

## Sorption–Desorption of Alachlor and Linuron in a Semiarid Soil As Influenced by Organic Matter Properties after 16 Years of Periodic Inputs

JOSÉ DORADO,\* CRISTINA LÓPEZ-FANDO, MARÍA-CRISTINA ZANCADA, AND GONZALO ALMENDROS

Centro de Ciencias Medioambientales, CSIC, Serrano 115B, 28006 Madrid, Spain

The effect of management practices on soil potential for regulating the residual concentration of pesticides was examined in samples from a Calcic Haploxeralf in Toledo (central Spain). Sorption–desorption of alachlor and linuron was found to depend on inputs of lignocelulosic wastes or cattle manure for the past 16 years. For a given herbicide, the soil sorption capacity ( $K_f$ ) follows the order control < crop residues < manure, which is consistent with the organic C content in the soil samples. Some structural characteristics of the soil humic acid as revealed by visible and infrared spectroscopies and analytical pyrolysis were useful to forecast the sorption–desorption intensity. Simple and multiple linear correlation analyses illustrate enhanced sorption of alachlor and linuron in soil plots where slightly altered soil organic matter accumulated (positive correlations with the intensity of infrared lignin signature band and with the methoxyphenol yields after pyrolysis of the humic acids and negative correlation with the aromaticity as pointed out by the optical density at 465 nm). Linuron showed a preference for soils with humic acids of low molecular weight and low degree of internal cross-linking, as inferred from the positive correlation with the ratio between optical densities at 465 and 665 nm. Under the conditions of the present experiment, agricultural practices including organic amendments seem to have a beneficial effect in the control of leaching and sorption of pesticides.

**KEYWORDS:** Herbicides; organic matter; humic acid; regression models

### INTRODUCTION

Soil management practices involving periodic organic inputs often lead to changes in soil quality through progressive modification of the composition of the soil organic matter (1). These changes are expected to have a significant bearing on important physicochemical properties of the soil, mainly cation exchange capacity and sorptive interactions with agrochemicals. Soil quality is a vague term that could be defined by diverse properties, including those regulating the composition of the soil solution, which are straightforwardly related to the bioavailability of pollutants (2, 3).

Several studies dealing with soil quality have focused on the quantitation of organic matter in soil. Comparatively less attention has been paid to changes in the quality of the organic C forms and their possible functional relationships with the environmental role of the organic matter (4).

Herbicide leaching toward the groundwater is controlled to a large extent by the processes of sorption. Alachlor (a chloroacetanilide) and linuron (a phenylurea) are herbicides extensively used throughout the world for preemergence control of annual grasses and broadleaf weeds. The sorption of alachlor

and linuron on soil has been the subject of previous studies (5–11). However, a precise knowledge for the major mechanisms involved in their sorption process is not currently available. Despite the above literature indicating that the sorption of these herbicides is positively related with the amount of soil organic C, other compositional features of the sorbate require further systematic investigations.

One of the most important problems in agricultural areas of central Spain is the low level of organic matter in soils. In this context, practices including organic amendments such as manure or lignocelulosic wastes are often considered within the framework of an environmentally friendly, sustainable management to improve the soil physicochemical properties. However, the changes in the chemistry of the soil solution due to these external organic inputs are still poorly understood (12–16).

Assuming that information on the behavior of pesticides in soil is needed to forecast their potential leaching and contamination of the groundwater, a study of the effect of periodic organic inputs on the sorption and desorption of alachlor and linuron has been performed.

### MATERIALS AND METHODS

**Chemicals and Soils.** Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N'*-(methoxymethyl)acetamide] and linuron [*N*-(3,4-dichlorophenyl)-*N'*-

\* Corresponding author (telephone +34-91-7452500; fax +34-91-5640800; e-mail [jose.dorado@ccma.csic.es](mailto:jose.dorado@ccma.csic.es)).

methoxy-*N*'-methylurea], both of analytical grade, were obtained from Chem Service (West Chester, PA).

A Calcic Haploxeralf (17) from Toledo (central Spain), with a sandy loam texture, was used in this study. Soil samples were taken from plots included in the International Organic Nitrogen Long-Term Experiment (IOSDV) coordinated by the Justus Liebig University in Giessen, Germany, in which 22 European centers are involved. The experiment was set up as a split-plot design with three spatial replications of each treatment, organic amendments as main plots and N mineral fertilizations as subplots. The organic treatments consisted of (i) control plots without organic inputs, (ii) plots receiving 3000 kg ha<sup>-1</sup> of barley straw every year and ~2500 kg ha<sup>-1</sup> of rape crop top-dressing on soil as green manure amendment every 3 years, and (iii) plots treated with 30000 kg ha<sup>-1</sup> of 2-year-old cattle manure every 3 years. The mineral nitrogen application levels were (i) no mineral N input and (ii) mineral fertilization with 100 kg ha<sup>-1</sup> of 33.5% NH<sub>4</sub>-NO<sub>3</sub>. An additional dose of 30 kg ha<sup>-1</sup> of 33.5% NH<sub>4</sub>NO<sub>3</sub> was added to prevent microbial N immobilization when barley straw was used as amendment.

