

THE ADSORPTIVE BEHAVIOR OF ATRAZINE AND ALACHLOR IN ORGANIC-POOR SEDIMENTS

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ABSTRACT

A sediment mixing approach was taken to systematically vary the organic carbon (oc) and clay content (cm) of a suite of organic-poor, clay-rich sediments. Organic carbon content ranged from 3.2 to 0.4% and clay content ranged from 24 to 51%. Atrazine and alachlor were shown to sorb to both natural organic carbon and clay minerals. Partition coefficients to natural organic carbon (K_{oc}) were found to be 196 and 436 liters/kg organic carbon for atrazine and alachlor, respectively. Partition coefficients to the clay fraction were found to be 1.8 and 3.0 liters/kg clay for atrazine and alachlor, respectively. Retardation factors calculated using partition coefficients that ignore numerical phase sorption are low by factors of 2.6 to 2.8 in the subsoils used in this study.

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INTRODUCTION

Triazine and acetanilide herbicides are the most commonly used classes of pre-emergence broadleaf herbicides. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) form the vast majority of the herbicides used in the mid-continent region of the United States. In the region, atrazine is the most widely used herbicide and is commonly detected in ground- and surface-waters. A recent water quality survey in Wisconsin suggests that as many as 15% of all Wisconsin dairy farms have wells contaminated by atrazine (Wisconsin DATCP, 1989). Alachlor originating from typical agricultural usage (as well as from accidental spills, etc.) has also been found in drinking water supplies (U.S. Environmental Protection Agency, 1986).

A key process in the transport of herbicides to the water table is sorption to the solid matrix through which it percolates. Sorption of pollutant molecules affects not only the physical transport of the molecule, but also affects chemical reactivity either directly or indirectly (e.g., Wolfe et al., 1986; Zepp and Scholtzhauer, 1981; Macalady and Wolfe, 1985). In addition, sorption alters solution phase concentrations and therefore alters solution phase reactions. A complete process-level understanding of the sorptive behavior of these widely used herbicides is of prime importance to the understanding of their overall behavior in the subsurface.

The adsorptive behavior of nonionic organic pollutants usually is presumed to be controlled by the organic carbon portion of the solid. This generalization is supported by numerous studies performed on a variety of non-ionic organic pollutants and sediment/solid sorbents (e.g., Kenaga and Goring, 1978; Bailey and White, 1970; Yaron and Saltzman, 1978; Wahid and Sethunathan, 1978). The studies demonstrate that pollutant sorption to sediments is proportional to the organic carbon (oc) content of the sediment. Other surfaces such as clays or oxides are less active and for many sediments do not contribute significantly to total sorption.

This has led to the development of a carbon referenced sorption parameter (K_{oc}):

$$K_{oc} = C_{oc} / C_w \quad (1)$$

where C_{oc} = μg pollutant/g solid organic carbon
 C_w = μg pollutant/ml water.

K_{oc} is related to the partitioning to any natural sediment (K_p) by multiplying by the organic carbon fraction of the sediment;

$$K_p = (K_{oc})(foc) \quad (2)$$

where K_p = $\mu\text{g pollutant/g sediment}$
 f_{oc} = weight fraction organic carbon in sediment.

Sorption of this type is driven by the hydrophobic nature of the pollutant molecule. Hydrophobic sorption is not being driven by polar group interactions, ionic bonding, or chemisorption.

This adsorptive dependence on organic carbon content leads to the common behavioral model in which adsorption of nonionic pollutants occurs only in the organic-rich topsoil. Adsorption in organic-poor subsoils is assumed to be minimal. This model may be incorrect for molecules such as atrazine or alachlor which are not strongly hydrophobic especially if the soils are organic-poor and clay-rich or if loading is great enough that the pollutant leaches through the topsoil. The possibility may arise that adsorption to inorganic material plays a role in the behavior of atrazine and alachlor in the unsaturated zone beneath the topsoil.

