Long-term tillage effects on soil metolachlor sorption and desorption behavior

Guangwei Ding [a], Jeffrey M. Novak [b], Stephen Herbert [a], Baoshan Xing [a,*]

[a] *Department of Plant and Soil Sciences, Stockbridge Hall, University of Massachusetts,*
P.O. Box 37245, Amherst, MA 01003, USA
[b] *USDA-ARS-Coastal Plains Soil, Water and Plant Research Center, Florence, SC 29501, USA*

Abstract

Sorption and desorption are two important processes that influence the amount of pesticides retained by soils. However, the detailed sorption mechanisms as influenced by soil tillage management are unclear. This study examined the sorption and desorption characteristics of metolachlor [2-chloro-N-(2-ethyl-6-methyphenyl)-N-(2-methoxy-1-methylethyl)-acetamide] using the soil samples collected from the long-term conservation tillage (CnT) and conventional tillage (CT) research plots established in 1979 in Darlinton, SC. Humic acid (HA) and humin were extracted from the soils and used in the sorption experiments along with the whole soil samples. The sorption experiments were conducted using a batch-equilibration method. Three sequential desorption rinses were carried out following the sorption experiments. By comparing metolachlor sorption and desorption results we observed hysteresis for all soil samples and their organic matter fractions. Sorption nonlinearity (N) and hysteresis were dependent on the structure and composition of soil organic matter (SOM), e.g., Freundlich isotherm exponents (N) of HA and humin from CnT were higher than those of CT treatment, which may be related to high aromaticity of SOM fractions in CT treatment. Sorption capacity (K_f') was positively correlated with soil organic carbon (SOC) content. These results show that long-term tillage management can greatly affect metolachlor sorption and desorption behavior probably by qualitative differences in the structural characteristics of the humic substances.
© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metolachlor; Soil organic matter; Sorption; Hysteresis; Tillage

1. Introduction

Sorption and desorption are important processes that influence the mobility and bioavailability of hydrophobic organic compounds (HOCs) in the soil environment. A number of soil properties have been shown to affect the retention of HOCs in the soil profile, including organic matter content, soil acidity, soil texture, and clay mineralogy (Johnson and Sims, 1993; Chefetz et al., 2000; Hundal et al., 2001). These soil properties also affect the sorptive behavior of pesticides in soil.

Pesticide distribution patterns within soils are controlled by a complex series of equilibrium interactions between pesticides and soil components. Pesticides in the liquid phase are readily available for plant uptake and leaching. Pesticides sorbed to solid phases are generally regarded as being slowly available for plant uptake because of strong bonding forces and slow desorption kinetics. Soil minerals and soil organic matter (SOM) are major components that influence the sorption magnitude

* Corresponding author. Tel.: +1-413-545-5212; fax: +1-413-545-3958.
E-mail address: bx@pssci.umass.edu (B. Xing).

of organic chemicals including pesticides. The reactive mineral components are silicate clays, oxyhydroxides, and amorphous materials of Fe and Al. Agricultural practices generally do not substantially change contents and characteristics of soil mineral components due to their inert chemical nature, for example, there are no marked differences in clay contents between conservation tillage (CnT) and conventional tillage (CT) plots after 18 years (Novak et al., 1996). Thus, sorption by minerals should not vary greatly with agricultural tillage practices. However, the change in quantity and quality (e.g., structures) of SOM by agricultural practices can be significant and may potentially alter sorption behavior, mobility, and biological activity of pesticides in soils (Novak et al., 1996).

Metolachlor is a pre-emergence herbicide used commonly for corn, soybean, and peanut in the USA and has been detected in surface and groundwater systems (Ritter, 1990; Maas et al., 1995). Information regarding metolachlor sorption and desorption characteristics in soil is necessary to predict its fate in the soil environment. Evaluation of long-term tillage effects on pesticide sorption and desorption will be important to southeastern Coastal Plain soils, which are regarded as having a high pesticide leaching potential because of high precipitation, sandy textures, and low SOM levels (Kellog, 1993). Seybold and Mersie (1996) investigated the sorption and desorption of metolachlor in two soils from Virginia and showed that differences in the composition of organic matter and/or the amounts of other components (e.g., clay) play a significant role in the sorption process. Johnson and Sims (1993) found a significant positive correlation between SOM and sorption of metolachlor ($r = 0.925$) and noted that the spatial variability of SOM was similar to that of metolachlor sorption coefficients. They further reported that the variability of sorption coefficients in a field soil could be more readily estimated by measuring the variability of SOM.