Soil samples were collected with a spade from the surface (0–20 cm), air-dried, homogenized, and passed through a 2 mm sieve. Soil particle size distribution was analyzed by using the densimeter method with no previous hydrogen peroxide treatment (18). Soil pH was determined in water (1:2.5 w/w). Oxidizable C was measured according to the modified Walkley–Black method based on wet oxidation with sulfochromic mixture and further titration of the digest with Mohr's salt (19). Total N was analyzed via micro-Kjeldahl digestion and available P according to the procedure of Bray and Kurtz (20). Available K, Ca, and Mg were extracted with 1 M NH<sub>4</sub>OAc (pH 7).

**Organic Matter Fractionation.** Quantitative analysis of organic matter fractions was based on standard procedures (21). A previous physical separation of the light soil fraction (free organic matter) was carried out by flotation in 2 M H<sub>3</sub>PO<sub>4</sub>. The soil residue was shaken with 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> for 1 h and centrifuged at 2600g for 10 min, and the extraction was repeated two times. The soil residue after centrifugation was subjected to four successive extractions with 0.1 M NaOH. Aliquots of the total humic extract obtained by aggregating the alkaline supernatant solutions after centrifugation were taken to determine their concentration in C or to precipitate the humic acid (HA) fraction after acidification with H<sub>2</sub>SO<sub>4</sub> (1:1 v/v) to pH 1 and centrifugation at 2600g. The acid-soluble fraction (fulvic acid, FA) was calculated by difference with the C content in the total extract. Finally, the nonextractable organic matter (humins) was calculated by difference between the total organic C and the above-mentioned organic fractions.

The remaining humic extract after quantitation was acidified with HCl to pH 1 for the preparative precipitation of the HAs. The acidified extract was siphoned to remove the yellowish supernatant solution, and the precipitated HA was separated from the remaining supernatant solution by centrifugation at 3020g for 10 min and then redissolved in 0.5 M NaOH. The solution with sodium humate was centrifuged at 43500g for 10 min, and the insoluble sediment with clay impurities was discarded, whereas the new, alkaline supernatant solution was reprecipitated with HCl and dialyzed in distilled water until salt-free (no reaction with AgNO<sub>3</sub>). The resulting HA suspension was dried at 40 °C and kept for chemical analyses.

Visible spectra of HAs were obtained from solutions of 200 mg of C L<sup>-1</sup> of HAs in 0.02 M NaHCO<sub>3</sub> (22) by using a Shimadzu UV-240 spectrophotometer. The optical densities at 465 nm (*E*<sub>465</sub>) and 665 nm (*E*<sub>665</sub>) were recorded, and the resulting *E*<sub>465</sub>/*E*<sub>665</sub> ratio was considered to be inversely related to the molecular weight of HA (23). The infrared (IR) spectra in the 4000–600 cm<sup>-1</sup> range were acquired from KBr pellets (2.0 mg of HA in 200 mg of KBr) with a Bruker IFS28 Fourier transform infrared spectrophotometer. A digital method based on the subtraction of the original spectrum from a multiple of its second derivative (24) was used for resolution enhancement.

The HAs were also examined by analytical pyrolysis in a Horizon Instruments unit attached to a Varian Saturn 2000 gas chromatograph (GC)–mass spectrometer system. The HA samples were heated on ferromagnetic wires at a Curie temperature of 510 °C for 5 s. The pyrolytic interface was set to 250 °C, and the GC oven was programmed from 50 to 100 °C at 32 °C min<sup>-1</sup> and then up to 320 °C at a rate of

6 °C min<sup>-1</sup>. The injection port was cooled by a liquid CO<sub>2</sub> cryogenic unit, which was programmed between –30 °C (1 min) to 300 °C at 20 °C min<sup>-1</sup>. A fused-silica capillary column coated with CPSil (25 m × 0.32 mm × 0.4 μm) was employed. Compounds corresponding to the chromatographic peaks were identified by their electron impact mass spectra (70 eV). Ion traces for the main series of homologues and isomer compounds were reconstructed to check for the occurrence of specific pyrolysis products in the chromatogram.

The main analytical characteristics of soil and soil HAs are shown in Table 1.

**Sorption–Desorption Experiments.** Air-dried soil samples (5 g) were treated in triplicate in 25 mL test tubes with 10 mL of herbicide solution containing 5, 10, 15, 20, 30, 40, or 50 mg L<sup>-1</sup> alachlor or linuron. The sorption was studied using a batch equilibrium method. The suspensions were equilibrated in a dark chamber at 20 °C after mechanical shaking for 12 h and left in contact for another 12 h, which represents conditions enough to achieve practically complete equilibrium between the phases under study (25). Preliminary experiments under slightly different conditions indicated no significant changes in repeated measurements after 12 and 24 h, suggesting no important effect of photodegradation or of chemical or biological degradation. Following equilibration, the suspensions were centrifuged for 10 min at 48200g, and an aliquot (~3 mL) of the supernatant solution was filtered through a 0.2 μm syringe tip filter. The herbicide concentration was determined by derivative ultraviolet spectroscopy as a linear function of the intensity of one spectral maximum selected for each herbicide: 267 nm for alachlor and 253 nm for linuron (26). One of the advantages observed for the method used with regard to alternative, extraction-required GC methods is that accurate quantitation of most pesticides in the supernatant equilibrium solution is possible even when high molecular weight, nonvolatile adducts are formed between pesticide and dissolved organic matter from the soil. In the conditions of the experiment, the detection limit of the pesticides studied was ~0.5 mg L<sup>-1</sup>. To minimize the background effects in the different samples, a control water-soluble extract was prepared for each plot and used in the reference cell of the spectrophotometer for digital baseline subtraction before the spectrum of the supernatant solution of the soil–herbicide suspensions was obtained. In the derivative spectra most of the interfering background effects were removed, and accurate measurement of peak intensity (in the second derivative occurring as sharp valleys in a horizontal baseline) was possible in comparable conditions. No attempt was made to control the ionic strength through the use of additional electrolytes in the measurement solution due to preliminary experiments suggesting that highest repeatability under the above conditions where the release of interfering UV-colored extractives from the amended soils could lead to sample-dependent sensitivity for the solution pesticide.

