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Sorption of the Herbicide Mefenacet in Soils

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The knowledge of the sorption behaviors for chemicals is helpful to understand the consequences that may arise from their controlled or uncontrolled distribution to the soil compartment. For instance, movements towards deeper soil zones and to groundwater, the uptake and eventual metabolism by plants or micro-organisms, and the volatility of pollutants may be influenced by the soil sorption. Thus, sorption studies have become an essential part in hazard and risk assessment.

Mefenacet, [2-(2-benzothiazolyl-oxy)-N-methyl-N-phenylacetamide], exhibits a low water solubility of 4.0 mg/L and a melting point with 134.8°C. It belongs to the acetamide herbicides and is used to control weeds in transplanted rice of paddy field in the tropical and temperate zones, particularly in some countries of Asia. In recent years it has been put into use in China as an alternative to butachlor, which is found to inhibit the growth of paddy rice and induce the tolerance of Barnyard-grass (Heli Geng et al. 1999). Some investigations have been carried out on its mode of action (Fedtke 1991), biological/physicological activity (Fedtke 1987; Heli Geng et al. 1999), toxicity (Shigehisa et al. 1998), monitoring (Shigehisa et al. 1998), etc., however, quantitative data on the sorption of mefenacet by soils are sparse and seldom reported.

This work investigated the sorption behaviors of mefenacet in six typical agricultural soils from different regions in China. The sorption characteristics are essential for assessing its environmental fate and for input into site-specific simulation models for these soils.

MATERIALS AND METHODS

Mefenacet (98% pure) was obtained from Chang Zhou Pesticides Factory, and was monitored by HPLC to assure that no interference impurity had occurred. Heptane used in this study was analytical reagent grade supplied from Tian Jin Chemical Reagents Factory.

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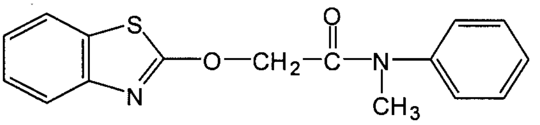


Figure 1. Chemical structure of mefenacet

Soils used in this study were collected from six different regions in China. Soil samples were taken from the surface layer (0-20 cm), air-dried, and passed through an 80-mesh sieve. Soil properties determined (Page et al. 1982) were: pH in 0.01M $CaCl_2$ with soil/solution of ratio 1:1, organic matter content by the Walkley-Black procedure, particle-size by the Bouyoucos gravimeter method.

The sorption experiment was conducted by the batch equilibrium technique. A 0.01M solution of $CaCl_2$ was used as an aqueous phase, to make phase separation easier and to simulate an ionic strength similar to that of a natural soil solution. Different soil/solution ratios were applied for different soils according to these soil properties, respectively. Preliminary evaluations found that mefenacet sorption equilibrium was attained within a 24 hours period.

The soil was weighed into a 50 ml flask and then, a 0.01M $CaCl_2$ solution (25.00 ml) containing a known concentration of mefenacet was added. The stoppered container was shaken automatically for 24h at the constant temperature of 25±1°C. At the end of the shaking period, 15 ml suspension was taken and centrifuged at 3000 rpm/min for 30min. 10.00 ml of the resulting clear solution was sampled and transferred into a stoppered small test-tube with 3.00 ml of heptane as extractant. After the extraction, 2.5ml of the heptane solutions were taken out to determine the absorbence at 218.6 nm against the corresponding soil blank with an ultraviolet/visible spectrophotometer (Shimadzu UV-2201). Under the chosen measuring conditions, the extraction efficiencies for mefenacet was up to 93% and the detection limit of 0.5 mg/L in heptane was achieved. The concentration of mefenacet in the aqueous phase could be calculated according to its concentration in the heptane phase read from the plot of absorbence versus concentration previously generated in heptane. The amount of mefenacet sorbed was computed simply by the difference between the initial and equilibrium concentrations in the aqueous phase.

For the determination of the sorption isotherms, six initial concentrations ranging from 0.2 to 2.1 mg/L were used. All treatments were performed in duplicate, and blank samples containing only dissolved mefenacet without any soil were prepared and handled in parallel with each set of batch experiments to qualify the losses. In all cases, there was not significant decrease from volatilization after 24h of shaking at 25°C.

RESULTS AND DISCUSSION

The primary properties of these soil substrates, which are relevant to understand the sorption behaviors, are summarized in Table 1. According to their properties (organic matter content, pH value, clay content), the six different soils were classified into two categories using statistical cluster analysis with the Euclidian average distance, where the category I comprises the Black, Chao soils and sediment while category II includes the Red, Yellow-brown and Clay soils. It is obvious that the organic matter content in the category I is higher.