SOM is heterogeneous and varies with agricultural practices. The variation in quality of SOM can strongly influence sorption capacity of metolachlor. However, there are very limited studies regarding the effect of changes in SOM quality on metolachlor sorption. In our previous paper (Ding et al., 2002), we showed that tillage system markedly changed the structure and composition of SOM in a southeastern Coastal Plain soil. The objectives of this study were to investigate the sorption and desorption behavior of metolachlor by different soil components (soil, humic acid, or humin) and to evaluate metolachlor sorption and desorption mechanisms as influenced by the long-term tillage systems. Humic acid (HA) is defined as the fraction of humic substances that is soluble in alkaline but not in acidic solutions. Humin can be described as the fraction that is insoluble in an aqueous solution at any pH value. These two fractions make up the bulk of SOM, thus, it is critical to study metolachlor sorption by the two fractions.

2. Materials and methods

2.1. Site description and sorbent preparation

Soil samples were collected from long-term CnT and CT research plots at the Clemson University Pee Dee Research and Education Center (Darlington, SC). CnT completely eliminated disking and field cultivation for weed control. CT consisted of multiple diskings (0–15 cm) and use of field cultivators (0–5 cm) to maintain a relatively weed-free soil surface and to incorporate crop residues, fertilizers, and lime. The plots have been in several types of rotations including continuous corn, corn–wheat–soybeans, and corn–wheat–cotton. Detailed management practices were reported previously (Novak et al., 1996). A bucket auger was used to collect soil cores from Ap horizon (0–15 cm), which were subsampled at three depths (0–5, 5–10, and 10–15 cm), at random locations within each plot. Then, soil samples were composited, air-dried, and sieved (2 mm). However, soil samples from only two depths (0–5 and 10–15 cm) were used in this study.

HA was extracted by the methods of Swift (1996) with some modifications. The soil samples were extracted by 0.1 M $Na_4P_2O_7$ three times (Ding et al., 2001). It should be noted that not all HA and fulvic acid were extracted due to the limited number of extractions. After separating the supernatant solution of the $Na_4P_2O_7$ extraction, the residues (crude humin) were placed in a plastic bottle, treated with HF (3.5% v/v) and continuously mixed with a magnetic stir bar (Preston and Newman, 1995). The mixture in the bottle was stirred for 4 h on a magnetic plate, and the stir bar was taken out to remove clinging magnetic particles. After centrifugation, the supernatant was discarded and filled with fresh HF solution, and the stir bar was replaced. Removal of mineral substances with HF was repeated six times, but the stir bar was only used for the first three to four treatments due to a decline of magnetic particles. After the last HF wash, the de-ashed humin was washed with deionized water three times before transferring into a shallow dish for air-drying. Spectra of HA and humin were obtained by using the CPMAS–TOSS (cross-polarization magic-angle-spinning and total sideband suppression) ^{13}C NMR techniques (Xing et al., 1999). Major peak areas were integrated and calculated by chemical shift ranges (Xing et al., 1999; Mao et al., 2000; Ding et al., 2002). The aromaticity calculation was based on the method of Hatcher et al. (1981). Selected chemical properties of HAs and humins are listed in Table 1.

Table 1
Chemical property of sorbents

	C (%)	Aliphatic-C (%) (0–108 ppm)	Aromatic-C (%) (108–162 ppm)	Aromaticity[a] (%)
HA CnT1[b]	51.2	58.9	28.2	32.4
HA CT1	53.2	52.6	31.8	37.7
Humin CnT1	7.18	47.9	34.1	41.5
Humin CT1	7.82	40.4	47.7	54.1

[a] Expressed in terms of aromatic-C as a percentage of the aliphatic-C + aromatic-C (Hatcher et al., 1981), (108–162 ppm)/(0–162 ppm).

[b] 1 referring to 0–5 cm depth.

2.2. Sorption and desorption experiments

Metolachlor was purchased from the Crescent Chemical Company (Hauppage, NY) and ^{14}C-labeled metolachlor was obtained from the Ciba-Geigy Company (Greensboro, NC). The compound has a $\log K_{ow}$ (K_{ow} =octanol/water partition coefficient) of 3.45 and solubility of 530 mg l^{-1}.

Sorption experiments were conducted using a batch-equilibration method (Yuan and Xing, 2001) in 8-ml screw-cap vials with Teflon-lined septa. The background solution was 0.01 M CaCl$_2$ with 200 μg ml^{-1} HgCl$_2$ as a biocide. The ^{14}C-labeled metolachlor, along with its non-radioactive stock solutions, was mixed with sorbents (soil, HA, or humin) at different solid to solution ratios (from 8 to 200) to achieve 30–70% uptake of metolachlor. Nine different initial concentrations were used, which were evenly spaced on the log scale. The initial metolachlor concentrations ranged from 0 to 250 μg ml^{-1}. Each point was run in duplicate. Two blanks without sorbent were run for each initial concentration. The vials were agitated on hematology mixers that produced a gentle, rotating motion. After mixing, suspensions were centrifuged at 1100g (3000 rpm) to obtain a clear solution. The solute in the solution was determined by liquid scintillation counting (20 min per sample; Beckman LS 3801, CA) using 1 ml sample and 12 ml scintillant solution. Blanks (1 ml background solution and 12 ml scintillant solution, average count of 37 dpm/ml) were subtracted from all sample values. A three-day sorption experiment was used because preliminary sorption experiments showed no significant concentration changes between three- and seven-day sorption.