The same samples after the sorption studies were also used for determining successive desorption of alachlor and linuron. After sorption equilibrium (24 h), the suspension was centrifuged for 10 min at 48200g, and then 6 mL of the supernatant solution was replaced by 6 mL of distilled water. The flasks were shaken for 4 h, which was considered to be long enough to reach the desorption equilibrium (27), and centrifuged again. This process was repeated four times. The herbicide concentration in the supernatant solution after each desorption step was determined as indicated above, by derivative ultraviolet spectroscopy, and the amount of alachlor and linuron still sorbed onto the soil after each desorption process was calculated by difference.

To compare the isotherms, all sorption data were described by Freundlich-type equations of the form

$$S = K_f C^n$$

where *S* is mg of herbicide sorbed per kg of soil, *C* is the herbicide concentration in solution after equilibrium (mg L<sup>-1</sup>), and *K<sub>f</sub>* and *n* are constants relative to the affinity of the sorbent for the sorbate [*K<sub>f</sub>* = amount of herbicide sorbed for an equilibrium concentration of 1 mg L<sup>-1</sup>, and *n* = degree to which sorption is a function of concentration (linearity of the isotherm)].

The partition coefficient *K<sub>d</sub>* (equilibrium ratio of the herbicide concentration associated with the soil to the herbicide concentration in the surrounding aqueous solution) was determined for the different soils

**Table 1.** Soil and Soil Humic Acid Characteristics in Experimental Plots from Calcic Haploxeralf Subjected to Different Management Practices

	soil plot						LSD <sup>c</sup>
	control		crop residues <sup>a</sup>		manure <sup>b</sup>		
	0 N input	100 kg of N input ha <sup>-1</sup>	0 N input	100 kg of N input ha <sup>-1</sup>	0 N input	100 kg of N input ha <sup>-1</sup>	
soil characteristics							
sand <sup>d</sup>	78.1	81.3	84.2	70.7	84.1	71.7	3.5
silt <sup>d</sup>	9.7	8.2	8.7	7.9	7.1	7.4	1.1
clay <sup>d</sup>	12.2	10.5	7.1	21.4	8.8	20.9	2.5
pH	6.9	5.7	7.1	7.5	5.5	5.9	0.9
organic C <sup>e</sup>	4.6	5.1	7.3	9.6	6.8	7.2	0.5
N <sup>e</sup>	0.6	0.5	1.1	1.1	0.5	0.7	0.2
P <sub>2</sub> O <sub>5</sub> <sup>f</sup>	195	100	530	623	110	170	131
K <sup>f</sup>	245	190	1250	790	310	340	67
Ca <sup>f</sup>	1785	940	1220	2900	650	2190	1179
Mg <sup>f</sup>	142	173	136	246	75	264	51
free organic matter <sup>g</sup>	9.3	14.7	10.7	6.2	18.5	8.0	6.3
humic acid <sup>g</sup>	14.4	17.4	25.5	24.5	18.9	16.7	1.5
fulvic acid <sup>g</sup>	39.6	36.6	30.2	30.2	37.4	40.5	6.8
nonextractable humin <sup>g</sup>	34.3	29.4	31.8	37.6	23.2	33.5	4.5
soil humic acid characteristics							
E <sub>465</sub> (optical density at 465 nm)	0.83	0.84	0.72	0.63	0.82	0.79	0.44
E <sub>465</sub> /E <sub>665</sub> optical density ratio	5.17	5.56	5.81	6.12	5.94	6.07	0.16
IR 1510 <sup>h</sup>	29.7	26.5	44.9	50.2	33.5	41.2	7.7
IR 1420 <sup>h</sup>	18.6	15.0	31.6	29.8	21.0	26.9	4.8
IR 1130 <sup>h</sup>	15.9	13.2	33.3	34.3	20.1	25.4	4.3
IR 1030 <sup>h</sup>	14.4	12.6	21.6	21.9	14.1	17.2	3.5
total alkanes <sup>i</sup>	5.2	5.5	3.4	7.2	4.8	4.6	3.7
total alkenes <sup>i</sup>	5.5	7.5	6.0	6.1	5.4	4.8	1.0
total alkylbenzenes <sup>i</sup>	2.6	7.6	2.7	5.2	3.5	6.2	1.7
total fatty acids <sup>i</sup>	22.9	4.4	39.8	11.8	26.3	13.2	34.4
total indenes <sup>i</sup>	0.6	0.6	0.2	0.2	0.6	0.1	0.1
total phenols <sup>i</sup>	7.5	6.3	14.8	30.7	18.2	30.9	7.2
total methoxyphenols <sup>i</sup>	5.6	4.7	12.7	26.7	15.8	26.5	6.0
total guaiacols (2-methoxyphenols) <sup>i</sup>	3.5	3.4	7.3	14.3	10.1	16.6	1.7
total syringols (2,6-methoxyphenols) <sup>i</sup>	2.2	1.5	6.2	12.7	6.0	10.3	4.0
syringols/guaiacols ratio <sup>i</sup>	0.7	0.4	0.8	0.9	0.6	0.6	0.2
syringols/total methoxyphenols ratio <sup>i</sup>	0.4	0.3	0.5	0.5	0.4	0.4	0.1
guaiacols/total methoxyphenols ratio <sup>i</sup>	0.6	0.7	0.6	0.6	0.6	0.5	0.1
methylsyringol + methylguaiacol <sup>i</sup>	0.8	0.6	1.8	7.5	2.1	4.2	2.6
propenylsyringol + propenylguaiacol <sup>i</sup>	0.7	0.4	1.7	1.9	1.2	1.5	0.3

