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Adsorption and Degradation of Metolachlor in Alluvial Soils: Effect of Poultry Litter

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Abstract

Soils in the Southern Mississippi Valley Alluvium (MLRA 131) have low organic matter content (< 20 g kg^{-1}) and application of poultry (Gallus gallus domesticus) litter to these soils may improve their quality. However, after litter application, chemical weed control practice such as herbicide application for row crop production remains the same. In soils where soybean [*Glycine max* (L.) Merr.] is grown, metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl] acetamide] is applied as a pre-emergent herbicide to control broadleaf and annual grasses. There is an opportunity for metolachlor to leach to the groundwater during and after rainfall events. We hypothesize that metolachlor applied to these alluvial soils amended with poultry litter may degrade rapidly when compared to unamended (control) soils. Soil samples were collected from the top 10 cm of Commerce silt loam (Aeric Fluvaquents) and Sharkey clay (Vertic Haplaquepts). The samples were air dried and amended with poultry litter to increase the organic matter content to 20 g kg^{-1}. Control samples received no poultry litter but were subjected to similar protocols as the amended samples. Batch experiments indicated significant increase in metolachlor adsorption for the amended soils, although adsorption was higher in Sharkey clay. Kinetics experiments showed that equilibrium was established 2 h for Commerce silt loam and 24 h for Sharkey clay. Metolachlor degradation was 6 times faster in the amended Commerce soil and 2.5 times faster in the amended Sharkey soil. Degradation rate in the amended Commerce soil was 2.3 times faster than the amended Sharkey clay. We conclude that adding poultry litter to these alluvial soils will increase metolachlor adsorption and further increase rates of degradation. However, appropriate amounts of poultry litter when applied, are promising for enhancing remediation of metolachlor.

Keywords: Adsorption, degradation, metolachlor, poultry litter.

Introduction

Production of Gallus gallus domesticus (poultry) has increased in the United States over the past five years. Increase in production means increase in the quantity of manure. This manure is mixed with wood shavings or sawdust (bedding materials) and is classified as litter. The litter is usually applied to pasture, added to animal diet, or stockpiled as means of disposal. However in most cases, the litter is stockpiled in fields in the vicinity of poultry production facilities. Since most poultry producers do not have enough pasture to dispose of the litter produced at their facilities, efforts are being made to transport the material to row crop production areas.

Soils in the Southern Mississippi Valley Alluvium (MLRA 131) have low organic matter content. Application of poultry litter to these low organic carbon (< 20 g kg^{-1}) soils may improve their quality. However, after litter application, weed control for row crop production (herbicide application) remains the same. In soils where soybean [*Glycine max* (L.) Merr.] is grown, metolachlor is applied as pre-emergent herbicide to control broadleaf and annual grasses. This herbicide is an acetanilide with water solubility of 488 mg L^{-1} at 20°C and is known to undergo many dissipation processes when placed in soils (Weber, 1991). Eighty two percent of surface water samples collected from 312 locations in 14 states contained metolachlor at a maximum concentration of 138 µg L^{-1} (Bouchard et al., 1982). A previous study showed soil from a 0 to 20-cm depth had higher metolachlor adsorption than the soil from a 40 to 50 cm depth and suggested that the lower adsorption of the subsoil was attributed to lower organic matter content (Lui and Cibes-Viade, 1992). Metolachlor adsorption was highest in the 0-to 8-cm soil depth of a silt loam that contained 1.1% organic matter (Barnes et al., 1992). Earlier study showed that metolachlor adsorption was highest in soil planted with clover followed by vetch and wheat (Johnson, 2001). The increase in metolachlor adsorption was also attributed to increased organic carbon content (Johnson, 2001). Enhancement of herbicide degradation by crop resi-

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dues amended soils has been investigated (Kinniburgh, 1986; Wagner and Zablotowicz, 1997; Johnson, 2001; Salim and Zhu, 2005). Further, soil organic matter has often been considered the dominant sorptive phase for pesticides in soil-water systems (Sheng et al., 2001; Martin-Neto et al., 2001). Since poultry litter addition to soil will increase the organic matter content of the soil, it is essential to assess how such amendment affects metolachlor fate in soils. It was the objective of this study to quantify adsorption and degradation of metolachlor in two poultry litter amended alluvial soils.

Materials and Methods

Soil samples were collected from the top 10 cm of two alluvial soils from the Southern Mississippi Delta region. The soils were Commerce silt loam (Fine-silty, mixed, nonacid, thermic Aeric Fluvaquents) and Sharkey clay (Very-fine, montmorillonitic, thermic Vertic Haplaquepts). The Commerce soil had a pH of 6.0 and consisted of 231, 635, 144 and 9.7 g kg^{-1} sand, silt, clay and organic carbon (OC), respectively. The Sharkey soil had a pH of 6.3 and consisted of 124, 240, 636 and 12.7 g kg^{-1} sand, silt, clay and OC, respectively. All samples were air dried and amended with poultry litter to increase the OC content to 20 g kg^{-1}. Control samples received no poultry litter but were subjected to similar protocols as the amended samples.

