

# Effect of Organic Amendments on Herbicide Sorption as Related to the Nature of the Dissolved Organic Matter

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It has been assessed the influence of four organic amendments (OA) consisting of two commercial humic amendments (liquid LF and solid SF) from olive-mill wastes, a solid urban waste (SUW), and a sewage sludge (SS) on the sorption properties and leaching potential of simazine and 2,4-D. A sandy soil (TR) and a sandy-clay soil with a relatively high montmorillonite content (A) were treated with the diverse OA. Dissolved organic matter (DOM) was extracted from the amendments, the soils, and the amended soils and studied by fluorescence spectroscopy. A humification index (HIX) was calculated from the fluorescence data. Sorption was determined with the batch technique. Spectroscopical studies revealed that the DOM of the LF differs from the other OA by having a very low ability to absorb and to fluoresce and by its very low HIX values, which indicates that the LF contains large amounts of nonhumified material and consists of small molecules. On the other hand, the SF amendment contains the highest amounts of highly humified material and a large number of carboxylic groups. Amended soils sorbed simazine and 2,4-D to a greater extent than the untreated soils, except in the case of simazine sorption in the LF amended soil A, which had a lower simazine sorption than the original soil. The small molecules of DOM in the LF compete with simazine for montmorillonite sorption sites in soil A. This is not the case for 2,4-D, since this herbicide does not sorb on montmorillonite. In the case of the soil TR, with a lower montmorillonite content, there is no competition between simazine and the LF molecules for sorption sites. Soils amended with the highly humified SF were the best sorbents for simazine but not for 2,4-D, which can be attributed to repulsion between negatively charged 2,4-D molecules and COO<sup>-</sup> groups, which are more abundant in SF.

## Introduction

Soil applied herbicides reach surface and groundwater by losses associated with runoff and leaching processes (1). These losses are attenuated by the natural process of sorption by soil solids, mainly those constituting the soil colloidal

fraction (2). Soils of low organic carbon content have a low capacity for retarding pesticide mobility (3–5), since soil organic matter, especially humic substances, is the primary adsorbent for pesticides (6, 7). Consequently, organic amendments (OA), commonly used to enrich soils of low organic matter content and to increase structural stability (8), can be also used to modify surfaces of soils and subsurface materials to promote adsorption and reduce pesticide contamination of groundwater (3, 4, 9–14).

In addition to solid organic matter, the incorporation of OA to soils also introduces soluble organic matter (DOM). DOM has been shown to reduce sorption of pesticides due to DOM-pesticide interactions and/or competition between DOM molecules and pesticide molecules for sorption sites (15–17). This decrease in sorption would enhance transport and increase the risk of groundwater contamination. Consequently, the effect of the OA addition is not easy to predict, especially when liquid amendments are applied.

The aim of this study was to assess the influence of four OA (two commercial humic amendments, a solid urban waste residue, and a sewage sludge) on sorption of the herbicides simazine (6-chloro-*N,N*-diethyl-1,3,5-triazine-2,4-diamine) and 2,4-D (2,4-dichlorophenoxy)acetic acid), with special emphasis on the role of DOM, which can significantly influence the amount of chemical available for leaching through the soil profile and the risk of groundwater contamination.

## Materials and Methods

**Herbicides, Soils, and Amendments.** Simazine is a colorless solid of melting point 226 °C, vapor pressure 810 nPa, and water solubility (20 °C) 5 mg L<sup>-1</sup> (18). Reported Koc values can vary from 190 to 360 (19). The simazine used was of high purity (>98%) purchased from Riedel-de Haën (Germany). 2,4-D is a colorless solid of melting point 140.5 °C, vapor pressure 53 Pa, and water solubility (25 °C) 620 mg L<sup>-1</sup> (18). Depending on pH, Koc values vary from 28 to 200 (20). The 2,4-D used was the high purity compound (>98%) purchased from Sigma (St. Louis, MO).