The background solution for desorption experiments was prepared by mixing the 0.01 M CaCl$_2$ and 200 μg ml^{-1} HgCl$_2$ with test sorbents using the same solid to solution ratio as described previously, but without metolachlor. Then, the suspension was mixed at the room temperature (25 ± 2°) for the identical length of time as the sorption or desorption experiment. After appropriate time of mixing, the bottle was centrifuged at

1100g for 30 min and the supernatant was collected for use as the background solution for desorption experiments. By using this background solution, we expected to have replenished any dissolved and colloidal substances lost (from the sorbent) in the discarded fluid, and thus ensured that solution chemistry was not changed during the desorption cycles (Xia and Pignatello, 2001).

Desorption experiments were conducted in sequential decant-refill steps immediately following the completion of sorption experiments. At the end of sorption experiments, solids were separated from the aqueous solution by centrifugation at 1100g for 30 min and 1 ml aliquot of supernatant was withdrawn from each vial for liquid scintillation counting. Then about 4 ml of the remaining supernatant (depending on the sorbent) were replaced with the same volume of the background solution prepared as above, by weight to the precise amount. After dilution, the vials were shaken on the hematology mixers for three days. The suspension was centrifuged and 1 ml aliquot of supernatant was extracted for analysis. The above process was repeated for two more cycles. The metolachlor concentration present in the supernatant solution after each desorption cycle was determined by liquid scintillation counting. Desorbed metolachlor was calculated at each desorption stage. The amount of metolachlor remaining on sorbents at each desorption stage was calculated as the difference between the initial sorbed amount and the final desorbed amount. Both the duplicates, rather than the average for each experiment were reported on the isotherms.

All sorption and desorption data were fitted to the logarithmic form of the Freundlich equation:

$$\log x/m = \log K_f + N \log C, \tag{1}$$

where x/m (μg g^{-1}) is the sorbed concentration and C (μg ml^{-1}) is the final solution concentration. The K_f and N values are the Freundlich coefficients, and the latter is often used as the index of isotherm nonlinearity (Yuan and Xing, 2001).

We used reduced concentration, C_r [solubility (S_w)-normalized solution concentration, $C_r = C/S_w$] to replace C in Eq. (1). The C_r is dimensionless. Then, K_f was converted to K_f' (modified Freundlich coefficient). The values of K_f' as calculated from C_r can be conveniently normalized to organic carbon (OC) content ($K_{foc}' = 100K_f'/\%OC$) (Carmo et al., 2000; Chen et al., 1999).

Desorption hysteresis was calculated as the ratio of Freundlich exponents for desorption to sorption, i.e., N_d/N_s (subscripts d and s refer to desorption and sorption, respectively) (Barriuso et al., 1994; Yuan and Xing, 2001). The lower the hysteresis index, the higher the degree of hysteresis (i.e., more difficult to desorb).

3. Results and discussion

3.1. Sorbent properties

Sandy soil from the long-term tillage plots at the Clemson University was used in our experiment. The OC contents were 1.54% (0–5 cm) and 0.35% (10–15 cm) in the soil of CnT plots. For CT treatments, OC contents were 0.85% (0–5 cm) and 0.54% (10–15 cm), respectively. The top soil (0–5 cm) of CnT contained significantly higher soil organic carbon (SOC) than that of CT treatment. As reported by Novak et al. (1996), the lack of physically mixing of plant residue resulted in a build up of SOC in the top few cm of CnT in the Norfolk soil. Thus, 20 years of CnT management has resulted in an increase in the SOC content in the top 0–5 cm layer of the unfractionated Norfolk soil. This result was consistent with the reports by Bruce et al. (1990) and Unger (1991) that CnT management can increase both the carbon content of the soil surface horizon and crop yield. Increased SOC, coupled with increased surface residues, can improve soil productivity by increasing the capture and infiltration of water and reducing erosion (Langdale et al., 1992).

The HA from the top soil (0–5 cm) of CnT treatment contained higher aliphatic-C (0–108 ppm) and lower aromatic-C (108–162 ppm) than that of CT plots (Table 1). The humin fractions showed the same trend as for HA. This observation is consistent with the enhanced decomposition of plant residue in the CT plot. Previously, we also examined O/R ratios (reactive oxygen-containing to recalcitrant functional groups), based on the peak heights generated from DRIFT spectra (diffuse reflectance infrared Fourier transform). The high O/R ratio of HA was observed in the top soil (0–5 cm) of CnT, indicating that SOM was more biologically active (Ding et al., 2002). Compared with humin, HA was derived mainly from more recent vegetation input. Humin is usually regarded as the alkali-insoluble fraction of SOM which is associated with or encapsulated by minerals (Baldock and Skjemstad, 2000). Thus, humin exhibits a more recalcitrant structure than HA.