Many organic pollutants are extremely hydrophobic and strongly partition onto the organic phase. This hydrophobic nature is manifested by very low water solubilities (S) and very high octanol-water partition coefficient (K_{ow}). Pesticides exhibit solubilities that range in value from 10^{-3} mg/liter to 10^3 mg/liter and K_{ow} values that range from 10^2 to 10^6 (Kenaga and Goring, 1980). Atrazine and alachlor have relatively high solubilities ($S = 70$ mg/liter and 240 mg/liter, respectively) and relatively low octanol water partition coefficients ($K_{ow} = 10^{2.7}$ and $10^{2.6}$, respectively) and as such are not overly hydrophobic.

Previous workers have noted that inorganic surfaces, especially clays with a high cation exchange capacity (CEC), can play an important role in adsorption of organic pollutants (Means et al., 1982; Harris and Sheets, 1965; Walker and Crawford, 1968). Adsorption to inorganic surfaces becomes important when the weight fraction clay:weight fraction organic carbon ratio (cm/oc) of the sediment exceeds 30 (Karickhoff, 1984). This is particularly true for organics with polar functional groups. Inorganic sorption may be a contributing factor to the observed nonlinearity of certain $\log K_{oc}:\log K_{ow}$ relationships (Karickhoff, 1984). It has also been reported that K_{oc} values for sand sized particles within a sediment are as much as an order of magnitude less than the K_{oc} value from the fine grained portion of the sediment (Karickhoff et al., 1979). This apparent change in K_{oc} may be due to a contribution to total sorption by inorganic sorption onto the clays in the fine grained portion of the sediment.

The behavioral model tested holds that herbicide sorption is controlled primarily by partitioning onto organic carbon until the cm:oc ratio exceeds a critical value (approximately 30) at which point partitioning onto a mineral phase becomes important. The active mineral surface is presumed to be a high CEC clay (montmorillinite or illite). In this model, adsorption in the unsaturated zone beneath the topsoil is not minimal and may play a significant role in the movement of these pollutants in the subsurface.

MATERIALS AND METHODS

Two soils, one a topsoil and the other a subsoil directly beneath, were collected from the University of Wisconsin-Milwaukee campus. Both soils are classified as Kewaunee silt loam. They were characterized for soil pH, total organic carbon (TOC) and cation exchange capacity (CEC). Soil pH was measured in a 1:1 (by weight) soil:water mixture. TOC was measured in a Carlo Erba C-H-N analyzer and CEC was determined by Na^+ saturation of the exchange sites following the procedure of Polemio and Rhodes (1977).

Batch adsorption experiments were carried out on samples with a constant sediment:water ratio of 5. Capillary gas chromatography (GC) with an ECD detector was used to detect atrazine and alachlor. To compensate for differences in the volume of sample injected into the GC, simazine and propachlor were used as internal standards for atrazine and alachlor, respectively. Each batch was equilibrated on a wrist action shaker for at least 48 hr, separated by centrifugation and the herbicide concentrations in water and sediment phases measured. Water phase concentrations were determined by direct injection on the GC. Sediment phase concentrations were determined after methanol extraction. The GC was calibrated against methanol and water based stock solutions. All experiments were conducted in triplicate and results averaged. Controls were performed to check for losses due to hydrolysis or other degradation reactions.

All herbicides were obtained from Ultra Scientific. The methanol used was HPLC-grade (Aldrich).

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RESULTS AND DISCUSSION

The two soil samples were chosen to be similar in all respects except organic carbon content. Both soils had 20 meq/100 g CEC and a pH of 7.4. Organic carbon content of topsoil and subsoil were 3.2% and 0.39%, respectively. Adsorption experiments on the two soils are complete. Table 1 contains all the pertinent data.

Table 1. Characteristics of end member soils and sorption data. †

	Topsoil	Subsoil
Soil pH	7.4	7.4
CEC (meq/100 g)	21 ± 3	21 ± 1
% Clay Content	24	51
% O.C.	3.24 ± 0.21	0.39 ± 0.05
K _p (atrazine)	8.2 ± 0.8	2.6 ± 0.1
K _p (alachlor)	17.2	4.8
Apparent K _{oc} (atrazine)	254 ± 24	752 ± 42
Apparent K _{oc} (alachlor)	530	1,372

†Values are given ± one standard deviation.