The top 50 cm of two soils, TR and A, were sampled, air-dried, and sieved to pass a 2 mm mesh. The organic amendments (OA) used were the commercial liquid organic amendment Fertiormont (LF), the solid commercial amendment Fertiormont (SF), a solid urban waste residue (SUW), and a sewage sludge (SS). The LF and SF amendments are two commercial amendments derived by composting the liquid and solid waste, respectively, of the olive-mill process. The SUW was a composted municipal waste from Huelva (Spain), and the SS was a compost supplied by the municipal sewage treatment plant in Sevilla (Spain).

In the laboratory, the OA were added to the original soils at a rate of 10% (w/w). Physicochemical properties of the original (unamended) soils TR and A and the amended soils were determined and are given in Table 1, and characteristics of the OA are given in Table 2. The organic carbon (OC) content of the soil samples and organic matter (OM) content of the OA were determined by dichromate oxidation (21). The pH was determined in a 1:2 (w/w) soil/deionized water mixture.

**Characterization of DOM: Spectroscopical Studies.** For DOM extraction, the three solid OA (SF, SUW and SS), original soils (TR and A), and amended soils were treated with a solution of 4 mM CaCl<sub>2</sub> (1:2 w/v) and shaken for 10 min. The goal was to mimic to some extent in situ elution processes (22). The samples were then centrifuged at 4000 rpm for 15 min in order to facilitate their filtration, which was done

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**TABLE 1. Clay Mineralogy (I = Illite, K = Kaolinite, M = Montmorillonite) and Selected Chemical Properties of TR and A Soils and Amended TR and A Soils**

soil sample	pH	OC %	sand %	silt %	clay % (I, K, M)	Fe <sub>2</sub> O <sub>3</sub> %
TR	7.1	0.66	75	9.0	16 (60,20,20)	4.3
TR+LF	6.5	1.94	75	9.0	id	id
TR+SF	7.7	1.06	75	9.0	id	id
TR+SUW	7.7	0.90	75	9.0	id	id
TR+SS	7.6	1.54	75	9.0	id	id
A	7.9	0.76	54	23	23 (40,10,50)	2.6
A+LF	7.2	1.00	54	13	id	id
A+SF	7.8	1.40	54	13	id	id
A+SUW	7.9	1.60	54	13	id	id
A+SS	7.6	1.90	54	13	id	id

**TABLE 2. Characteristics of the Organic Amendments**

organic amendment	LF	SF	SUW	SS
dry matter (%)	31	85	80	84
pH	5.1	9.4	7.8	6.1
organic matter (%)	25.7	31.5	27.7	20.3
C/N	13.8	15.8	16.5	10.3
N <sub>Kjeldahl</sub>	0.9	1	0.8	1.5
P <sub>2</sub> O <sub>5</sub> (%)	0.21	0.87	0.98	5.1
K <sub>2</sub> O (%)	2.2	3.23	0.48	0.48
CaO (%)	0.27	6.5	4.51	12.5

with polycarbonate filters (0.4  $\mu$ m pore diameter). The LF amendment was diluted with bidistilled water. The concentration of dissolved organic carbon (DOC) in the extracts and the diluted LF was measured, after acidification and sparging for 1 min to drive out carbonates, with a Shimadzu 5050 Total Organic Carbon Analyzer and their absorption at 254 nm with a Hitachi U-1000 Spectrophotometer. The absorptivities ( $\text{dm}^3 \text{m}^{-1} \text{mg}^{-1}$ ) of the extracts at 254 nm were calculated by dividing their absorption at that wavelength with their DOC concentrations and multiplying by 100.