3.2. Metolachlor sorption

Sorption of metolachlor by soil, HA, and humin from CnT and CT treatments is shown in Figs. 1 and 2, respectively. The detailed metolachlor sorption parameters are listed in Table 2. Sorption of metolachlor by soil, HA, and humin was well described by the Freundlich model (Figs. 1 and 2, Table 2). Sorption of metolachlor was nonlinear ($N < 1$) for all soil samples and their SOM fractions in this investigation.

Sorption of metolachlor was much higher in the soils with high amounts of OC than in the soils containing low OC contents (Tables 1 and 2). These results are in
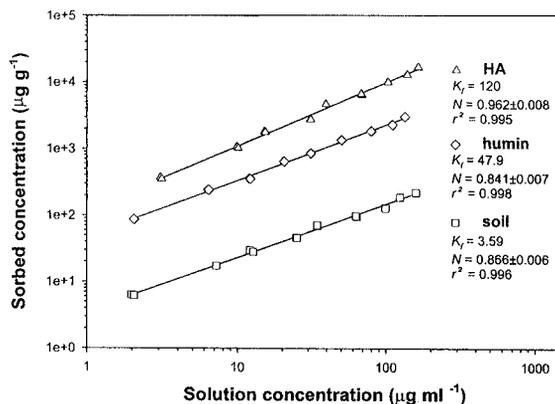

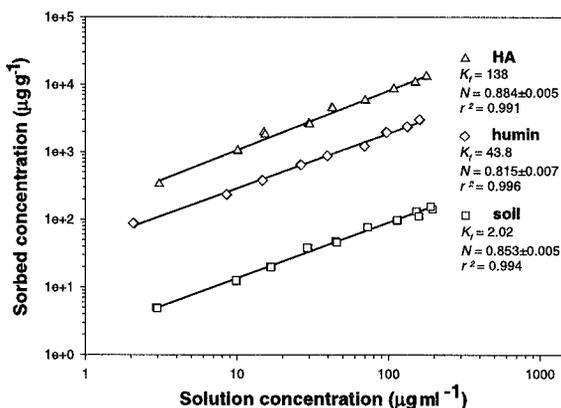Fig. 1. Sorption of metolachlor in soil, HA, and humin (CnT, 0–5 cm).

Fig. 2. Sorption of metolachlor in soil, HA, and humin (CT, 0–5 cm).

agreement with the report by Novak et al. (1996). After characterizing the impact of two different tillage systems (CnT vs CT) on sorption of atrazine and fluometuron by the Norfolk loamy sand soil, they demonstrated that tillage and soil depth affected SOC contents in the tillage systems. Thus, atrazine and fluometuron sorption was significantly different with tillage system and soil depth. In our study, correlation analyses between OC and modified sorption coefficient (K'_f) showed that sorption of metolachlor was highly related ($r = 0.93$, $P = 0.05$) to the amount of organic materials in the soil, HA, or humin fractions. Previous investigators also indicated that metolachlor sorption by soils was related to OC and clay contents of soils (Kozak et al., 1983; Peter and Weber, 1985). Similarly, Carmo et al. (2000) reported that sorption of naphthalene and phenanthrene was a function of OC for heterogeneous soil materials.

Table 2
Sorption parameters of metolachlor in soils and their SOM fractions

Sample	N	$\log K_f$ ($\mu g\,g^{-1}$) ($\mu g\,ml^{-1}$)$^{-N}$	K_f' ($\mu g\,g^{-1}$)	K_{foc}' (μg (g of OC)$^{-1}$)
Soil				
CnT1[a]	0.866 ± 0.006	0.55 ± 0.004	5.78×10^2	3.75×10^4
CnT2[b]	0.811 ± 0.007	0.10 ± 0.003	1.99×10^2	5.69×10^4
CT1	0.853 ± 0.005	0.31 ± 0.005	3.56×10^2	4.19×10^4
CT2	0.835 ± 0.005	0.14 ± 0.004	2.89×10^2	5.35×10^4
HA				
CnT1	0.962 ± 0.008	2.08 ± 0.008	4.99×10^4	9.74×10^4
CT1	0.884 ± 0.005	2.14 ± 0.009	3.54×10^4	6.65×10^4
Humin				
CnT1	0.841 ± 0.007	1.68 ± 0.008	9.44×10^3	1.31×10^5
CT1	0.815 ± 0.007	1.64 ± 0.008	7.31×10^3	9.35×10^4

[a] 1 referring to 0–5 cm depth.
[b] 2 referring to 10–15 cm depth.

