Poa pratensis* L. leaves can be predicted from the isotherm: $Q_S = 59.8\ C_e + 4.18$ ($r^2 = 0.793$). The K value for the isotherm was 59.8 ± 13.8.

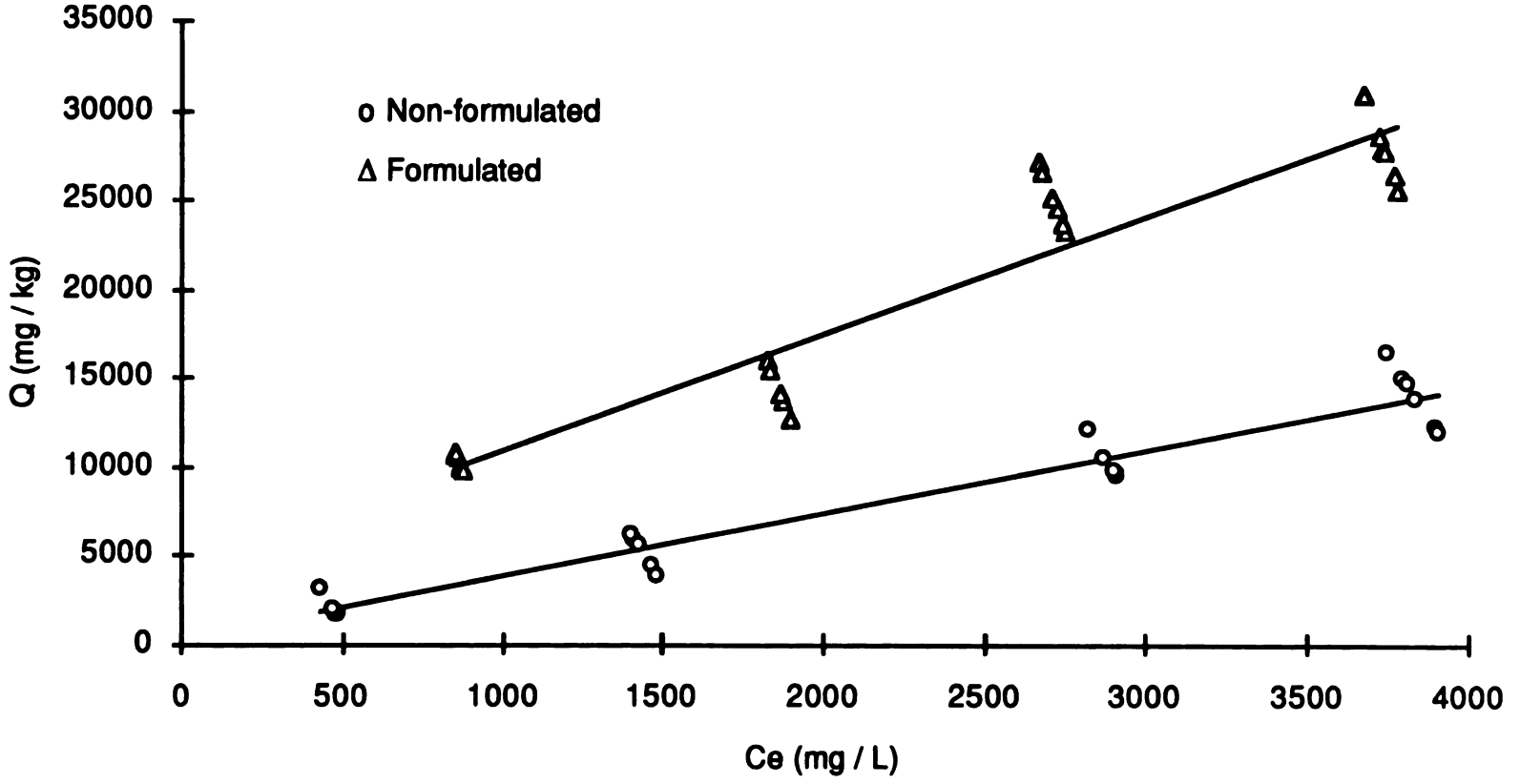


Figure 11. Acetanilide formulated with *Primo®* blank. Sorption of formulated acetanilide by *Poa pratensis* L. leaves can be predicted from the isotherm: $Q_S = 6.58\ C_e + 4390$ ($r^2 = 0.899$). The K value for the isotherm is 6.58 ± 0.97.

Table 5. K, K_{OC}, and K_{OM} values for leaves and thatch.

Compound	Leaves			Thatch		
	K	K_{OC}*	K_{OM}**	K	K_{OC}	K_{OM}
acetanilide	3.53 ± 0.42	9.34 ± 1.11	4.63 ± 0.55	6.32 ± 0.28	15.9 ± 0.70	7.70 ± 0.34
ethoprop	32.4 ± 2.40	85.7 ± 6.35	42.5 ± 3.15	16.2 ± 0.69	40.7 ± 1.73	19.7 ± 0.84
1,2,4-tcb	167 ± 7.29	442 ± 19.3	219 ± 9.55	19.2 ± 1.13	48.2 ± 2.84	23.4 ± 1.38
fenarimol	155 ± 13.3	410 ± 35.2	203 ± 17.4	86.5 ± 6.92	217 ± 17.4	105 ± 8.43
phenanthrene	2520 ± 307	6670 ± 812	3300 ± 402	793 ± 80.4	1990 ± 202	966 ± 97.9

*The percent organic carbon of the leaves was 37.8 ± 2.8, and the percent organic carbon of the thatch was 39.8 ± 0.9.
**The percent organic matter of the leaves was 76.3 ± 1.0, and the percent organic matter of the thatch was 82.1 ± 4.0.