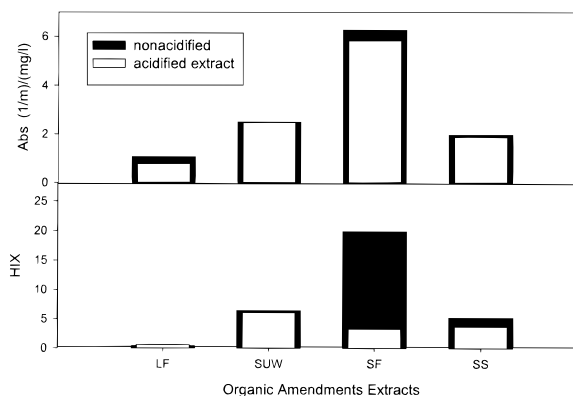
Fluorescence spectra were recorded from 300 to 480 nm under excitation at 254 nm using a Hitachi F-2000 Fluorescence Spectrophotometer. To take account of fluctuations in lamp output and detector sensitivity, the maximal intensity  $I_{\text{max}}$  (arbitrary units, AU) of fluorescence was corrected by dividing it with the maximum of the Raman peak ( $I_{\text{corr}}$ ). This correction is a simplification, since not all areas of the emission spectra vary to the same extent over time. However, it has proven to be adequate in numerous unpublished investigations and in ref 23. Analogous to absorptivity, the relative fluorescence (RF,  $\text{AU dm}^3 \text{mg}^{-1}$ ) was calculated

$$\text{RF} = I_{\text{corr}} / [\text{DOC}]$$

where  $I_{\text{corr}}$  is the fluorescence maximum in arbitrary units, and DOC the concentration of dissolved organic carbon. Fluorescence emission spectra can be strongly influenced by concentration (24). This was avoided by diluting samples with bidistilled water to an optical density below 0.1  $\text{cm}^{-1}$  before measurement. Self-quenching could be corrected with multiplication with  $e^A$ , where A is the absorption ( $\text{cm}^{-1}$ ) at the excitation wavelength (23).

A humification index HIX was calculated from the fluorescence data as follows (23)

$$\text{HIX} = \frac{\sum_{W1=435}^{480} I_{W1}}{\sum_{W1=300}^{345} I_{W1}}$$



**FIGURE 1. Absorptivity (Abs) and humification indexes (HIX) of the organic amendments LF, SUW, SF, and SS nonacidified and acidified extracts.**

where Wl is the wavelength in nanometers and  $I_{Wl}$  is the fluorescence intensity at this wavelength. Since this is an "internal" parameter, no corrections were necessary.

Absorption and fluorescence spectra measurements were taken before and after acidification by the addition of 30  $\mu$ L 2 N HCl to 3 mL of extract (pH = 2).

**Sorption Studies.** Sorption studies were performed using the batch equilibration procedure. Duplicate samples of 5 g of each soil were treated with 10 mL of simazine solutions of initial concentrations ( $C_i$ ) ranging from 0.5 to 10  $\mu$ M or with 10 mL of 2,4-D with  $C_i$  of 5 to 100  $\mu$ M. The suspensions were shaken at  $20 \pm 2$   $^{\circ}\text{C}$  for 24 h and then centrifuged at 31000 g at the same temperature. Previously, it was checked that equilibrium was reached before 24 h and that no measurable degradation occurred during this period. Equilibrium concentrations ( $C_e$ ) in the supernatants were determined by HPLC under the following conditions: Nova-Pack C18 column of 150 mm length  $\times$  3.9 mm i.d.; flow rate, 1 mL  $\text{min}^{-1}$ ; eluent system, 70:30 water-acetonitrile mixture for simazine and 55:45  $\text{H}_3\text{PO}_4$  (pH=2)-methanol for 2,4-D and UV detection at 230 nm. Differences between  $C_i$  and  $C_e$  were assumed to be the amounts sorbed ( $C_s$ ). Sorption isotherms were fit to the Freundlich equation ( $C_s = K_f C_e^{n_f}$ ) and  $K_f$  (relative sorption capacity) and  $n_f$  (sorption intensity) coefficients calculated. The fitted equation was used, when convenient, to calculate sorption distribution coefficients ( $K_d$ ) at selected  $C_e$  and also  $K_d$  normalized to the OC content ( $K_{oc}$ ).