<sup>a</sup> Amendment with barley straw (3000 kg ha<sup>-1</sup> per year) plus rape crop top-dressing (2500 kg ha<sup>-1</sup> every 3 years). <sup>b</sup> Amendment with 2-year-old cattle manure (30000 kg ha<sup>-1</sup> every 3 years). <sup>c</sup> Least significant difference ( $P = 0.05$ ). <sup>d</sup> Grams per 100 g. <sup>e</sup> Grams per kilogram of soil. <sup>f</sup> Milligrams per kilogram of soil. <sup>g</sup> Grams of C per 100 g of soil C. <sup>h</sup> Peak intensity (absorbance units) in the resolution-enhanced IR spectrum. <sup>i</sup> Major pyrolysis products (cumulative peak areas as percentage of the total ion chromatogram).

from the fit of the experimental sorption isotherms ( $K_f C^n = K_d C$ ) by calculating the average value from the different herbicide concentrations used in this study, whereas the organic C partition coefficient  $K_{OC}$  (equilibrium ratio of the amount of herbicide sorbed per unit mass of organic C in soil to the concentration of the herbicide in the solution) was assessed from the formula  $K_{OC} = (K_d/\% \text{ organic C}) \times 100$ .

**Statistical Procedures.** Simple and multiple linear regression models (in the latter case using backward automatic variable selection) were used to relate soil and soil humic acid properties to herbicide sorption.

## RESULTS AND DISCUSSION

**Sorption Experiments.** Sorption isotherms of alachlor and linuron in samples from control plots and soils treated with barley straw and rape crop residues or with 2-year-old cattle manure, both with and without mineral N fertilization, are shown in **Figures 1** and **2**, respectively. Isotherms of sorption for both herbicides are L-type, according to the classification of Giles (28), suggesting high affinity of these soil samples for alachlor and linuron at low herbicide concentrations. Independently of the mineral N fertilization, the initial part of the curve (below 10 mg L<sup>-1</sup>) shows an increasing slope from the control to the amended plots, which indicates a greater affinity for these herbicides as levels of soil organic C increase.

The Freundlich constants  $K_f$  and  $n$ , and the corresponding correlation coefficients ( $r^2$ ), for the nonlinear curves are given in **Tables 2** and **3**. In general, the isotherms fit the Freundlich sorption equation with  $r^2$  values  $> 0.98$  for both herbicides. In the case of alachlor (**Table 2**) the  $K_f$  values ranged between 0.77 for the control soil with mineral N fertilization and 2.94 for the soil amended with manure and mineral N fertilization, whereas for linuron (**Table 3**) the  $K_f$  ranged from 2.29 for the control soil with N fertilization to 4.02 for the soil amended with manure and mineral N. For both herbicides the increasing  $K_f$  values varied in the order control < crop residues < manure, paralleling the organic matter content of the soil samples.

The  $K_d$  values (**Tables 2** and **3**) follow the same trend as the  $K_f$  values (i.e., the higher the sorption capacity, the higher the organic C content: manure > crop residues > control). The values of  $K_{OC}$  are not significantly different ( $P > 0.05$ ) between soil treatments for either of the herbicides studied and varied on average from 164 L kg<sup>-1</sup> for alachlor to 254 L kg<sup>-1</sup> for linuron, suggesting a lower potential sorption for alachlor than for linuron in the soil samples studied. Due to the sorption performance not paralleling the total molecular surface of the sorbates (29), additional processes could be playing roles such as the hydrophobicity of specific sorbate molecular regions and/