Table 6. Comparison of K_{OC} values for leaves and thatch with empirical estimations of K_{OC} from the literature.

Compound	Determined		K_{OC}(soil) Estimations		
	log K_{OC} leaves	log K_{OC} thatch	Hassett et al. (1980)*	Chiou et al. (1979)**	Karickhoff (1984)***
acetanilide	0.97	1.20	1.74	3.38	1.12
ethoprop	1.93	1.61	2.32	4.00	1.15
1,2,4-tcb	2.65	1.68	3.12	4.59	3.48
fenarimol	2.61	2.34	3.49	5.04	5.05
phenanthrene	3.82	3.30	4.27	5.53	5.63

* Log K_{OC} = -0.68 log $S_W(\mu g\ ml^{-1})$ + 4.273.

** Log K_{OC} = -0.557 log $S_W(\mu mol\ L^{-1})$ + 4.277. This equation was originally expressed as K_{OM}, but K_{OC} = 1.74 K_{OM} was used for conversion.

*** Log K_{OC} = -0.83 log S_W(mole fraction) - 0.01 (mp - 25°C) - 0.93. S_W(mole fraction) = S_W(molar) x 18/1000 for the hydrophobic solutes, and the mp for liquids was set at 25°C.

DISCUSSION

Hydrophobic organic compounds are less strongly sorbed by hydrophobic sorbents when formulated with surfactants (Kile and Chiou, 1989), or when they are in the presence of dissolved humic materials (Chiou et al., 1986 and 1987). A formulation's surfactants form micelles that solubilize organic compounds (active ingredients) (WSSA, 1982). When phenanthrene was formulated with *Primo®* blank, the K_{leaves} value decreased drastically from 2520 ± 307 to 59.8 ± 13.8 (Fig. 10). Acetanilide, when formulated with *Primo®* blank, had its K_{leaves} value increased from 3.53 ± 0.42 to 6.58 ± 0.97 (Fig. 11). Therefore, the surfactants had the opposite effect on acetanilide relative to phenanthrene. Acetanilide was more strongly sorbed to leaves with the *Primo®* blank; however, the increase in sorption was minimal for this the most water soluble compound evaluated. Based on these results and work by Kile and Chiou (1989), Pick et al. (1984) and Liu et al. (1992), the effects of surfactants on pesticide sorption to *Poa pratensis* L. leaves and thatch appear to be significant.

If the solvents, surfactants and other ingredients in a pesticide formulation volatilize or degrade in the turf, then the effect of formulations may be minimal. Turf managers will often water in pesticides immediately following an application to make them less susceptible to volatilization and photodecomposition, and this increases the likelihood that the watering in of the formulation will effect the sorption of the applied pesticide. This also minimizes the risk of human exposure to the active ingredients. Many of the pesticides

(active ingredients) used on turf are relatively water insoluble (Balogh and Anderson, 1992).

The application of hydrophobic organic compounds to turf is a very common practice, and the leaves should intercept a large percentage of an application (Stahnke et al., 1991). Once these hydrophobic compounds come in contact with the leaves they may not be readily desorbed because of the high K_{leaves} values expected for such hydrophobic compounds. If the compounds are desorbed, they will then come into contact with the thatch layer. The chance of degradation is very great for such compounds because of the long residence time that results from the tortuosity of their pathway through the thatch (Taylor and Blake, 1982; and Hurto et al., 1980).

Numerous studies conducted on cotton have demonstrated the removal of pesticide residues from leaves decreases with time, but usually more than 50% of the mass of residue on the leaves could be removed with as little as 7 mm rainfall (McDowell et al., 1985) when applied within 24 h after treatment (Pick et al., 1984; Smith et al., 1987; Southwick et al., 1983; and Willis et al., 1991, 1992b, 1994). Once the water in the formulation dries from the leaf surface, leaving the surfactant residue and the organic solute on the leaf surface, the effect of the formulation's surfactants should be minimal. However, Pick et al. (1984) found pesticides in formulations were not as tightly bound to leaves as might be expected based on the active ingredient's hydrophobicity. Stahnke et al. (1991) found that even after posttreatment irrigation nearly all (95%) of a pendimethalin (S_W = 0.275 mg L^{-1}) treatment could be recovered from *Poa pratensis* L. 'Touchdown' leaves. The effect of the surfactants, solvents and emulsifiers in formulations will result in deeper initial leaf penetration of a pesticide than would be expected from the active ingredient's properties.