Batch and Kinetics Experiments

A high purity metolachlor (99.2% purity) was obtained for the study (Ultra Scientific, North Kingstown, RI) and prepared in 50 µM $CaCl_2$ background solution. For the batch study, 5 g of soil (oven-dry soil basis) and 15 mL of the metolachlor solution at concentrations of 0, 2, 4, 10, 16, and 20 mg L^{-1} were transferred to 25 mL glass centrifuge vials that were sealed with Teflon-lined screw caps. All metolachlor-soil mixtures were done in three replicates. Each vial was concealed with aluminum foil paper to prevent degradation by light. The soil-solution mixtures were shaken on a reciprocating shaker at 150 rpm for 24 h at room temperature (approx. 23^{0}C). Subsequently, the vials were then centrifuged at 3500 rpm for 30 min. and removed for filtration of the supernatant. For the kinetics study, 15 mL of herbicide solution at a concentration of 2.4 mg L^{-1} was added to 5 g of soil (7.2 mg kg^{-1}). The metolachlor-soil mixture was shaken at approximately 230C on a reciprocating shaker at 150 rpm for 0, 1, 2, 12, 24, 48, 72, 96 and 120 h. Each shaking time had three replicates and at the end of a shaking time the vials were removed and centrifuged at 3500 rpm for 30 min. until separation of the liquid and solid phases occurred. The supernatant was then filtered.

Supernatants for both batch and kinetics experiments were filtered through disposable 0.45 µm nylon filters and the filtrates were analyzed for metolachlor using a DX 500 High Performance Liquid Chromatography (HPLC) system (Dionex Corp., Sunnyvale, CA). The system consisted of an AD20 UV/visible detector operated at a wavelength of 220 nm. About 5 mL filtrates were transferred to polyvials, capped and placed on an AS40 autosampler (Dionex Corp., Sunnyvale, CA). By automation, the samples were injected into a Zorbax HPLC C-18 column (4.6 mm i.d x 25 cm; MAC-MOD Analytical, Chadds Ford, PA) with 80:20 acetonitrile:water ratio as the mobile phase at a flow rate of 1 mL min^{-1}. Losses to vial and filtration were determined and found to be negligible from the blank samples that consisted of only metolachlor solutions. The adsorbed concentration, S, (mg kg-1) was calculated as the difference between the initial concentration and the concentration at equilibrium, C_e (mg L^{-1}). For the batch experiment, metolachlor adsorption was described by the Freundlich equation for soils treated with and without poultry litter:

$$S = K_f C_e^{N} \qquad [1]$$

$$\ln S = \ln K_f + N \ln C_e \qquad [2]$$

where K_f (mgL$^{-1/n}$ kg^{-1} L$^{1/n}$) is the Freundlich coefficient and N is an empirical constant or the slope in Eq. [2]. Nonlinear regression techniques were used to derive K_f and N coefficients for Eq. [1].

Incubation Experiment

Incubation of metolachlor was conducted in triplicate in 500-mL beakers containing 250 g (oven-dry soil basis) of soil at 10% gravimetric water content. Eighty milliliters of herbicide solution (31.25 mg L^{-1}) were applied to yield a metolachlor application rate of 10 mg kg^{-1} of soil with a total gravimetric water content of approximately 36%. The soil in each container was mixed carefully with a stainless steel spoon. All containers were covered with perforated aluminum foil paper and allowed to incubate at 23°C in the dark for 504 h (21 d), and water content was adjusted to maintain 36% water content. About 20 g of soil was taken from each container at 0, 1, 24, 72, 120, 168, 336, and 504 h during incubation and analyzed for herbicide. The samples were air-dried and 5 g of soil from each sample was transferred to 50 mL vials with Teflon screw caps. To ensure that the extraction effectiveness was acceptable, percent recoveries of the herbicides were investigated using the same extraction procedure. Thirty milliliters of a 4:1 methanol:water mixture were added to each sample and shaken on a reciprocating shaker at 150 rpm for 8 h. The vials were centrifuged at 3500 rpm for 30 minutes. Aliquots (10 mL) from each vial were taken, filtered as above, concentrated, and analyzed using HPLC procedure. Degradation was based on first-order decay with governing model as follows:

$$\frac{dC_t}{dt} = -kt \qquad [3]$$

and integrating Eq. [3] gave

$$C_t = C_o e^{-kt} \qquad [4]$$

where C_t is herbicide concentration at time, t, C_o is initial concentration and k is the degradation coefficient. Percentage of metolachlor degraded was based on the concentration at the first sampling time after initial addition. Based upon the k values, half-life ($t_{1/2}$) of metolachlor was calculated for each treatment.