Again, when we compared K_{foc}' values (K_f' normalized to the OC content), for the same treatment (Table 2), K_{foc}' was larger in humin than that of HA. Differences between K_{foc}' values may suggest that organic matter in humin had a greater impact on sorption of metolachlor than in HA. One possible interpretation is that the characteristics of the organic matter (e.g., aromaticity) varied (Table 1) among the organic fractions and could lead to differences in sorption capacity. However, K_{foc}' values of both HA and humin were larger than soil, which was probably caused by the structural conformation changes during the extraction and/or de-ashing processes. After the removal of non-mineral bound organic matter fractions (i.e., fulvic acid and HA), humin might have exposed more sorption sites. Similarly, by changing the chemical and physical conformation, HA might take more "expanded and open" structures that are accessible to metolachlor molecules. By investigating 1-naphthol sorption with different organic matter fractions of several soil samples, Salloum et al. (2001) reported that organic matter physical conformation and accessibility are important in contaminant sorption. Similarly, they observed an increase in sorption after removal of HAs and fulvic acids.

The metolachlor sorption isotherms (Figs. 1 and 2) were characterized by different N values (Table 2). For the same treatment, N values followed the order: HA > soil > humin. As an example, the order of N values for top layer (0–5 cm) of CT plots was: HA (0.884) > soil (0.853) > humin (0.815). This order is expected from the dual-mode sorption model (Xing and Pignatello, 1997; Xing, 2001b), following the order in the degree of glassy or condensed nature of the organic matter. The more condensed (glassy) the organic matter, the more nonlinear the sorption isotherm (lower N value). Higher N values for metolachlor sorption in HA (i.e., smaller deviation from linearity) may indicate

that the degree of HA heterogeneity in terms of sorption sites was low as compared with humin fractions. The smaller the N values, the more heterogeneous (McGinley et al., 1993; Yuan and Xing, 1999). More specifically, after $Na_4P_2O_7$ extractions, the loosely bound fractions (HA and fulvic acids) were removed and the more tightly bound, condensed fractions (humins) were left behind. Therefore, more competition and decreased isotherm linearity were observed in humin fractions. Xing and Pignatello (1997) examined sorption of low-polarity compounds in glassy poly(vinylchloride) and SOM and reported that the N values for 1,2-dichlorobenzene and 1,3-dichlorobenzene declined in the following order: peat-HA > peat > peat-humin, consistent with our current results. Our results with naphthalene sorption by a mineral soil and its humic fractions had the same trend (unpublished).

3.3. Metolachlor desorption

Results of metolachlor desorption by soil, HA and humin are shown in Figs. 3–5, respectively. All the data fitted well with the Freundlich model. Hysteresis was observed for all isotherms.

Desorption is commonly observed to be biphasic, involving a relatively fast initial release of sorbed solute followed by a prolonged and increasingly slower release as desorption proceeds. This trend implies that some fractions of solute may be irreversibly bound to soil components (Weber et al., 1998). Hysteresis is conceptually considered as the result of binding in two source areas: site-specific binding and physical entrapment. The amount desorbed may represent the sum of readily desorbable or weakly retained metolachlor fractions. Differences in hysteresis were observed between the initial concentrations and between different sorbents. For example, at the lower initial concentrations, desorption
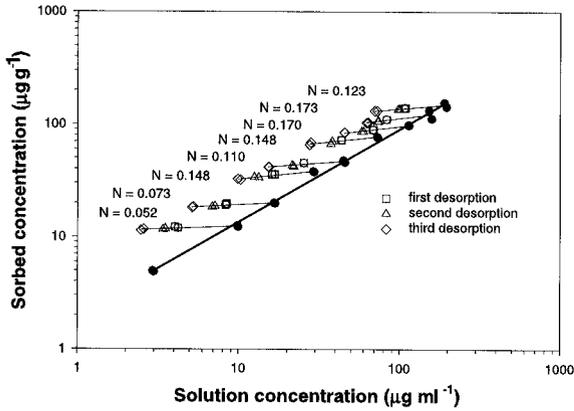
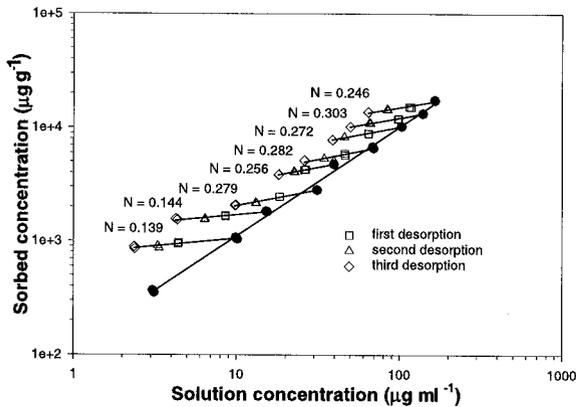Fig. 3. Sorption–desorption of metolachlor in soil (CT, 0–5 cm).