**Table 2.** Freundlich Constants and Corresponding Coefficients for Alachlor Sorption and Desorption in Control and Amended Calcic Haploxeralf

soil plot	isotherm	$C_{\max}^a$ (mg L <sup>-1</sup> )	$K_f$ (mg kg <sup>-1</sup> )	$n$	$r^{2\ b}$	$K_d^c$ (L kg <sup>-1</sup> )	$K_{OC}^d$	$K^e$	$H^f$
No Mineral N Fertilization									
control	sorption		0.94	0.91	0.991	0.74	163		
	desorption	50	5.61	0.42	0.946			499	2.16
	desorption	40	4.92	0.42	0.924			423	2.17
	desorption	30	4.95	0.40	0.969			427	2.26
crop residues <sup>g</sup>	sorption		0.97	1.00	0.996	0.97	143		
	desorption	50	no <sup>i</sup>	no	no			no	no
	desorption	40	no	no	no			no	no
	desorption	30	no	no	no			no	no
manure <sup>h</sup>	sorption		2.34	0.80	0.986	1.35	185		
	desorption	50	no	no	no			no	no
	desorption	40	no	no	no			no	no
	desorption	30	no	no	no			no	no
Mineral Fertilization with 100 kg of NH <sub>4</sub> NO <sub>3</sub> ha <sup>-1</sup> (33.5% N)									
control	sorption		0.77	0.99	0.998	0.75	147		
	desorption	50	7.56	0.36	0.812			887	2.72
	desorption	40	8.09	0.30	0.854			956	3.30
	desorption	30	5.04	0.39	0.829			558	2.56
crop residues <sup>g</sup>	sorption		1.99	0.82	0.989	1.24	173		
	desorption	50	no	no	no			no	no
	desorption	40	no	no	no			no	no
	desorption	30	no	no	no			no	no
manure <sup>h</sup>	sorption		2.94	0.80	0.984	1.65	173		
	desorption	50	no	no	no			no	no
	desorption	40	no	no	no			no	no
	desorption	30	no	no	no			no	no

<sup>a</sup> Solution concentration before desorption is initiated. <sup>b</sup> Correlation coefficient. <sup>c</sup> Distribution coefficient ( $K_d = S/C$ ). <sup>d</sup> Organic carbon distribution coefficient [ $K_{OC} = (K_d/\% C) \times 100$ ]. <sup>e</sup> Percent change in the sorption–desorption  $K_f$  value =  $(K_{f,des} - K_{f,sor}/K_{f,sor}) \times 100$ . <sup>f</sup> Hysteresis coefficient ( $H = n_{sor}/n_{des}$ ); subscripts “sor” and “des” indicate sorption and desorption, respectively. <sup>g</sup> Amendment with barley straw (3000 kg ha<sup>-1</sup> per year) plus rape crop top-dressing (2500 kg ha<sup>-1</sup> every 3 years). <sup>h</sup> Amendment with 2-year-old cattle manure (30000 kg ha<sup>-1</sup> every 3 years). <sup>i</sup> “no” indicates that desorption was not observed (the detection limit was ~0.5 mg L<sup>-1</sup>).

or a partial contribution of the lower molecular weight of linuron in favoring diffusion processes within microporous organic matrices. On the other hand, when the sorption isotherms were compared with coefficients calculated in terms of the total organic C content in the soil samples (data not shown), no significant differences were observed depending on the soil management system. This suggested that the influence of the dose of organic matter prevailed on that from specific properties of the different types of organic matter added.

The significant ( $P < 0.05$ ) correlation coefficients between different properties of the soil or its isolated HAs and the Freundlich ( $K_f$ ) and distribution ( $K_d$ ) sorption coefficients of both herbicides are shown in **Table 4**. In general, the coefficients suggest that sorption increases with the organic matter content. The positive correlations of the sorption coefficients with the total C content and the intensity of the 1030 cm<sup>-1</sup> band in the IR spectra of HAs (mainly due to vibrations of residual carbohydrate structures and lignin methoxyl groups indicating that the concentration of these oxygen-containing functional groups at least behaves as a surrogate indicator of matricial sorptive potential), as well as the negative correlations with the  $E_{465}$  (aromaticity), suggest that most of the sorptive performance of the soil samples studied depends on the inputs of recent organic matter not yet transformed into humic substances.

In fact, in both herbicides  $K_f$  and  $K_d$  were significantly correlated with the total amount of HAs but also with soil HAs properties indicating a selectively preserved lignin domain in the HAs (**Table 4**). For example, diagnostic IR bands for lignin methoxyphenol units such as 1510, 1420, and 1130 cm<sup>-1</sup> (**Figure 3**) showed a positive correlation with  $K_f$  and  $K_d$  for alachlor and linuron. This agrees with the analytical pyrolysis of HAs, which also indicates that herbicide sorption depends

on the occurrence of young organic matter (positive correlation with the pyrolytic yield of methoxyphenols) rather than of matured soil organic matter (negative correlations with the yields of nontypical lignin fragments, i.e., indenes). In this sense, the relative yields of syringyl-type phenols behave also as indicators of the performance of the sorptive mechanisms. In fact, syringyl compounds prevail on guaiacyl compounds in the case of less condensed lignins, with comparatively low degrees of internal cross-linking, which could explain the positive correlations observed between sorption and the syringols/guaiacols and the syringols/total methoxyphenols ratios.

Assuming that the mechanisms involved in the sorption process may have great complexity, the factors implicated could be better understood after multiple regression models using backward automatic variable selection of those variables with significant contribution to the inertia of the total system. The standardized (mean = 0; standard deviation = 1) coefficients reveal the relative importance of the factors related with the sorption of both herbicides (**Table 5**). The multiple regression models confirm the affinity of alachlor for soil samples with a high proportion of organic matter (correlation of  $K_d$  with organic C), which coincides with previous research (9) suggesting a dominant role of the total amount of organic matter on the sorption of chloroacetanilide herbicides.