Statistical Analysis

The distribution coefficient, K_f, of a herbicide is directly influenced by the clay and OC contents of the soil. Both clay and OC components of the soils in this study were thought to likely influence adsorption of the metolachlor. Consequently, a factorial design was used to assess all possible combinations of K_f in the batch study under soil and poultry litter amendment. For the batch and incubation experiments, factor A was soil type and factor B was poultry litter. For the kinetics study, factor A was poultry litter, factor B was soil and factor C was time. Analysis of variance (ANOVA) was used to determine factor significance and comparisons were made using the least significant difference (LSD) at the 5% level of probability. Criteria for estimating the goodness-of-fit of a model to data are the root mean square error, RMSE, and coefficient of determination (r^2) (Kinniburgh, 1986). These statistical criteria were used in estimating degradation rates and adsorption of metolachlor. However, only r^2 was reported in this study. The k, N and r^2 values were determined by nonlinear regression techniques using the JMP statistical discovery software (SAS Institute, Inc.).

Results and Discussion

Metolachlor Adsorption

Addition of poultry litter to the soils increased metolachlor affinity. Metolachlor adsorption parameters for the Commerce and Sharkey soils are presented in Table 1. The Freundlich model indicated good fit to the experimental data for all isotherms the isotherms presented in Figure 1. Irrespective of poultry litter application, K_f values in the Sharkey soil were generally much higher than the Commerce soil. The K_f values for unamended and amended Commerce soil were 0.50 L kg^{-1} and 2.09 L kg^{-1} and for the Sharkey soil were 1.97 L kg^{-1} and 2.90 L kg^{-1}, respectively.

Metolachlor Adsorption Kinetics

Adsorption kinetics for metolachlor in both Commerce and Sharkey soils with and without poultry litter treatment are presented in Figure 2. Metolachlor adsorption in the Sharkey soil with and without poultry litter was rapid during the shaking period from 1 to 120 h. However, equilibrium was established in 24 h and shaking beyond 24 h had no significant effect on adsorption. Similar trend was observed for the Commerce soil with or without poultry litter but equilibrium was established in 2 h.

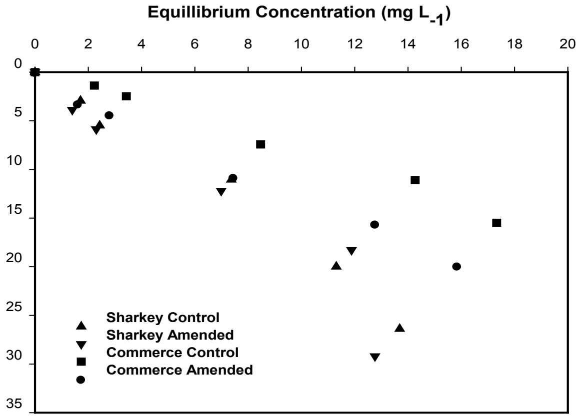

Figure 1. Adsorption isotherms for metolachlor by poultry litter amended and control Commerce and Sharkey soils.

Table 1. Mean values of distribution coefficient (K_f), empirical constant, degradation rate constant (k) and half-life ($t_{1/2}$) for metolachlor in poultry litter amended and control Commerce and Sharkey soils.

		Adsorption Parameters			Degradation Parameters		
Soil	Poultry Litter	K_f	N	r^2	k	$t_{1/2}$¶	r^2
		$mg^{1-1/n}\,kg^{-1}\,L^{1/n}$			day^{-1}	day	
Commerce	Amended	2.09a‡	0.803(0.040)†	0.99	0.286(0.0012)†	2.4a‡	0.97
	Control	0.59b	1.156(0.081)	0.98	0.048(0.0002)	14.4b	0.95
Sharkey	Amended	2.90c	0.811(0.097)	0.96	0.125(0.0004)	5.5c	0.99
	Control	1.97a	0.959(0.092)	0.97	0.050(0.0002)	13.9b	0.96

¶ Half-life [$t_{(1/2)}$ = 0.693/k]. † Means in parentheses are standard errors. ‡ Means followed by the same letter in each column are not significantly different at the 5% level of probability.

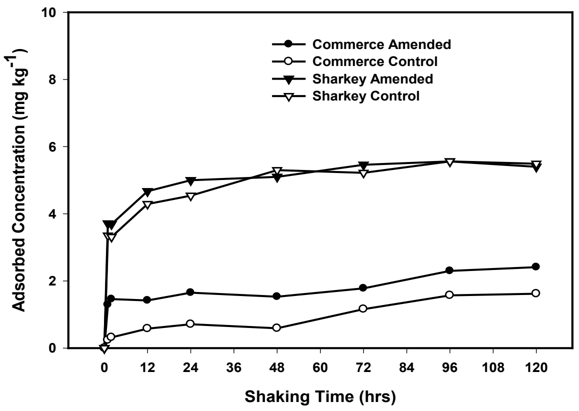

Figure 2. Adsorption kinetics of metolachlor in poultry litter amended and control Commerce and Sharkey soils.