## Results and Discussion

**Characterization of DOM: Spectroscopic Studies.** The absorptivity values (Abs) and humification indexes (HIX) (Figure 1) reveal that the LF amendment differs from the other organic amendments by having a very low ability to absorb and to fluoresce. The very low HIX values indicate that LF contains great amounts of relatively nonhumified material. On the contrary, Abs and HIX values of the SF DOM show that this amendment contains the highest amounts of highly humified material. The grade of humification of SUW and SS organic amendments is between that of LF and SF.

The normalized fluorescence spectra of the OA reveal the great difference between the LF and the other OA (Figure 2). The LF amendment has its maximal fluorescence intensity in the region near 300 nm. In this region, less complicated and nonhumified material tend to fluoresce. The maximal fluorescence intensity of the other OA extracts appear at wavelengths greater than 400 nm, indicating that their fluorescence is dominated by more complicated molecules which are typical for humic materials (23, 25–27). The maximal intensity of SF extract is shifted even more toward

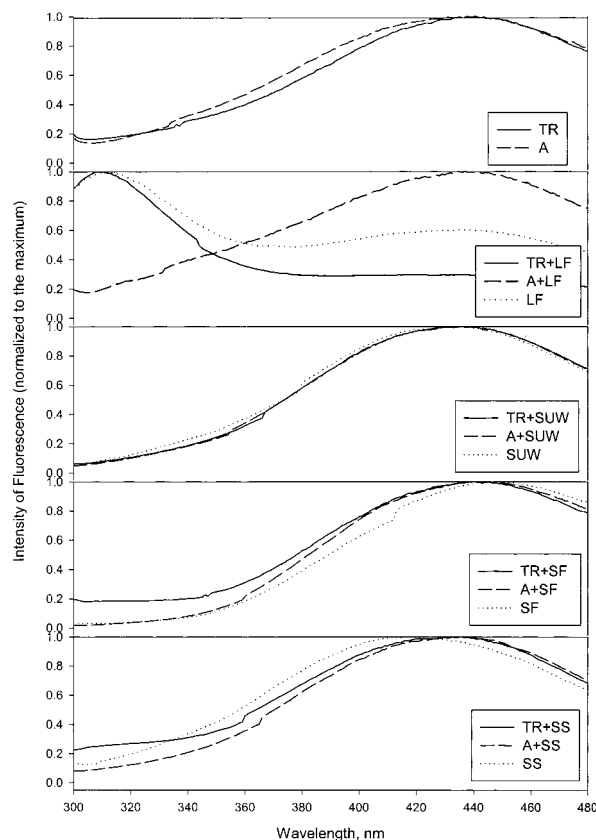


FIGURE 2. Normalized fluorescence spectra of soils TR and A, amendments (LF, SUW, SF, and SS) and amended soils TR+LF, A+LF, TR+SUW, A+SUW, TR+SF, A+SF, TR+SS, and A+SS.

TABLE 3. Dissolved Organic Carbon ( $\text{mg L}^{-1}$ ) of Extracts of Organic Amendments (OA) and Soils (Original and Amended TR and A Soils)

sample	+LF	+SUW	+SF	+SS	unamended
TR					20.1
A					28.2
OA	$6.83 \times 10^4$	400.6	2000	300.4	
TR+OA	2600	50.71	200.3	100.6	
A+OA	300.8	70.29	100.6	60.27	

the red region indicating a more complicated, presumably aromatic, nature for the DOM of this OA.

Absorptivity is hardly affected by acidification in all the OA, whereas the effect of acidification on  $\text{RF}_{\text{DOC}}$  (data not shown) and HIX (Figure 1) is major in the case of SF. Acidification lowers the intensity of the fluorescence spectra of DOC, due to withdrawal of electrons from aromatic structures ( $\pi$ -electron system) and to changes in the spatial structure of DOM upon protonation (28). The strong reaction to protonation of SF indicates a higher amount of carboxylic groups in this amendment than in the other OA.