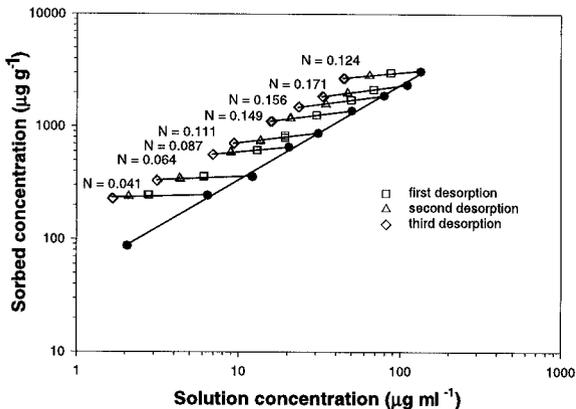Fig. 4. Sorption–desorption of metolachlor in HA (CnT, 0–5 cm).

Fig. 5. Sorption–desorption of metolachlor in humin (CnT, 0–5 cm).

isotherm N values were smaller than the higher concentrations for all three different sorbents of both tillage systems (soil, HA, and humin) (Figs. 3–5, respectively). This is as expected, because there were only a limited

number of high energy sites in SOM matrix that would be filled first and the proportion of metolachlor molecules in these sites was higher at lower concentrations. On the other hand, at high concentrations, the limited high-energy sites (resistant fraction) were saturated and the proportion of resistant fractions would be lower at high concentrations than that at lower concentrations, thus, overall desorption was easier. However, at the highest concentration, the N values of metolachlor desorption isotherm for all our experiments tended to decrease. This may be due to the creation of more holes or sorption sites upon the removal of metolachlor molecules. Xia and Pignatello (2001) reported as the concentration increases, the sorbate causes dilation (swelling) of the sorbent, then, converting the glassy to the rubbery phase. With subsequent desorption due to the removal of sorbate molecules, these new holes can trap more sorbate molecules, which are resistant to desorption. Consequently, at the highest concentration, desorption isotherms for all three sorbents became more nonlinear as compared to that from the adjacent, few lower concentration points (Figs. 3–5). We surmised that the first eight initial concentrations might not be high enough to alter SOM matrix and create new sorption sites.

Comparisons of the hysteresis index between soil, HA, and humin from CnT and CT treatment are shown in Figs. 6 and 7, respectively. The hysteresis index followed the order of HA > soil > humin (again, the lower the index, the higher the hysteresis, the more resistant to desorption), which is the same order of N values for these three sorbents (see above). Yuan and Xing (2001) reported the similar results between hysteresis index and N values for several cation-treated HAs. This means that when HA is compared to humin, humin has a relatively more rigid structure (rich in glassy or condensed phase). Our explanation for this behavior is that a larger proportion of irreversible (energetic) sites existed in humin due to its rigid SOM structure and conformation.
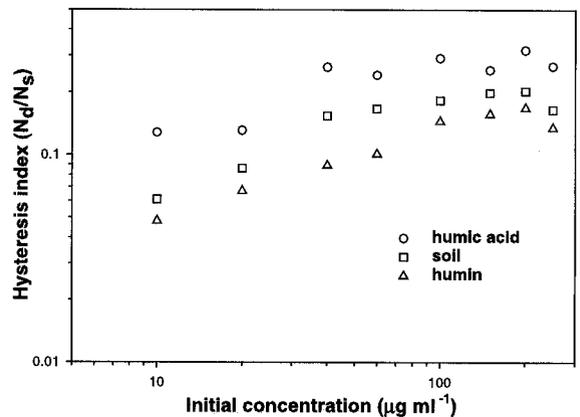

Fig. 6. Comparison of hysteresis index of soil, HA, and humin fractions (CT, 0–5 cm).
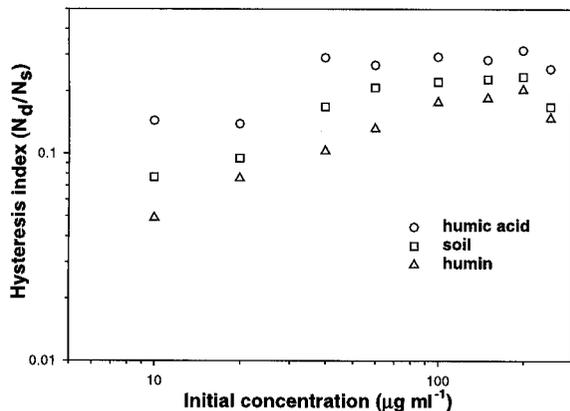
Fig. 7. Comparison of hysteresis index of soil, HA, and humin fractions (CnT, 0–5 cm).