The linearity of the sorption isotherms ($r^2 > 0.922$), over the concentration (C_i) ranges tested, indicates that sorption resembles a partitioning phenomena rather than an adsorption (surface) phenomena on *Poa pratensis* L. leaves and thatch (Chiou and Schmedding, 1982). This theory is further supported on leaves by the linear relationship between the experimentally determined K_{leaves} values and K_{ow} values. The sorption of the organic compounds to *Poa pratensis* L. leaves is analogous to the partitioning of the compound between two immiscible solvents (octanol and water) at concentrations from 10 - 80% of the water solubility of a given nonionic organic compound.

From Figures 1-5 and Table 4, it is apparent that most isotherms do have a y-intercept close to zero. When the standard deviations of the y-intercept values are considered, the regression line would include the origin without drastically changing the K values. The isotherm for 1,2,4-trichlorobenzene produced a y-intercept that was significantly less than zero (-84 ± 21). If the isotherms are not linear at lower concentrations (<10 % of S_w), the nonlinear portion of the isotherm may resemble the L-type isotherms described by Weber and Miller (1989) where a portion of the isotherm has an exponential increase or decrease in Q_s vs. C_e at lower concentrations. Ironically, these lower concentrations may be a more realistic portrayal of the actual quantity of residue reaching the thatch layer in the field. If these lower concentration ranges are nonlinear, the thatch isotherms may resemble the nonlinear isotherms reported by Dell et al. (1994) for thatch. Additional data is needed at these lower concentrations (<10 % of S_w) to determine the sorption characteristics in this region of the isotherm.

The more hydrophobic (lower S_w) the organic compound, the greater the K_{leaves} and K_{thatch} values for both sorbents, with one exception. Fenarimol

had a lower K_{leaves} value than expected for a compound with a water solubility of only 14 mg L^{-1}. Fenarimol did not behave as predicted by its K_{ow} of 3.40. Fenarimol's K_{ow} and K_{leaves} were lower than the K_{ow} (4.02) and K_{leaves} for 1,2,4-trichlorobenzene. Since the K_{oc} values were usually much greater for leaves than for thatch (acetanilide being the only exception), the *Poa pratensis* L. leaves are a more hydrophobic sorbent than thatch (Figure 6). This seems reasonable since thatch is primarily made up of "sclerified vascular strands of stems and leaf sheaths, intact fibrous roots, nodes and crown tissue" (Hurto et al., 1980) that are primarily lignin (Ledeboer and Skogley, 1967) with very limited amounts of plant cuticle. The leaves are covered with hydrophobic cuticular waxes.

The K_{oc} and K_{om} values for all 5 of the nonionic organic compounds evaluated are listed in Table 5. The leaves and thatch had nearly identical percent organic carbon (OC) and organic matter (OM), thereby the same divisor in the equation $K_{oc} = K$ / (OC fraction). The K_{oc} and K_{om} values have proven useful for comparing the hydrophobicity of sorbents with different OC and OM contents (Hassett and Banwart, 1989; Chiou, 1989; Boyd et al., 1990). Dell et al. (1994) observed slightly lower K_{oc} values for thatch than soil (Table 7) for chloroneb (1,4-dichloro-2,5-dimethoxybenzone), triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-1-(1 *H*-1,2,4-trizol-1-*g*-1)butanone] and vinclozolin [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione] indicating these compounds would not have as strong sorption to *Poa pratensis* L. thatch organic carbon as they would to soil organic carbon. Table 8 lists the log K_{ow}, log K_{oc} for thatch (39.8% OC), and log K_{oc} for soil (see Appendix G) for the 5 organic compounds evaluated in this study. The leaf K_{oc} values are always greater than the thatch Koc values with the exception of acetanilide.

Table 7. Log K_{OW}, log K_{OC} (thatch) and log K_{OC} (soil) from Dell et al. (1994).

Compound	log K_{OW}	log K_{OC} (Thatch)*	log K_{OC} (soil)**
chloroneb	2.71	2.72	2.85
triadimefon	2.39	2.46	2.54
vinclozolin	3.01	3.14	3.20

* *Poa pratensis* L. cv Wabash turf (thatch = 30% OC).
** Silty clay loam soil with 3.1% OC.

Table 8. Log K_{OW}, log K_{OC} (thatch) and log K_{OC} (soil) for nonionic organic compounds.

Compound	log K_{OW}	log K_{OC} (Thatch)	log K_{OC} (leaves)	log K_{OC} (soil)*
acetanilide	1.74	1.20	0.97	-----
ethoprop	3.59	1.61	1.93	1.85
1,2,4-tcb	4.02	1.68	2.65	2.94
fenarimol	3.40	2.34	2.61	2.78
phenanthrene	4.57	3.30	3.82	4.59

* K_{OC} values for various sorbents are listed in Appendix G with references.

Both thatch and leaf K_{OC} values were lower than soil Koc values for 1,2,4-trichlorobenzene, fenarimol and phenanthrene. Dell et al. (1994) observed this same result, but their K_{OC} values for thatch were closer to both the K_{OC} values for soil and K_{OW} values. The soil K_{OC} value for ethoprop was greater than the thatch K_{OC} value but slightly less than the leaf K_{OC} value. A soil K_{OC} value for acetanilide was not found in the literature. In both this study and Dell et al. (1994), the thatch organic carbon was less hydrophobic than soil organic carbon and 1-octanol. Turfgrass leaves and thatch have a much greater mass of organic carbon than soils, but soil organic carbon (matter) is a more hydrophobic sorbent. Turfgrass leaves and thatch will have a greater sorption capacity than soil organic carbon (matter) because of the abundance of organic carbon (matter) in these sorbents.