Table 1. Selected physico-chemical properties of the soils investigated

Soils	Source	PH (water:soil=1:1)	Organic matter content OM (%)	Clay content (%) (<0.002mm)
Black soil	Wudalianchi, Hei long-jiang	7.80	3.24	27.2
Sediment	Yangtze River, Nanjing	7.80	1.52	23.6
Chao soil	Fengqiu, Henan	7.95	1.35	10.9
Red soil	Yingtan, Jiangxi	5.59	0.76	32.3
Yellow-brown soil	Nanjing, Jiangsu	7.10	0.39	30.1
Clay soil	Jiangning, Jiangsu	7.91	0.16	29.8

Fitting the linear and Freundlich sorption equations respectively to the experimental data resulted in the linear and Freundlich sorption coefficients, K_d and K_f,, and the constants, 1/n, for the sorption of mefenacet by six soils. Table 2 gives the values of K_d , K_f and 1/n.

The correlation coefficients r shown in Table 1 indicate that the sorption behaviors of mefenacet in soils are well represented by the linear and Freundlich sorption equations. According to the values of K_d and /or K_f, the strength of mefenacet sorbed to soils seems relatively higher compared to some herbicides applied in China currently, such as imazethapyr, imazapyr and triclopyr. It is suggested that mefenacet is likely to be sorbed strongly to soils and not to leach into the deeper soil layers.

Moreover, it is found that the numerical differences among K_d and /or K_f within a category are lower than that between two categories, and values of K_d and /or K_f in the category I are greater, revealing that the sorption of mefenacet by soils in the category I is stronger than that in the category II. The degree of the sorption of mefenacet among six soils increases in the order: Black soil > Sediment > Chao soil > Red soil > Clay soil > Yellow-brown soil.

Table 2. Sorption parameters of mefenacet on soils at 25°C

Soils	Sorption models				
	Linear sorption model $X_s = K_d \cdot C_e$		Freundlich sorption mode $X_s = K_f \cdot C_e^{1/n}$		
	K_d (SE)	r	K_f (SE)	1/n (SE)	r
Black soil	8.7810 (1.2118)	0.9555	10.6256 (1.0809)	0.5158 (0.08169)	0.9533
Sediment	7.8473 (0.5937)	0.9860	8.6268 (1.0760)	0.7563 (0.07630)	0.9802
Chao soil	3.8320 (0.4443)	0.9680	4.5604 (1.0704)	0.5599 (0.07424)	0.9666
Red soil	2.4876 (0.1734)	0.9881	2.3208 (1.0830)	0.9598 (0.09682)	0.9802
Yellow-brown soil	1.1213 (0.05766)	0.9935	1.0397 (1.0616)	1.1182 (0.07472)	0.9912
Clay soil	1.7592 (0.1133)	0.9898	1.7576 (1.0909)	1.0569 (0.1060)	0.9805

[a] X_s denotes the amount of mefenacet sorbed on soil at equilibrium ($mg \cdot kg^{-1}$);
[b] C_e is the equilibrium concentration in solution ($mg \cdot L^{-1}$);
[c] The values of X_s and C_e were the average of two replications.

In general, sorption to the soil for hydrophobic compounds can be understood as a partitioning process between a polar aqueous and a nonpolar organic phases (Oepen et al. 1991). This process is commonly assumed to be the major mechanism for sorption of nonionic organic compounds from water to soil, and mineral adsorption is expected to be mostly suppressed by water owing to their unfavorable polarities for competitive adsorption on polar mineral surfaces (Chiou et al. 1983). Thus, the competition of mefenacet against water molecules for sorption sites on minerals is likely to show that the partition process would be predominate and for the sorption coefficients, there is the tendency to increase with the increasing of organic matter contents (except the soil E). On the basis of the partition mechanism and the isotherms with no indication of curvature (Chiou et al. 1979), the linear sorption model is selected in our study to describe the sorption behaviors of mefenacet by soils.

The simple equation showed as below was developed by regression analysis between the linear sorption coefficient (K_d) of mefenacet and soil organic matter contents (OM%):