Based on a solid-state ^{19}F-NMR study on hexafluorobenzene (HFB) sorption by sediments, Cornelissen et al. (2000) observed HFB in sediment at rapidly desorbing sites with a resonance at −125.5 ppm, whereas HFB at slowly desorbing sites with a resonance at −165.6 ppm. They inferred that the difference in desorption kinetics was related to differences between the proportion of HFB sorbed at high or low energy sorption sites. Readily desorbing solute had more linear sorption, whereas the slowly desorbing solute fractions (i.e., resistant) showed more nonlinear sorption. Their conclusion is in line with the results from this study; more nonlinear sorption (low N) is associated with low hysteresis index (more difficult to desorb) and the opposite is also true.

The hysteresis index of both whole soil and extracted fractions was higher under CnT than CT treatments. For example, at the initial concentrations of 10, 60, and 150 $\mu g\,ml^{-1}$, the hysteresis index for HA in CnT plots was 0.144, 0.266, and 0.283, respectively, while for CT, it was 0.128, 0.242, and 0.256, respectively. This means that sorbed metolachlor molecules in the humic fractions of CT treatment are more difficult to desorb than in those of CnT treatment. The difference of hysteresis index between CnT and CT treatments may be related to SOM structure, which is discussed below.

After investigation of sorption/desorption of naphthalene, phenanthrene, and α-naphthol by cation-saturated HA, Yuan and Xing (2001) showed that there was a positive correlation ($r^2 > 0.90$) between hysteresis index and N values of sorption isotherms. This correlation was anticipated because the same sources may have caused both sorption nonlinearity and hysteresis. In another study, Xing (2001a) reported that the N values of naphthalene and phenanthrene sorption decreased proportionally with increasing aromaticity of HA. Thus, low hysteresis index in CT treatments (as compared to

CnT) may be caused by the relatively high aromatic carbon contents (Table 1).

From the above discussion, it is concluded that the most likely cause of metolachlor hysteresis is due to irreversible or slowly reversible sorption, which is consistent with the results reported by Zhu and Selim (2000). Metolachlor sorbed at the lowest energy sites went into solution when desorption commenced. Then, the desorption became increasingly more difficult with an increase in the number of desorption steps as a result of the high resistance of the molecules sorbed in energetic sites.

4. Conclusions

Nonlinear sorption isotherms for metolachlor were observed in all whole soil samples and their organic fractions (HA and humin for CnT and CT treatments). The N value of HA and humin from CnT1 was higher than that of CT1, which may be caused by a higher degree of aromatic character in the SOM fractions of the CT1 treatment. The order of sorption capacity (K'_{foc}) was humin > HA > soil. The hysteresis index of both HA and humin in the CnT plots was higher than that of CT treatment. The metolachlor molecules sorbed in humic fractions in CT would be more difficult to release than in CnT system. For the same treatment, the hysteresis followed the HA < soil < humin order, indicating metolachlor sorption and desorption are dependent on the characteristics of different fractions. Long-term tillage management can change the composition and structure of SOM fractions, thus, influencing metolachlor sorption. Overall, CnT increases SOM content and metolachlor sorption in surface soil although sorbed metolachlor in CT soils may be more difficult to desorb as indicated by the lower hysteresis index.

References

Baldock, J.A., Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Organic Geochem. 31, 697–710.

Barriuso, E., Laird, D.A., Koskinen, W.C., Dowdy, R.H., 1994. Atrazine desorption from smectites. Soil Sci. Soc. Am. J. 58, 1632–1638.

Bruce, R.R., Langdale, G.W., Dillard, A.L., 1990. Tillage and crop rotation effect on characteristics of a sandy surface soil. Soil Sci. Soc. Am. J. 54, 1744–1747.

Carmo, A.M., Hundal, L.S., Thompson, M.L., 2000. Sorption of hydrophobic organic compounds by soil minerals: application of unit equivalent Freundlich coefficients. Environ. Sci. Technol. 34, 4363–4369.

Chefetz, B., Deshmukh, A.P., Hatcher, P.G., 2000. Pyrine sorption by natural organic matter. Environ. Sci. Technol. 34, 2925–2930.

Chen, Z., Xing, B., McGill, W.B., 1999. A united sorption variable for environmental applications of the Freundlich equation. J. Environ. Qual. 28, 1422–1428.

Cornelissen, G., van Noort, P.C.M., Nachtegaal, G., Kentgens, P.M., 2000. A solid-state Fluorine-NMR study on hexafluorobenzene sorbed by sediments, polymers, and active carbon. Environ. Sci. Technol. 34, 645–649.

Ding, G., Mao, J.D., Xing, B., 2001. Characteristics of amino acids in humic substances. Commun. Soil Sci. Plant Anal. 32, 1991–2005.

Ding, G., Novak, J.M., Amarasiriwardena, D., Hunt, P.G., Xing, B., 2002. Soil organic matter characteristics as affected by tillage management. Soil Sci. Soc. Am. J. 66, 421–429.

Hatcher, P.G., Schnitzer, M., Dennis, L.W., Maciel, G.E., 1981. Aromaticity of humic substances in soils. Soil Sci. Soc. Am. J. 45, 1089–1094.