Dell et al. (1994) had a thatch with 30% OC, and the thatch in this study was 39.8 ± 0.9% OC. Therefore, the thatch from Dell et al. (1994) may have been in a more decomposed state and more closely resembled soil organic carbon than the thatch in this study. *Poa pratensis* L. leaves and thatch have a strong affinity for hydrophobic organic compounds due to their high OC contents, but the hydrophobicity of the organic carbon in the leaf and thatch tissues seems to be less than that of soil organic carbon.

The empirical estimates of K_{OC} compiled by Green and Karickhoff (1990) may be successful for predicting K_{OC} values for organic compounds if the compound's family is taken into consideration, but the K_{OC} range for these empirical equations is 10 - 10^6 (Table 6). Empirical estimates for K_{OC} were usually greater than the experimentally determined K_{OC} values. All of the K_{OC} equations were derived from soil sorption research. It was interesting that the soil K_{OC} values from the literature are also greater than the experimentally determined K_{OC} values in this study. Therefore, the usefulness of such

correlations with soil values must be scrutinized. Based on the results of this study, the empirical estimates of K_{OC} derived for soils (Green and Karickhoff, 1990) should not be used to predict K_{OC} values for *Poa pratensis* L. leaves and thatch.

The differences in sorption by cuticular waxes between species has been shown to be negligible in at least one instance (Kerler and Schönherr, 1988a), who found sorption differences by needles from various coniferous tree species were due to the surface area of the needles rather than the nature of the cuticular membrane (Schreiber and Schönherr, 1992). Therefore, the sorption of hydrophobic compounds to various turfgrass species' leaves should be similar. Future research will have to address, the hydrophobicity and state of decomposition of the thatch layer under dissimilar turfgrass systems.

In the batch-suspension isotherm determinations, equilibrium was achieved in 4 h (Appendix C) for both acetanilide (S_W = 5405 mg L^{-1}) and phenanthrene (S_W = 1 mg L^{-1}). Future research should determine if equilibrium is achieved on leaves or thatch under field conditions. Assuming the compound does not have a long residence time on the leaves, due to removal with water from the sprayer solution or posttreatment irrigation, equilibrium would probably not be achieved with leaves. Equilibrium might be achieved on leaves if a turf was treated when wet, and it remained wet for an extended period of time. Otherwise the assumption can be made that the compound will be deposited in the thatch soon after an application. In the thatch, where infiltration rates are minimal until the thatch is thoroughly wet (Taylor and Blake, 1982; Hurto et al., 1980), the residence time of an organic compound on organic thatch tissues may be very long. Equilibrium would probably be reached in the thatch layer, and the K_{thatch} values determined by the batch-suspension method would be valid predictors of nonionic organic

compound sorption in the field. As stated earlier, the effect of the formulation should be considered in all future pesticide sorption work. Determination of nonequilibrated sorption to turfgrass leaves and thatch would be the optimum way of determining if the batch-suspension method is an accurate predictor of sorption in the field.

The relationships between K_{ow} or S_w and the K values for leaves and thatch are shown in Figures 8 and 9. The regression lines for leaves and thatch intersect in both figures. Therefore, at log S_w values (mol L^{-1}) greater than -2 and log Kow values less than 2.5, we can expect thatch to be a stronger sorbent than leaves. This is contrary to what was observed for the more hydrophobic compounds. The intersections in Figures 8 and 9 indicate that compounds with a log S_w (mol L^{-1}) of approximately -2 and log K_{ow} of approximately 2.5 would have equal K values for leaves and thatch.

Future research should address the differences in thatch sorption at different sites under various management strategies. The effects of formulations will need to be addressed, because the chemical parameters of the active ingredients in pesticides are not the only factors involved in distribution of a compound in the turfgrass system. Finally, there is a need for non-equilibrium sorption studies on turfgrass to determine the applicability of batch-suspension data to field sorption of pesticides.

APPENDICES

APPENDIX A

GRINDING EFFECTS ON THATCH SORPTION

All thatch was gently washed to remove as much soil as possible and to achieve a more uniform sorbent. Before washing the thatch was 38.6 ± 3.9% organic carbon, and after washing it was 39.8 ± 0.9% organic carbon. A sample of the thatch was then ground to 2 mm. The sorption of acetanilide at 500 mg L^{-1} (C_i) was determined by another batch-suspension experiment with 6 replications on both ground and unground thatch. The quantity sorbed (Q_S) and K values for this experiment are listed in the table below. The batch-suspension experiments showed how sorption was not effected by grinding, but the standard deviation for both quantity sorbed and the K values was decreased by grinding. If sorption isotherms are consistent with a partitioning mechanism rather than adsorption, grinding would not be expected to affect sorption. The variability in sorption with unground thatch was acceptable, and the chance of increasing adsorption sites was eliminated by using only unground thatch. All thatch samples were washed but left unground for the remainder of the batch-suspension experiments.