In fact, several authors have suggested that multifunctional hydrogen bonding involved in the sorption of alachlor on organic substrates (30) and charge transfer ( $\pi$ ) bonds between the benzene ring of the herbicide and the aromatic units of soil organic matter could be the most efficient mechanisms involved in alachlor sorption on HAs in soils (6, 9).

In our case, linuron sorption was significantly correlated with an index of the molecular size of soil humic substances (i.e.,



**Table 3.** Freundlich Constants and Corresponding Coefficients for Linuron Sorption and Desorption in Control and Amended Calcic Haploxeralf

soil plot	isotherm	$C_{max}^a$ (mg L <sup>-1</sup> )	$K_f$ (mg kg <sup>-1</sup> )	$n$	$r^2$ <sup>b</sup>	$K_d^c$ (L kg <sup>-1</sup> )	$K_{OC}^d$	$K^e$	$H^f$
No Mineral N Fertilization									
control	sorption		2.36	0.72	0.978	1.21	266		
	desorption	50	3.43	0.64	0.984			45.4	1.13
	desorption	40	3.38	0.59	0.974			43.4	1.22
	desorption	30	2.55	0.69	0.996			8.2	1.05
crop residues <sup>g</sup>	sorption		2.97	0.82	0.990	1.77	261		
	desorption	50	2.95	0.82	0.995			-0.6	1.00
	desorption	40	2.66	0.84	0.999			-10.5	0.98
	desorption	30	2.06	0.97	0.998			-30.7	0.85
manure <sup>h</sup>	sorption		3.81	0.79	0.982	2.03	278		
	desorption	50	2.64	0.90	0.998			-30.7	0.87
	desorption	40	1.80	1.04	0.998			-52.6	0.76
	desorption	30	1.96	1.04	0.998			-48.6	0.76
Mineral Fertilization with 100 kg of NH <sub>4</sub> NO <sub>3</sub> ha <sup>-1</sup> (33.5% N)									
control	sorption		2.29	0.78	0.982	1.36	267		
	desorption	50	3.42	0.68	0.984			49.3	1.15
	desorption	40	3.31	0.65	0.979			44.7	1.20
	desorption	30	2.61	0.74	0.996			13.9	1.05
crop residues <sup>g</sup>	sorption		3.62	0.75	0.999	1.75	245		
	desorption	50	2.95	0.85	0.998			-18.3	0.88
	desorption	40	2.50	0.87	0.997			-30.8	0.86
	desorption	30	2.26	0.92	0.999			-37.5	0.81
manure <sup>h</sup>	sorption		4.02	0.77	0.997	2.02	211		
	desorption	50	1.76	1.03	0.998			-56.1	0.75
	desorption	40	1.91	1.00	0.998			-52.4	0.77
	desorption	30	1.47	1.04	0.998			-63.4	0.74

<sup>a</sup> Solution concentration before desorption is initiated. <sup>b</sup> Correlation coefficient. <sup>c</sup> Distribution coefficient ( $K_d = S/C$ ). <sup>d</sup> Organic carbon distribution coefficient [ $K_{OC} = (K_d/\% C) \times 100$ ]. <sup>e</sup> Percent change in the sorption–desorption  $K_f$  value =  $(K_{f,des} - K_{f,sor}/K_{f,sor}) \times 100$ . <sup>f</sup> Hysteresis coefficient ( $H = n_{sor}/n_{des}$ ); subscripts “sor” and “des” indicate sorption and desorption, respectively. <sup>g</sup> Amendment with barley straw (3000 kg ha<sup>-1</sup> per year) plus rape crop top-dressing (2500 kg ha<sup>-1</sup> every 3 years). <sup>h</sup> Amendment with 2-year-old cattle manure (30000 kg ha<sup>-1</sup> every 3 years).

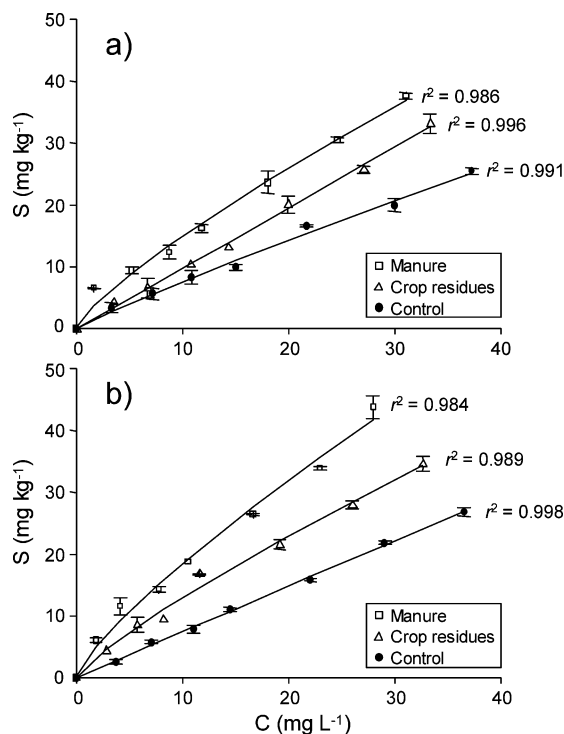
**Table 4.** Significant ( $P < 0.05$ ) Correlation Coefficients between Soil and Soil Humic Acid Parameters and the Freundlich ( $K_f$ ) and Distribution ( $K_d$ ) Coefficients of the Sorption of Alachlor and Linuron ( $P$  Value for the Fitted Model Is Given in Parentheses)