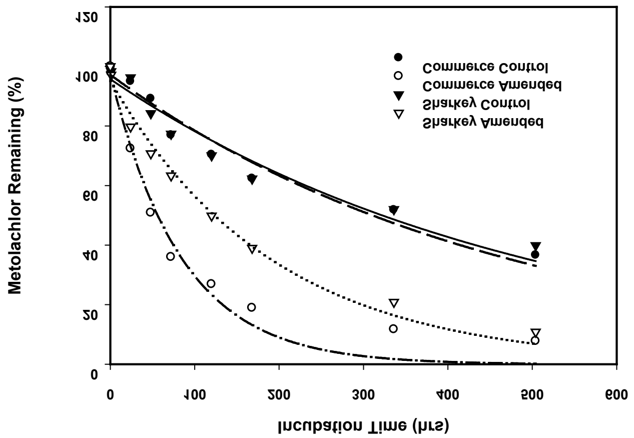

Figure 3. Decay of metolachlor in poultry litter amended and control Commerce and Sharkey soils. Lines represent fitted first-order reactions.

There was a consistently significantly greater adsorption by the amended Commerce soil than the control ($p \leq 0.05$). While no difference was observed between the treated and control Sharkey soil, adsorption was significantly greater and more consistent over time than the Commerce soil ($p \leq 0.05$). Although both soils are alluvial Mississippi Delta soils, Sharkey has 4 times more clay than Commerce that may have influenced metolachlor adsorption. Other researchers have shown a strong adsorption of metolachlor by Sharkey clay, although the soil was not treated with poultry litter (Selim et al., 1999). After 120 h of shaking, 33.5 and 75.0% of the initial metolachlor applied was adsorbed by the amended Commerce and Sharkey soils, respectively. For the control treatments, metolachor adsorption after 120 h was 22.5 and 76.2% of the initial herbicide applied, respectively.

Metolachlor Degradation

Metolachlor degradation as expressed in percent remaining is presented in Figure 3. The first-order decay model described degradation rates. Table 1 shows degradation rate constants were 0.048 day^{-1}for control and 0.286 day^{-1} for amended (Commerce); 0.050 day^{-1} for control and 0.125 day-1 for amended (Sharkey). The rate of degradation was 6 times faster (2.4 d) in the amended Commerce soil compared to the control (14.4 d) and was 2.3 times faster than the amended Sharkey soil (5.5 d). Metolachlor degraded 2.5 times faster in the poultry litter amended Sharkey soil than its unamended control. Degradation, however, did not significantly differ between both unamended soils. While the batch experiment indicated greater metolachlor adsorption in the two amended soils than the unamended controls, remediation of this herbicide is greatly enhanced under conditions where poultry litter is applied. From a previous study, it was observed that 43% of metolachlor degraded under reduced and oxidized conditions after 16 d of incubation in Forestdale silt loam, a Mississippi River Delta soil (Mulbah et al., 2000). After 14 d of incubation, 48% of metolachlor degraded in both control treatment of the Commerce and Sharkey soils; however, when poultry litter was added, 88 and 79% of metolachlor degraded, respectively.

Conclusion

Results of this study show that metolachlor adsorption and degradation were affected by addition of poultry litter to the two alluvial soils. Greater adsorption was observed in the Sharkey soil than in the Commerce soil. The clay contents in the Commerce and Sharkey soils are 144 and 636 g kg^{-1}, respectively. As shown in the batch experiment, there was higher adsorption of metolachlor in the Sharkey soil than in the Commerce soil irrespective of poultry litter application. This suggests that affinity of metolachlor to soil is also influenced by clay content. Degradation was highest in the amended Commerce soil followed by the amended Sharkey Soil. Disposal of poultry litter from production facilities to the Mississippi River Delta will not only increase the organic carbon pool of those soils, but it will also enhance degradation of herbicides. After 21 d of incubation, 89 and 92% of the total metolachlor applied was degraded. Since poultry litter is applied prior to herbicide application, metolachlor movement in the soil profile will be retarded thereby allowing for rapid degradation of the herbicide. Although groundwater in MLRA 131 is located in a confined aquifer, the potential for contamination may be further reduced when poultry litter is applied to the overlying soils for row crop production. Field studies are needed to quantify metolachlor fate in the vadose zone under conditions where poultry litter is used as an organic amendment.

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