The LF amendment has the highest concentration of DOC ( $\text{LF} \gg \text{SF} > \text{SUW} \geq \text{SS}$ ) (Table 3), since it is a liquid amendment. When soils TR and A, with similar DOC content, are treated with the diverse OA, the most interesting feature observed is the very different DOC concentration in the extracts of TR+LF and A+LF soils as summarized in Table 3: DOC is nearly 10 times higher in TR+LF than in A+LF, whereas in the case of the other OA, differences are not as high. These results suggest that DOM of LF associates to TR soil to a lesser extent than to A soil, as confirmed by the different fluorescence spectrum of these soil extracts (Figure 2). The normalized fluorescence spectrum of TR+LF soil is

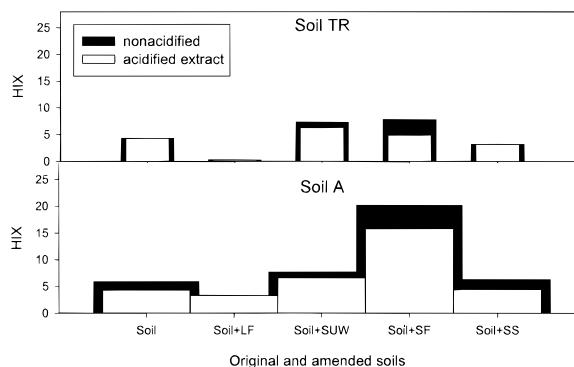


FIGURE 3. Humification indexes (HIX) of nonacidified and acidified extracts of unamended soils TR and A and amended soils TR+LF, A+LF, TR+SUW, A+SUW, TR+SF, A+SF, TR+SS, and A+SS.

very similar to that of the LF amendment, whereas in the case of A+LF soil, the peak of LF spectrum in the region near 300 nm, attributed to fluorescence of small molecules, does not appear. This indicates that these small molecules are sorbed to the soil and that there is mainly humified organic material in solution, as will be discussed later in the *Sorption studies* section. The differences observed between the two soils in their association with DOM of the different OA can also explain why the increase in OC upon amendment does not follow a consistent pattern (Table 3).

The fluorescence spectra of extracts of the soils amended with SUW, SF, or SS do not alter spectrum characteristics of the OA as much as LF amendment (Figure 2), although HIXs show some changes, specially in the case of SF and when extracts are acidified (Figure 3). The large decrease in HIX upon acidification of the SF amendment extract (Figure 1) is not observed in the case of acidified extracts of soils TR+SF and A+SF (Figure 3), indicating that a large number of molecules with carboxylic groups in the SF extract are sorbed on the TR and A soils. The lower HIXs (nonacidified and acidified) of TR+SF extract, when compared with SF and A+SF, indicate that highly humified organic molecules, probably with high content in carboxylic groups (negatively charged) sorb on TR soil to a higher extent than on soil A, probably due to the higher iron oxide (positively charged) content of TR soil (Table 1).

**Sorption Studies. Simazine.** Simazine sorption isotherms on TR and amended TR soils (TR+LF, TR+SF, TR+SUW, and TR+SS) are given in Figure 4a and simazine sorption isotherms in the A soil and amended A soils (A+LF, A+SF, A+SUW, and A+SS) in Figure 4b. Sorption coefficients are given in Table 4.  $K_f$  values, which measure relative sorption capacity, are higher in the amended soils than in the original TR soil due to the increase in OC, which has been shown to increase simazine sorption (14). At low solution concentrations, there are no significant differences between the OA. When a  $K_d$  is calculated at higher solution concentration ( $C_e = 10 \mu\text{M}$ ), differences are more significant. Adsorption increases in the following order:  $\text{TR} < \text{TR}+\text{SS} < \text{TR}+\text{LF} < \text{TR}+\text{SUW} < \text{TR}+\text{SF}$ . Although there is an overall increase in sorption upon amendment, there is not a clear direct correlation between OC and  $K_f$ , indicating that the nature of the OA is very important and that not all OM is equally efficient in sorption. Consequently, there is not a reduction in variability between soils when  $K_d$  ( $C_e = 10 \mu\text{M}$ ) is normalized to the OC content of the soils ( $K_{oc}$  in Table 4)). Natural organic matter in soil is not homogeneous in composition, degree of humification, or physicochemical properties. According to Xing and Pignatello (29), even within a single soil profile the percentage of aromatic constituents of humic acids changes with depth. Consequently, when soil organic matter is exogenous in origin (i.e. soil amendment),