Table 9. The effect of thatch grinding on acetanilide sorption

Thatch	Q_S (mg kg^{-1})	K
ground to 2 mm	0.87 ± 0.02	2.63 ± 0.09
unground	0.85 ± 0.13	2.62 ± 0.65

APPENDIX B

RADIO-LABELED COMPOUND PURITY AND SPECIFIC ACTIVITY

Acetanilide

Four-5 μl spots of acetanilide dissolved in methanol were placed on a silica gel 60A thin layer chromatography (TLC) plate and developed with acetone:carbon tetrachloride (3:2) for 0.5 h at 21° C. The plate was then placed in a desiccator at 21° C until dry. The spots was then observed under a UV lamp at 254 nm to determine the R_f (0.58). The plate was then scraped in 0.5 cm increments into separate scintillation vials containing 20 ml aqueous (Safety Solve) counting cocktail (Research Prod. Int. Corp.). Care was taken to place the visible spot into a vial by itself. Quantities of ^{14}C were then determined by liquid scintillation counting for 10 minutes on a Packard Tri-Carb Model 1500 liquid scintillation counter. All DPM values were corrected for background and quenching when necessary. The ^{14}C-acetanilide sample was determined to be >98% pure as indicated by Sigma Chem. Co.

The specific activity reported by Sigma was then verified by reverse-phase HPLC (Isco - Model 2300). The acetanilide/methanol solution was injected at 21° C with a flow rate of 1.75 ml min^{-1}. The mobile phase was 3:2 water:acetonitrile, while the stationary phase was a 5 μm x 3 cm x 4.6 mm, C18 column (Anspec-H1404). The samples were detected at 242 nm on a UV detector (Isco - V^4) and the peaks were integrated (Varian - Model 4290) to determine peak area. A standard curve was employed to determine acetanilide concentrations. The same volume that was injected into the HPLC was placed in liquid scintillation vials to determine the ^{14}C concentration. This method was

successful in verifying the specific activity reported by Sigma(2.2×10^9 Bq $mmol^{-1}$).

Ethoprop

Two-5 μl spots of ethoprop dissolved in methanol were placed on a silica gel 60A thin layer chromatography (TLC) plate and developed with hexane:acetone (4:1) at 21° C (R_f=0.6). The plate was then placed in a desiccator at 21° C until dry. The plate was developed in toluene:methanol: triethylamine (80:19:1) in the direction 90° from the first development (R_f = 0.3). The plate was again placed in a desiccator at 21° C until dry. The spots were observed under a UV lamp at 254 nm. The plate was then scraped in 0.5 cm increments into separate scintillation vials containing 20 ml aqueous (Safety Solve) counting cocktail (Research Prod. Int. Corp.). Care was taken to place the visible spot into a vial by itself. Quantities of ^{14}C were then determined by liquid scintillation counting for 10 minutes on a Packard Tri-Carb Model 1500 liquid scintillation counter. All DPM values were corrected for background and quenching when necessary. The ^{14}C-ethoprop sample was determined to be >96% pure as indicated by Rhone Poulenc.

The specific activity of the ^{14}C-ethoprop sample reported by Rhone Poulenc (1.8×10^8 Bq $mmol^{-1}$) was not verified.

1,2,4-Trichlorobenzene

Four-5 μl spots of 1,2,4-trichlorobenzene dissolved in methanol were placed on a silica gel 60A thin layer chromatography (TLC) plate and developed with iso-pentane for 0.5 h at 21° C. The spots was then observed under a UV lamp at 254 nm to determine the R_f (0.57). The plate was scraped in 0.5 cm increments into separate scintillation vials containing 20 ml aqueous

(Safety Solve) counting cocktail (Research Prod. Int. Corp.). Care was taken to place the visible spot into a vial by itself. Quantities of ^{14}C were determined by liquid scintillation counting for 10 minutes on a Packard Tri-Carb Model 1500 liquid scintillation counter. All DPM values were corrected for background and quenching when necessary. The ^{14}C-1,2,4-trichlorobenzene sample was determined to be >99% pure as indicated by Sigma Chem. Co. The above procedure must be done with care to minimize the volatilization of the very volatile 1,2,4-trichlorobenzene.

The specific activity of the ^{14}C-1,2,4-trichlorobenzene sample reported by Sigma (2×10^6 Bq $mmol^{-1}$) was not verified.

Fenarimol

Four-5 μl spots of fenarimol dissolved in methanol were placed on a silica gel 60A thin layer chromatography (TLC) plate and developed with ethyl acetate for 0.5 h at 21° C. The plate was placed in a desiccator at 21° C until dry. The spots was observed under a UV lamp at 254 nm to determine the R_f (0.54). The plate was scraped in 0.5 cm increments into separate scintillation vials containing 20 ml aqueous (Safety Solve) counting cocktail (Research Prod. Int. Corp.). Care was taken to place the visible spot into a vial by itself. Quantities of ^{14}C were determined by liquid scintillation counting for 10 minutes on a Packard Tri-Carb Model 1500 liquid scintillation counter. All DPM values were corrected for background and quenching when necessary. The ^{14}C-fenarimol sample was determined to be >97% pure as indicated by DowElanco.