	alachlor		linuron	
	$K_f$	$K_d$	$K_f$	$K_d$
soil characteristics				
organic C	0.89 (0.016)	0.96 (0.002)	0.92 (0.009)	0.91 (0.012)
N	0.94 (0.006)	0.89 (0.017)	0.85 (0.033)	ns <sup>d</sup>
P <sub>2</sub> O <sub>5</sub>	0.89 (0.016)	0.85 (0.032)	ns	ns
humic acid <sup>a</sup>	0.83 (0.041)	0.85 (0.032)	0.82 (0.044)	0.90 (0.014)
soil humic acid characteristics				
$E_{465}$ (optical density at 465 nm)	-0.94 (0.005)	-0.94 (0.006)	-0.84 (0.034)	ns
$E_{465}/E_{665}$ optical density ratio	ns	ns	0.81 (0.050)	0.85 (0.032)
IR1510 <sup>b</sup>	0.98 (0.001)	0.99 (0.001)	0.98 (0.001)	0.89 (0.017)
IR1420 <sup>b</sup>	0.93 (0.007)	0.92 (0.009)	0.97 (0.001)	0.89 (0.017)
IR1130 <sup>b</sup>	0.96 (0.002)	0.97 (0.002)	0.97 (0.001)	0.92 (0.009)
IR1030 <sup>b</sup>	0.97 (0.002)	0.93 (0.007)	0.92 (0.010)	0.84 (0.038)
total indenenes <sup>c</sup>	-0.91 (0.012)	-0.87 (0.026)	ns	ns
total methoxyphenols <sup>c</sup>	ns	0.82 (0.046)	0.83 (0.040)	ns
total syringols <sup>c</sup>	0.86 (0.029)	0.91 (0.012)	0.90 (0.016)	0.81 (0.050)
syringols/guaiacols ratio <sup>c</sup>	0.87 (0.023)	0.84 (0.037)	0.81 (0.050)	ns
syringols/total methoxyphenols ratio <sup>c</sup>	0.81 (0.050)	ns	0.83 (0.041)	0.81 (0.050)
guaiacols/total methoxyphenols ratio <sup>c</sup>	-0.83 (0.039)	ns	-0.88 (0.020)	-0.86 (0.026)
methylsyringol + methylguaiacol <sup>c</sup>	0.83 (0.043)	0.87 (0.025)	ns	ns
propenylsyringol + propenylguaiacol <sup>c</sup>	0.91 (0.012)	0.95 (0.004)	0.98 (0.001)	0.93 (0.007)

<sup>a</sup> Grams of C per 100 g of soil C. <sup>b</sup> Peak intensity in the resolution-enhanced IR spectrum. <sup>c</sup> Major pyrolysis products (cumulative peak areas as percentage of the total ion chromatogram). <sup>d</sup> Nonsignificant ( $P > 0.05$ ).

the  $E_{465}/E_{665}$  ratio). This could be interpreted as a role of mechanisms where diffusion processes favored by the flexibility and low degree of internal cross-linking of the organic sorbate would favor the retention of low molecular weight compounds, as suggested above. Linuron also showed a significant correlation coefficient between the  $K_f$  and the 1420 cm<sup>-1</sup> band of the

IR spectra, which indicates residual lignin structures. This also agrees with the positive coefficient between the  $K_f$  and the relative yield of syringols obtained after analytical pyrolysis. Concerning the mechanisms that could be involved with the above structures, Rae et al. (7) proposed that linuron interactions could result from a dual-mode sorption in which partitioning



**Figure 1.** Sorption isotherms fitted to Freundlich model ofalachlor [ $S = \text{mg}$  ofalachlor sorbed per kg of soil,  $C = \text{alachlor}$  concentration in solution ( $\text{mg L}^{-1}$ ) after equilibrium] on samples of control plots and soils amended with different organic inputs under two agronomical management systems: (a) without mineral N fertilization; (b) with  $100 \text{ kg of NH}_4\text{NO}_3 \text{ ha}^{-1}$  (33.5% N). Error bars indicate the standard deviations on three replications.