If hydrophobic, organic based sorption was the only sorptive process in operation, K_{oc} values would be independent of soil type. Inspection of the data shows that this is not the case. Sorption to the mineral portion of the soil is occurring. The partitioning of herbicide to the organic and mineral portion of a soil can be written:

$$K_p = (K_m)(cm)(fm) + K_{oc}(oc)(f_{oc}) \quad (3)$$

where

- K_p = total partition coefficient to sediment
- K_m = partition coefficient to inorganic surfaces
- K_{oc} = partition coefficient to organic surfaces
- cm = fraction mass of inorganic material in the whole sediment
- fm = adsorptively active portion of cm
- oc = fractional mass of organic material in the whole sediment (it is initially assumed that the entire mass of organic material is adsorptively active)
- f_{oc} = adsorption active portion of oc

Numerous studies (e.g., Karickhoff, 1984; Lyman et al., 1982) indicate the sediment independence of K_{oc} values, therefore, it is usually assumed that f_{oc} is constant and is incorporated into K_{oc} . If it is assumed that f_m is also constant, Eq. 3 reduces to:

$$K_p = (K_m)(cm) + K_{oc}(oc) \quad (4)$$

The two assumptions mean that organic matter in the soil does not "block" or change the adsorptive capacity of the mineral matter and vice versa. Experiments are currently underway that will provide information on f_m in this system.

Two independent determinations of K_p have been made for each herbicide, and two independent determinations of oc have been made. Since $cm = 1 - oc$, the only unknowns are K_{oc} and K_m . Two independent equations can be written, one each for topsoil and subsoil and solved for K_{oc} and K_m . Results are given in Table 2.

Table 2. Mineral and organic phase sorption coefficients.

Partition Coefficients	Atrazine	Alachlor
K_m (liters/kg clay)	1.8	3.0
K_{oc} (liters/kg organic carbon)	196	436

Although organic sorption appears dominant from the K_{oc} values, this is not the case when multiplied through by the relative amounts of organic and mineral matter. Sorption of atrazine to the mineral fraction accounts for 70% of the total in the subsoil and 21% in the topsoil. Equivalent values for alachlor are 63% and 17%, respectively. Sorption to the mineral portion of these soils is significant, even in the topsoil with an organic carbon content of > 3%.

When trying to predict the sorptive behavior of organic pollutants, the usual procedure is to either measure a K_p and convert to K_{oc} or to estimate K_{oc} from empirical $\log K_{oc} - \log K_{ow}$ relationships (e.g., Lyman et al., 1982). The resultant K_{oc} is then applied to the soil of interest and the only measurement needed to obtain a K_p for the soil is the % oc .

These K_p 's are then used to calculate the retardation of pollutant movement with respect to groundwater movement. The pertinent equation is:

$$r_f = 1 + \frac{(P_b)(K_p)}{n} \quad (5)$$

where r_f = advective velocity of groundwater divided by the velocity of pollutant (retardation factor)
 P_b = bulk density of soil
 n = soil porosity.

If representative values of P_b and n for the subsoil ($P_b = 1.6 \text{ g/cm}^3$ and $n = 0.4$) and the K_p derived from the actual K_{oc} (Table 2) are used, the retardation factor is calculated to be 4.0 and 7.8 for atrazine and alachlor, respectively. Values from $\log K_{ow} - \log K_{oc}$ estimates are similar. The actual retardation factor, based on the measured K_p (Table 1) is 11.1 and 20.0 for atrazine and alachlor, respectively.

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CONCLUSIONS

Atrazine and alachlor exhibit significant sorption to the mineral portion in the organic-poor (0.39% oc) subsoil. Retardation factors in the subsoil calculated using partition coefficients that ignore mineral sorption are low by factors of 2.6 to 2.8. The sorption of both herbicides to the mineral portion of organic-poor, clay-rich soils cannot be discounted.

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