TABLE 4. Simazine Sorption Coefficients for TR and A Soils and for These Soils Amended with LF, SF, SUW, and SS

soil	Kf	nf	r2	Kd (10 $\mu$ M)	Koc
TR	0.44 (0.37–0.51) <sup>a</sup>	0.83 $\pm$ 0.12 <sup>b</sup>	0.95	2.94 (2.38–3.63)	445
TR+LF	0.81 (0.70–0.94)	0.88 $\pm$ 0.13	0.96	6.19 (5.01–7.67)	320
TR+SF	1.11 (1.03–1.19)	1.16 $\pm$ 0.05	1.00	15.99 (14.63–17.48)	1550
TR+SUW	0.60 (0.48–0.74)	1.25 $\pm$ 0.18	0.96	10.69 (7.87–14.50)	1100
TR+SS	0.74 (0.61–0.90)	0.76 $\pm$ 0.15	0.92	4.26 (3.26–5.51)	280
A	2.14 (1.91–2.39)	0.78 $\pm$ 0.07	0.98	12.89 (11.67–14.28)	1700
A+LF	0.37 (0.35–0.38)	1.28 $\pm$ 0.11	1.00	7.12 (7.02–7.22)	712
A+SF	3.39 (3.35–3.42)	0.80 $\pm$ 0.01	1.00	21.53 (21.29–21.77)	1537
A+SUW	1.74 (1.67–1.81)	0.86 $\pm$ 0.03	1.00	12.62 (12.19–13.06)	788
A+SS	2.80 (2.65–2.97)	0.72 $\pm$ 0.05	0.99	14.96 (13.99–16.00)	700

<sup>a</sup> Numbers in parentheses are standard error about the mean Kf. <sup>b</sup> Numbers are nf  $\pm$  standard error.

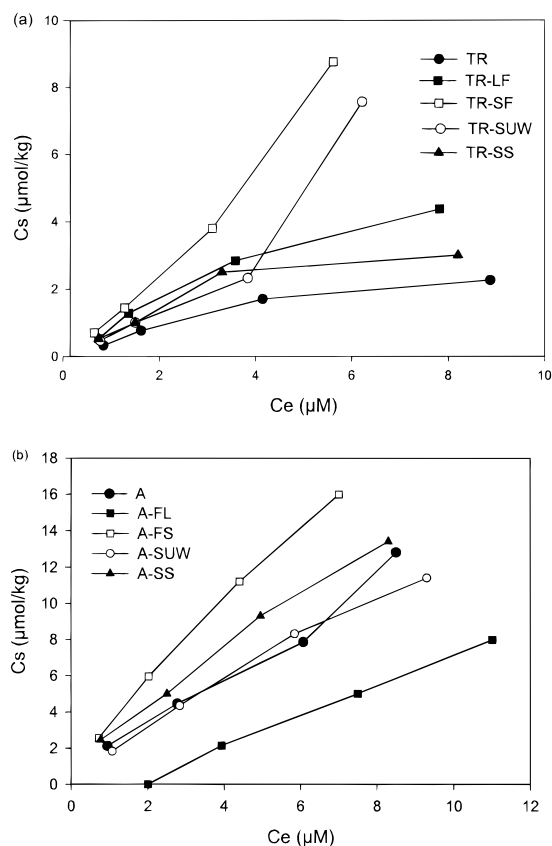


FIGURE 4. Simazine sorption isotherms in the TR soil and amended TR soils (a) and in A soil and amended A soils (b).

variability in sorption capacity of soils is expected. On another hand, the different OA may have altered the original sorptive-active soil constituents to a different extent, blocking surfaces or creating new surfaces available for sorption depending on the particular soil-pesticide system considered. Previous sorption studies with model soil colloid associations revealed that contribution of individual soil colloids (montmorillonite, iron oxides and humic acid) to simazine and 2,4-D sorption changes upon their interassociation (19, 20). The lower sorptive systems (TR, TR+LF, and TR+SS) show L-type isotherms (Figure 4a), which according to Giles et al. (30) correspond to a decrease of site availability as the solution concentration increases. The higher sorptive systems TR+SUW and TR+SF show S and C-type isotherm, respectively, which indicate the presence of more abundant sorptive sites and adsorption by partition between OM and solution.