The specific activity of the ^{14}C-fenarimol sample reported by DowElanco (2.5×10^8 Bq $mmol^{-1}$) was not verified.

Phenanthrene

Four-5 μl spots of phenanthrene dissolved in methanol were placed on a silica gel 60A thin layer chromatography (TLC) plate and developed with carbon tetrachloride for 0.5 h at 21° C. The plate was placed in a desiccator at 21° C until dry. The spots were observed under a UV lamp at 254 nm to determine the R_f (0.61). The plate was scraped in 0.5 cm increments into separate scintillation vials containing 20 ml aqueous (Safety Solve) counting cocktail (Research Prod. Int. Corp.). Care was taken to place the visible spot into a vial by itself. Quantities of ^{14}C were determined by liquid scintillation counting for 10 minutes on a Packard Tri-Carb Model 1500 liquid scintillation counter. All DPM values were corrected for background and quenching when necessary. The ^{14}C-phenanthrene sample was determined to be >99% pure as indicated by Sigma Chem. Co.

The specific activity reported by Sigma was verified by reverse-phase HPLC (Isco - Model 2300). The phenanthrene/methanol solution was injected at 21° C with a flow rate of 1.5 ml min^{-1}. The mobile phase was 3:1 acetonitrile:water, while the stationary phase was a 5 μm x 3 cm x 4.6 mm, C18 column (Anspec-H1404). The samples were detected at 254 nm on a UV detector (Isco - V^4) and the peaks were integrated (Varian - Model 4290) to determine peak area. A standard curve was employed to determine phenanthrene concentrations. The same volume that was injected into the HPLC was placed in liquid scintillation vials to determine the ^{14}C concentration. This method was successful in verifying the specific activity reported by Sigma (3.1×10^8 Bq $mmol^{-1}$).

APPENDIX C

TIME TO EQUILIBRIUM

Preliminary experiments showed equilibrium for acetanilide and phenanthrene was reached in 4 h. The initial solute concentrations for acetanilide and phenanthrene were 2700 mg L^{-1} and 0.4 mg L^{-1}, respectively. One-ml aliquots of phenanthrene and acetanilide supernatant were removed at 0, 0.2, 0.3, 0.5, 0.7, 0.8, 1.0, 1.3, 1.7, 2, 4, 12, and 24 h. The most widely used equilibration time in published isotherm studies is 24 h, and because there was no further sorption between 4 and 24 h, we chose a 24 h equilibration period (Figure 12). These results show that equilibrium is reached very quickly for both sorbents regardless of the water solubility of the solute evaluated.