Hundal, L.S., Thompson, M.L., Laird, D.A., Carmo, M., 2001. Sorption of phenanthrene by reference smectites. Environ. Sci. Technol. 35, 3456–3461.

Johnson, R.M., Sims, J.T., 1993. Influence of surface and subsoil properties on herbicide sorption by Atlantic coastal plain soils. Soil Sci. 155, 339–348.

Kellog, R.L., 1993. Protecting groundwater from contamination by pesticides. Renew. Res. J. 11, 8–13.

Kozak, J., Weber, J.B., Sheets, T.J., 1983. Adsorption of prometryn and metolachlor by selected soil organic fractions. Soil Sci. 136, 94–100.

Langdale, G.W., Mills, W.C., Thomas, A.W., 1992. Use of conservation tillage to retard errosive effects of large storms. J. Soil Water Conserv. 47, 257–260.

Maas, R.P., Patch, D.J., Peek, B.T., van Engelen, D.L., 1995. Pesticide in eastern North Carolina rural supply wells: land use factors and persistence. J. Environ. Qual. 24, 426–431.

Mao, J.D., Hu, W.G., Schmidt-Rohr, K., Davis, G., Ghabbour, E.A., Xing, X., 2000. Quantitative characterization of humic substances by solid-state carbon-13 nuclear magnetic resonance. Soil Sci. Soc. Am. J. 64, 873–884.

McGinley, P.M., Katz, L.E., Weber, W.J., 1993. A distributed reactivity model for sorption by soils and sediments. 2. Multicomponent systems and competitive effects. Environ. Sci. Technol. 27, 1524–1531.

Novak, J.M., Watts, D.W., Hunt, P.G., 1996. Long-term tillage effects on atrazine and fluometuron sorption in Coastal Plain soils. Agri. Ecosyst. Environ. 60, 165–173.

Peter, C.J., Weber, J.B., 1985. Adsorption mobility and efficacy of alachlor and metolachlor as influenced by soil properties. Weed Sci. 33, 874–881.

Preston, C.M., Newman, R.H., 1995. A long term effect of N fertilizer on the C-13 CPMAS NMR of de-ashed soil humin in a second-growth Douglas-fir stand of Coastal British Columbia. Geoderma 68, 229–241.

Ritter, W.F., 1990. Pesticide contamination of groundwater—a review. J. Environ. Sci. Health. B 25, 1–29.

Salloum, M.J., Dudas, M.J., McGill, W.B., 2001. Variation of 1-naphthol sorption with organic matter fractionation: the role of physical conformation. Organic Geochem. 32, 709–719.

Seybold, C.A., Mersie, W., 1996. Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine, hydroxyatrazine, and metolachlor in two soils from Virginia. J. Environ. Qual. 25, 1179–1185.

Swift, R., 1996. In: Sparks, D. (Ed.), Methods of Soil Analysis. Part 3 Chemical Method-SSSA Book Series no. 5. Soil Science Society of America, Madison, WI, pp. 1011–1069.

Unger, P.W., 1991. Organic matter, nutrient, and pH distribution in ni- and conventional-tillage semiarid soils. Agron. J. 83, 186–189.

Weber, W.J., Huang, W., Yu, H., 1998. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. 2. Effects of soil organic matter heterogeneity. J. Contam. Hydrol. 31, 149–165.

Xia, G.S., Pignatello, J.J., 2001. Detailed sorption isotherms of polar and apolar compounds in a high-organic soil. Environ. Sci. Technol. 35, 84–94.

Xing, B., 2001a. Sorption of naphthalene and phenanthrene by soil humic acids. Environ. Pollut. 111, 303–309.

Xing, B., 2001b. Sorption of anthropogenic organic compounds by soil organic matter: a mechanistic consideration. Can. J. Soil Sci. 81, 317–323.

Xing, B., Pignatello, J.J., 1997. Dual-mode sorption of low polarity compounds in glassy polyvinylchloride and soil organic matter. Environ. Sci. Technol. 31, 792–799.

Xing, B., Mao, J.D., Hu, W.G., Schmidt-Rohr, K., Davis, G., Ghabour, E.A., 1999. Evaluation of different solid-state C-13 NMR techniques for characterizing humic acids. In: Davis, G., Ghabour, E.A. (Eds.), Understanding Humic Substances: Advanced Methods, Properties and Applications. Royal Society of Chemistry, Cambridge, UK, p. 49.

Yuan, G., Xing, B., 1999. Site-energy distribution analysis of organic chemical sorption by soil organic matter. Soil Sci. 164, 503–509.

Yuan, G., Xing, B., 2001. Effects of metal cations on sorption and desorption of organic compounds in humic acids. Soil Sci. 166, 107–115.

Zhu, H., Selim, H.M., 2000. Hysteresis behavior of metolachlor adsorption–desorption in soils. Soil Sci. 165, 632–645.