In the case of the A soil (Figure 4b, Table 1), simazine sorption coefficients are higher than in TR, due to the higher OC and clay contents of A soil. Both soil components are

important in simazine soil sorption, although mechanisms involved are different: whereas simazine sorbs mainly by H-bonding or proton transfer to OM (31), sorption on clay minerals takes place as protonated species and/or as molecular species on hydrophobic microsites of montmorillonite surfaces (32). As in the TR soil, the changes in simazine sorption upon amendment in soil A do not indicate a clear correlation between OC and Kf. Furthermore, Koc values obtained for the same OA in the two soils are different, which clearly reveals how exogenous OM association with soil components alter their individual contribution to sorption. Sorption of simazine in A soil follows a very different pattern of increase (Table 4): A+LF < A < A+SUW < A+SS < A+SF. Isotherms for the original soil A and amended A soils A+SF, A+SUW, and A+SS soils are of L type, whereas A+LF isotherm is S-type as in the case of the TR soil, the higher sorption coefficients correspond to the SF amended soil. According to the fluorescence spectrum of DOM of SF (Figure 2), organic matter of SF is more aromatic and has higher HIX values (Figure 1) than the other OA, which would contribute to the higher sorption of simazine. By the contrary, simazine sorption on A+LF soil is significantly lower compared to the original soil A. As shown in fluorescence studies, the LF amendment is mainly constituted by small molecules and is only weakly humified. This low sorption of simazine can be attributed to interactions between small DOM molecules from LF and the soil surfaces. DOM molecules would adsorb on the active sites of the soil competing or displacing weakly sorbed simazine molecules. These results are consistent with the fluorescence spectrum of A+LF soil extract, which is significantly different from that of the LF spectrum (Figure 2). Similar results were observed by Bussinelli (16) for s-triazines in a desorption study with DOM from pig slurry and by Jin and O'Connor (33) and Celis et al. (34) for toluene and atrazine sorption on sewage sludge amended soil, respectively.

The very different results obtained for soil TR can be explained by considering the different composition of soils TR and A. The A soil has higher montmorillonite content and lower iron oxides content than the TR soil (Table 1). According to Celis et al. (32), montmorillonite is the main mineral soil colloid contributing to simazine sorption, whereas iron oxides do not sorb simazine. Our hypothesis is that montmorillonite would be responsible for the sorption of the small DOM molecules of LF amendment, which would compete with simazine molecules for the same surface active sites in soil A. The lower proportion of montmorillonite in TR would explain the similarity in the fluorescence spectra of LF and TR+LF (Figure 2), since these small DOM molecules would sorb to a lesser extent on the TR soil and remain in solution. Consequently, there is no competition with simazine for sorption sites on the TR soil. To corroborate the higher affinity of DOM from LF for montmorillonite than for iron oxide, we checked the sorption capacity for LF of Wyoming mont-

TABLE 5. 2,4-D Sorption Coefficients for TR and A Soils and for These Soils Amended with LF, SF, SUW, and SS