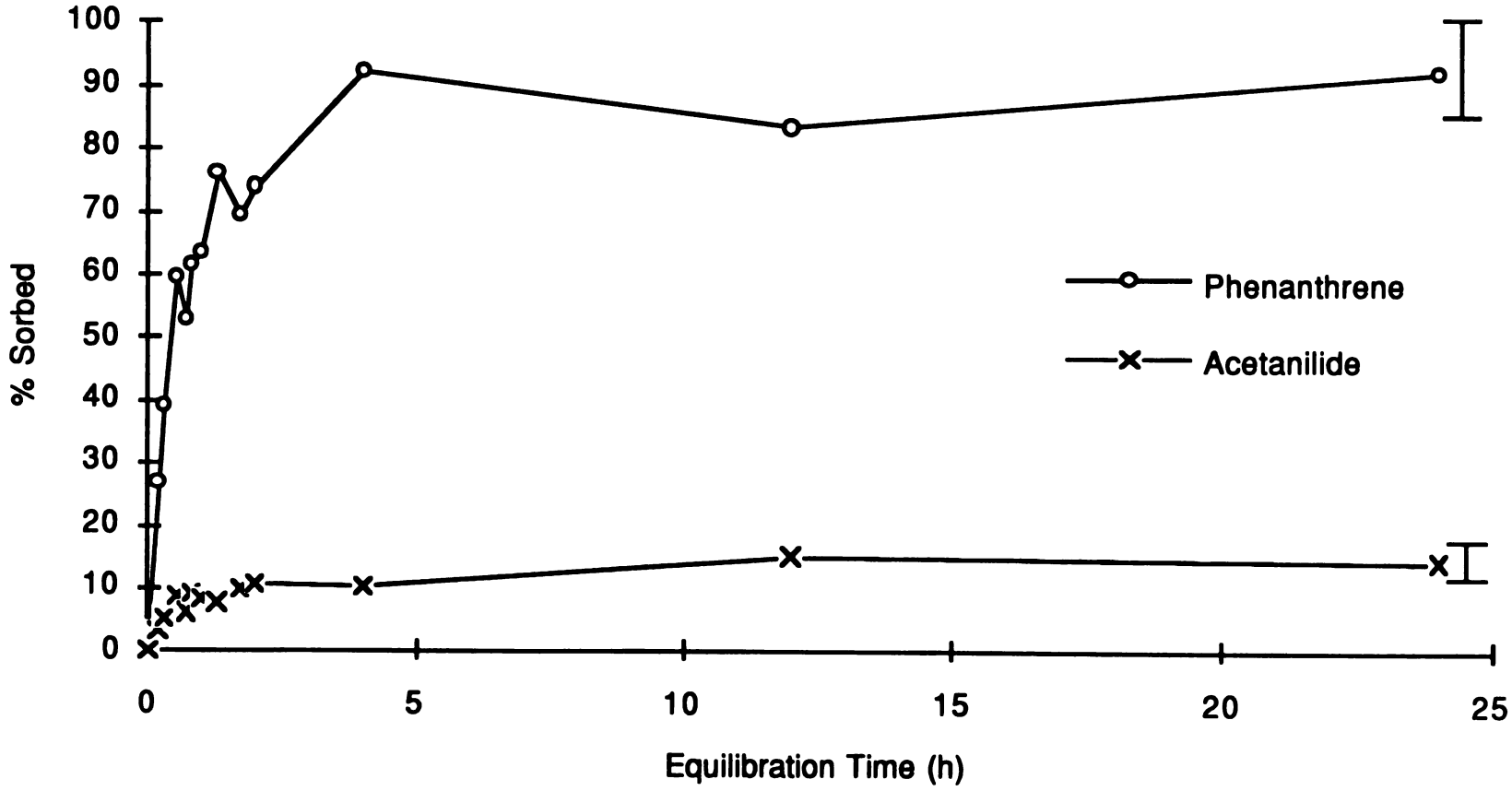


Figure 12. Time to reach equilibrium with the batch-suspension method on leaves

APPENDIX D

MICROBIAL ACTIVITY IN BATCH-SUSPENSION VIALS

A batch-suspension experiment was conducted with acetanilide at 500 mg L^{-1}. One gram of thatch was placed in each of 8 centrifuge tubes and half of the tubes were spiked with sodium azide at 10.0 g L^{-1}(Wahid et al., 1980). The tubes were shook for 48 h with 2 subsamples removed from each tube at 2, 4, 8, 24, 32, and 48 h. Differences in sorption may be due to the change in the solvent properties of the supernatant with the addition of sodium azide. Therefore, further studies with sterilized water and autoclaved sorbents may be necessary to determine if microbial degradation is a concern, but, based on these results, shaking tubes for longer then 24 h would not be advised (Figure 13). The 24 h equilibration time chosen appears to be safe from microbial degradation. Different results could be expected for less stable compounds.