$$K_d = 2.6120\ \mathrm{OM\%} + 1.0746 \qquad (1)$$

$$r = 0.8964,\ SE = 1.6094,\ N = 6$$

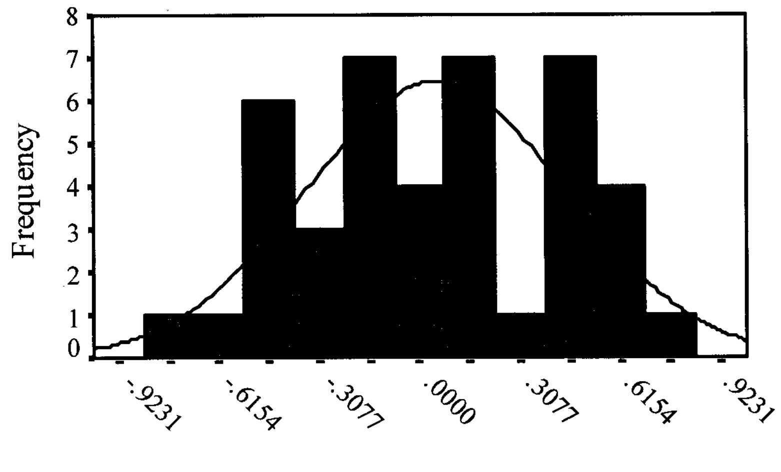
From the statistical table for testing significance of correlation coefficients, $r > r_{0.05}$ (= 0.811), which means the linear sorption coefficient and the soil organic matters were significantly correlated and nearly 90% of variation of K_d can be explained by the effect of the variable, OM%. The results demonstrate the importance of the soil organic matter in determining the sorption of mefenacet in soil-water system. Additionally, although there was a goodness of fit for the regression equation (1), its prediction performance should be further tested.

The method generally utilized to test the reliability of a regression equation is to divide the observations into two sets: one for use in developing the regression and the other for testing its prediction. This procedure, which is an excellent one to follow when sufficient data are available, became inconvenient when limited amount of data is obtained, and in this case a Monte Carlo technique (Summers et al. 1993) is more feasible. The Monte Carlo technique for testing the prediction performance of a regression equation permits the use of all data available as deriving the regression equation and does not require estimating degrees of freedom. These are especially important when the sample is small (Lund et al. 1970). Since only 6 observations were available in our present work, the Monte Carlo simulation was conducted to determine whether the prediction of the regression equation was reliable.

It was assumed that the predicted value (i.e. linear sorption coefficient (K_d)) is independent of the predictor (i.e. soil organic matter content (OM%)) when using Monte Carlo simulation to test the regression equation (1). Six bogus values of predicted value (K_d) were generated with a random number generator stochastically sampling from a normal distribution, which parameters were defined by the average (4.3047) and variation (3.2473^2) of observation values for K_d. A regression equation was developed between these six bogus values of K_d and the values of predictor (OM%), and the correlation coefficient of this spurious equation was recorded as r*. The predictor values were not changed in any manner when the spurious equations were derived; only the predicted values were varied. Repeating such a Monte Carlo simulation forty times resulted in 40 sets of 6 random numbers of K_d, as well as 40 spurious equations and their corresponding r* with the range from –0.02777 to 0.7590.

On the basis of results of Chi–square goodness-of-fit-test applied to the fitted empirical distribution of r*, obtained from the Monte Carlo simulation, the significance level (0.2738) greater than 0.05 suggests significant sufficiency of fit and no distinct difference from a normal distribution (Fig. 2). From the normal probability distribution of r*, it is known that at the probability of 0.95 exceeding a critical value of 0.7294 is required, in this case, to determine a significant difference between the values of r and r*. Since r (0.8964) in the equation (1) is greater than r* in our study, it can be regarded that the prediction by equation (1) considerably differs from the random prediction by spurious equations, therefore, the predictive reliability of equation (1) was verified by the Monte Carlo simulation method. Based on the equation (1), the K_d value of mefenacet could be predicted, to some extent, from OM% values of soils.

As compared, the "leave-one-out" method was also performed to test the prediction performance for regression equation (1), i. e., one of the observations was deleted, and the regression was rerun for the remaining 5 observations. The procedure was repeated 6 times, all of the regression statistics were averaged and



(Chi-square = 3.8878, Sig. level = 0.2738)

Figure 2. The empirical distribution of r*

obtained the averaged regression coefficient, constant, correlation coefficient and standard error were 2.7783, 0.9582, 0.9014 and 1.5452, respectively. It is seen that none of these averaged parameters for the diminished data sets is remarkably different from equation (1) developed for the full data set. However, when residuals for the deleted observations were respectively calculated from the difference between the observation and its corresponding predicted value, three deviated values were found and indicated predictive non-ideality. Thus, this aspect of investigations tested the predictive quality of the equation (1) and implied that the "leave-one-out" method is not that suitable to test the prediction performance for a small sample as the Monte Carlo simulation did.

In summary, mefenacet is strongly sorbed to soils in this study and it has a lower tendency to leach into deeper layers of soils. Within the range of concentrations in the experiment, the sorption behaviors of mefenacet in soils were appropriately characterized by linear sorption model. The soil organic matter was found to play an important role in the sorption of mefenacet by soils, and the sorption coefficients were observed to increase with the increasing of soil organic matter contents. A regression model of the linear sorption coefficient (K_d) versus soil organic matter content (OM%) was established with goodness of fit. Based on this regression equation, the K_d values of mefenacet could be predicted from values of OM% in soils, which would help to evaluate its potential leaching and its likelihood of groundwater contamination. The reliability of prediction was verified by means of a Monte Carlo simulation method.

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