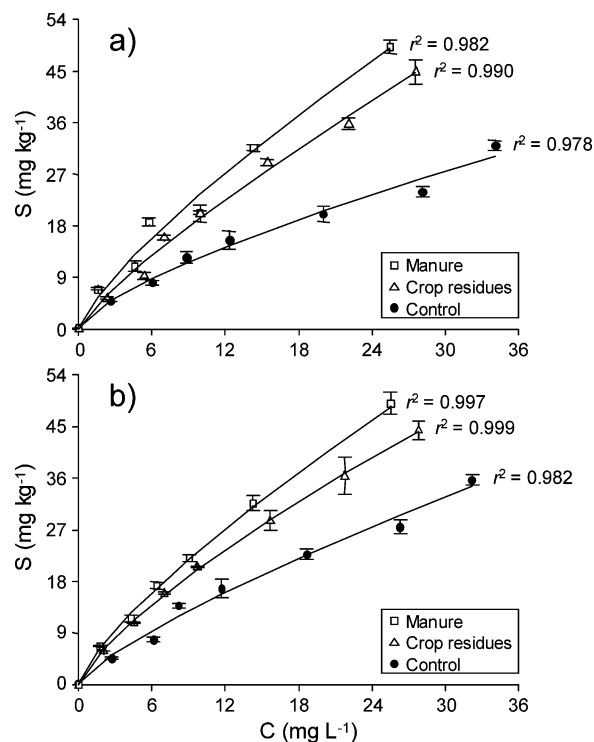
**Table 5.** Standardized Coefficients of Multiple Regression Functions<sup>a</sup> between Soil and Soil Humic Acid Parameters and the Freundlich ( $K_f$ ) and Distribution ( $K_d$ ) Coefficients of the Sorption of Alachlor and Linuron

independent variable	dependent variable			
	alachlor		linuron	
	$K_f$	$K_d$	$K_f$	$K_d$
soil characteristics				
organic C	ns <sup>e</sup>	0.121	ns	ns
humic acid <sup>b</sup>	ns	ns	ns	0.029
soil humic acid characteristics				
$E_{465}/E_{665}$ optical density ratio	ns	ns	0.177	0.130
IR1420 <sup>c</sup>	ns	ns	0.078	ns
IR1030 <sup>c</sup>	0.107	0.024	ns	ns
total indenes <sup>d</sup>	-1.143	-0.290	ns	ns
total syringols <sup>d</sup>	ns	ns	0.048	ns
methylsyringol + methylguaiaicol <sup>d</sup>	0.101	ns	ns	ns
propenylsyringol + propenylguaiaicol <sup>d</sup>	ns	ns	ns	0.305
$R^2$ statistic	99.863	99.988	99.970	99.892
$P$ value	<0.001	<0.001	<0.001	<0.001

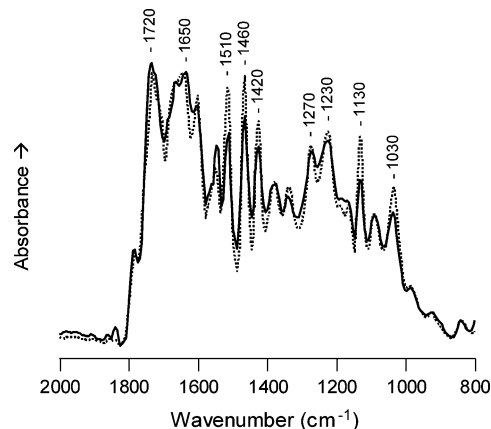
<sup>a</sup> Backward multiple regression, stepwise variable selection. <sup>b</sup> Referred to total soil organic C. <sup>c</sup> Peak intensity in the resolution-enhanced IR spectrum. <sup>d</sup> Major pyrolysis products (cumulative peak areas as percentage of the total ion chromatogram). <sup>e</sup> Nonsignificant ( $P > 0.05$ ).

(hydrophobic bonding and van der Waals attraction followed by repulsion of hydrophobic moieties) and site-directed (van der Waals) processes occur.

**Desorption Experiments.** The  $K_f$  and  $n$  values for desorption ofalachlor and linuron (Tables 2 and 3) were obtained by fitting



**Figure 2.** Sorption isotherms fitted to Freundlich model oflinuron [ $S = \text{mg}$  oflinuron sorbed per kg of soil,  $C = \text{linuron}$  concentration in solution ( $\text{mg L}^{-1}$ ) after equilibrium] on samples of control plots and soils amended with different organic inputs under two agronomical management systems: (a) without mineral N fertilization; (b) with  $100 \text{ kg of NH}_4\text{NO}_3 \text{ ha}^{-1}$  (33.5% N). Error bars indicate the standard deviations on three replications.



**Figure 3.** Resolution-enhanced infrared spectra ( $2000\text{--}800 \text{ cm}^{-1}$ ) of humic acids from untreated control plots (solid lines) and plots amended with cattle manure (dotted lines). The spectra shown correspond to plots that received no additional N fertilization.

the desorption data to the Freundlich-type equation. The  $n$  values for desorption isotherms ofalachlor in the control soil (Table 2) were lower than those for sorption isotherms, indicating an hysteretic desorption process (31). To a large extent, the values of the hysteresis coefficient ( $H = n_{\text{sor}}/n_{\text{des}}$ ) in the control soil were found to be independent of the maximum concentration ( $C_{\text{max}}$ ) before desorption is initiated and were similar (2.5 on average) to those reported for other chloroacetanilides in earlier sorption/desorption studies (32, 33). However, no desorption ofalachlor was observed in amended soils (Table 2). This suggests irreversible sorption due to binding ofalachlor to the organic materials added to the soils.

In the case of linuron, the  $n$  values obtained for the desorption isotherms were lower in the control soil but higher in the amended soils, irrespective of the mineral N fertilization. In addition, the irreversibility of the sorption process indicated by the  $K$  values (Table 3) was higher in the amended soils (mainly with cattle manure) than in the control soil, illustrating the significant effect of the management-induced changes in the organic matter on potential pesticide leachability (27, 31).

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