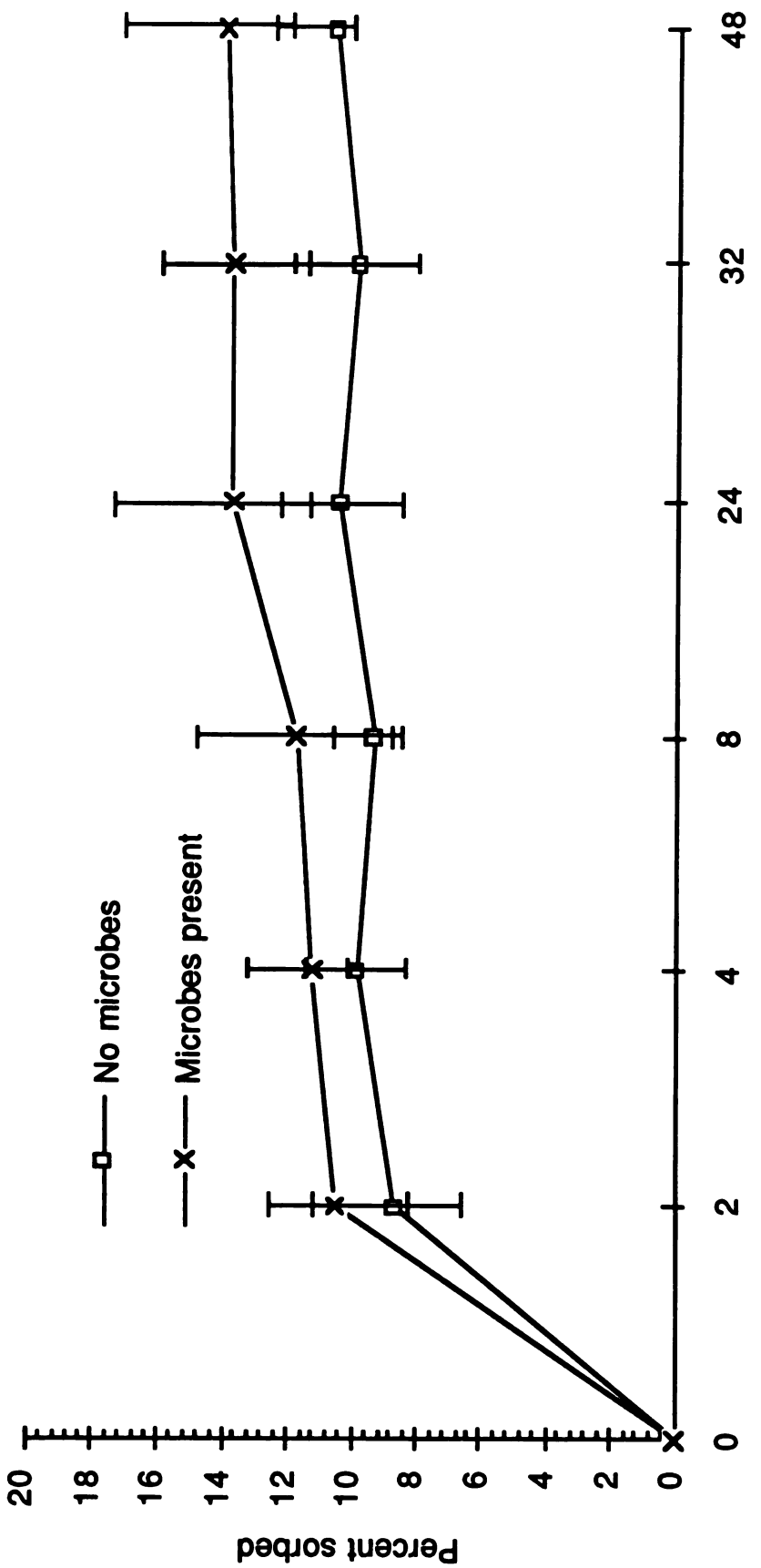


Figure 13. Microbial degradation of acetanilide during isotherm determination.

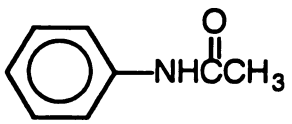
APPENDIX E

BATCH-SUSPENSION METHOD'S EFFECT ON PH

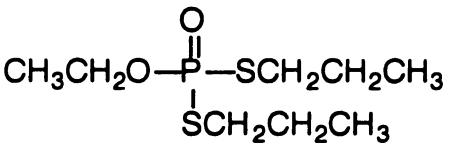
The change in pH of the supernatant in batch-suspension vials was determined after the 24 h equilibration period. The supernatant was decanted into a beaker, and the pH was determined with a pH meter (Fisher - Model 815MP) calibrated in the pH range from 4.0 - 7.0 with a 97.3% calibration efficiency. The pH of the leaf supernatant was 7.48 ± 0.48 initially and it dropped to 5.20 ± 0.94 after the 24 h equilibration period. The pH of the thatch supernatant dropped from 7.68 ± 0.39 to 7.28 ± 0.09 in the 24 h equilibration time. The thatch pH did not change as drastically due to the thatch's buffering capacity and/or its cation exchange capacity (CEC). The leaf supernatants pH decreased by the release of acidic (polar) organic matter into the solution during equilibration. These findings indicate buffering of the solution may be necessary when ionizable organic compounds such as 2,4-D are evaluated.

APPENDIX F

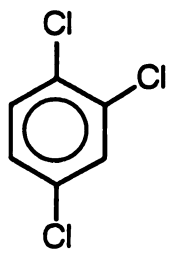
STRUCTURES FOR NONIONIC MODEL ORGANIC COMPOUNDS



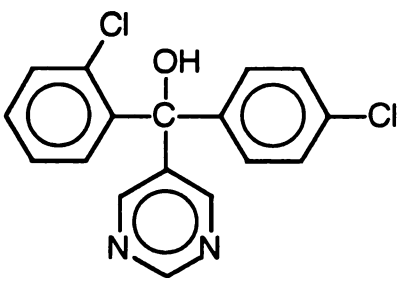
Acetanilide



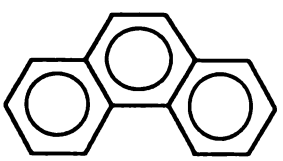
Ethoprop



1,2,4-Trichlorobenzene



Fenarimol



Phenanthrene

APPENDIX G

TABLE 10. LOG Koc VALUES FOR ORGANIC COMPOUNDS ON VARIOUS SORBENTS.

Compound	log K_{OC}	Sorbent	Reference
ethoprop	1.85	soil	Wauchope et al., 1992
1,2,4-tcb	0.55	river sediment (0.08% OC)	Swartzenbach and Westall, 1981
1,2,4-tcb	2.94	silt loam soil (1.9% OC)	Chiou et al., 1983
1,2,4-tcb	2.95	clay subsoil (0.05% OC)	Southworth and Keller, 1986
1,2,4-tcb	3.11	clay subsoil (1.2% OC)	Southworth and Keller, 1986
1,2,4-tcb	3.32	clay subsoil (0.11% OC)	Southworth and Keller, 1986
fenarimol	2.78	soil	Wauchope et al., 1992
phenanthrene	2.44*	activated carbon	Walters and Luthy, 1984
phenanthrene	3.15	clay subsoil (0.11% OC)	Southworth and Keller, 1986
phenanthrene	3.76	clay subsoil (0.05% OC)	Southworth and Keller, 1986
phenanthrene	3.77	clay subsoil (1.2% OC)	Southworth and Keller, 1986
phenanthrene	4.28	estuary sediment (4.0% OC)	Vowles and Mantoura, 1987
phenanthrene	4.36	pond sediment (3.27% OC)	Karickhoff et al., 1979
phenanthrene	4.59	silt loam soil (2.74% OC)	Schrap and Opperhuizen, 1989

* K value determined from Freundlich isotherm for activated carbon with an unknown % OC.

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