soil	Kf	nf	r2	Kd (100 $\mu$ M)	Koc
TR	—	—	—	—	—
TR+LF	0.93 (0.35–2.45) <sup>a</sup>	0.49 $\pm$ 0.26 <sup>b</sup>	0.77	8.46 (5.74–12.47)	400
TR+SF	1.6 (1.57–1.63)	0.44 $\pm$ 0.01	1.00	12.19 (12.10–12.28)	1200
TR+SUW	1.39 (1.36–1.40)	0.54 $\pm$ 0.01	1.00	17.06 (16.95–17.17)	1800
TR+SS	1.95 (1.55–2.45)	0.51 $\pm$ 0.08	0.96	20.51 (17.35–24.26)	1370
A	1.00 (ns)	0.2 (ns)	0.41	—	—
A+LF	0.91 (0.52–1.58)	0.73 $\pm$ 0.18	0.89	26.12 (17.95–38.02)	2600
A+SF	1.26 (0.83–1.91)	0.65 $\pm$ 0.13	0.93	25.06 (19.00–33.07)	1790
A+SUW	1.29 (0.83–1.99)	0.70 $\pm$ 0.14	0.93	32.73 (24.31–44.08)	2062
A+SS	1.22 (1.07–1.30)	0.74 $\pm$ 0.02	1.00	37.00 (35.34–38.71)	2000

<sup>a</sup> Numbers in parentheses are standard error about the mean Kf. <sup>b</sup> Numbers are nf  $\pm$  standard error.

morillonite (Clay Minerals Society) saturated in  $\text{Ca}^{2+}$  and poorly crystallized ferrihydrite synthesized according to Celis et al. (20). As in herbicide sorption studies, 10 mL of diluted LF (1 mL in 250 mL distilled water) was shaken with 50 mg of SWy-Ca or ferrihydrite for 24 h, centrifuged, and estimated the DOM remaining in solution (not sorbed) by UV absorbance measurements (285 nm) in an UV-Vis spectrophotometer. The pH's of the suspensions after 24 h shaking were 6.2 for the montmorillonite suspension and 5.4 for the ferrihydrite one. DOM sorption on montmorillonite (60%) was three times higher than on ferrihydrite (20%), thus corroborating our hypotheses. These results also explain the different degree of association of LF amendment OM to TR and A soils discussed previously (Figure 2 and Table 3).

**2,4-D.** 2,4-D did not sorb on the unamended soil TR, despite its relatively high iron oxide content (Table 1). Iron oxides have been shown to sorb 2,4-D anions through electrostatic interactions between negatively charged carboxylic groups and positively charged Fe oxide surface (20). However, negative layer charge of mineral soil colloids (phyllosilicates) can screen positive charge of iron oxides and explain why there is no measurable 2,4-D sorption on TR soil (20). Also the low organic matter content of TR soil, besides the anionic character of 2,4-D at the pH of the soil, can account for the lack of sorption measured on TR soil under the conditions studied. 2,4-D did sorb on TR soil when this soil was amended with the different OA (Figure 5a). Sorption isotherms were fit to the Freundlich equation and sorption coefficients Kf and nf are given in Table 5. As in the case of simazine, the different OA increased 2,4-D sorption to a different extent, and these differences are greater at high solution concentration (Kd at  $C_e = 100 \mu\text{M}$ ). For every organic amendment, sorption intensity nf of 2,4-D in the TR soil is much lower than for simazine, displaying L-type isotherms. Sorption increases in the order  $\text{TR} \ll \text{TR+LF} < \text{TR+SF} < \text{TR+SUW} < \text{TR+SS}$ .

Little sorption of 2,4-D on the original soil A was measured, and the sorption coefficients (Kf and nf) are not statistically significant ( $R^2 = 0.41$ ). Sorption coefficients Kf and nf are higher in amended A soils than in amended TR soils. As in TR soil, there is an overall increase in sorption upon the amendment but not a clear correlation with OC content. Also Koc values do not reduce variability in sorption neither between amendments nor between soils. Differences between the amendments are also more significant at higher solution concentrations. As for TR soil, sorption increases in the order  $\text{A} \ll \text{A+LF} < \text{A+SF} < \text{A+SUW} < \text{A+SS}$ . The lower sorption of 2,4-D on SF amended soils, when compared with SUW and SS (SF more aromatic than SUW and SS), can be attributed to repulsion between negatively charged 2,4-D molecules and  $\text{COO}^-$  groups, which are more abundant in SF. Consistently, the lower Koc value among the solid amended soils correspond to SF soils (Table 5).

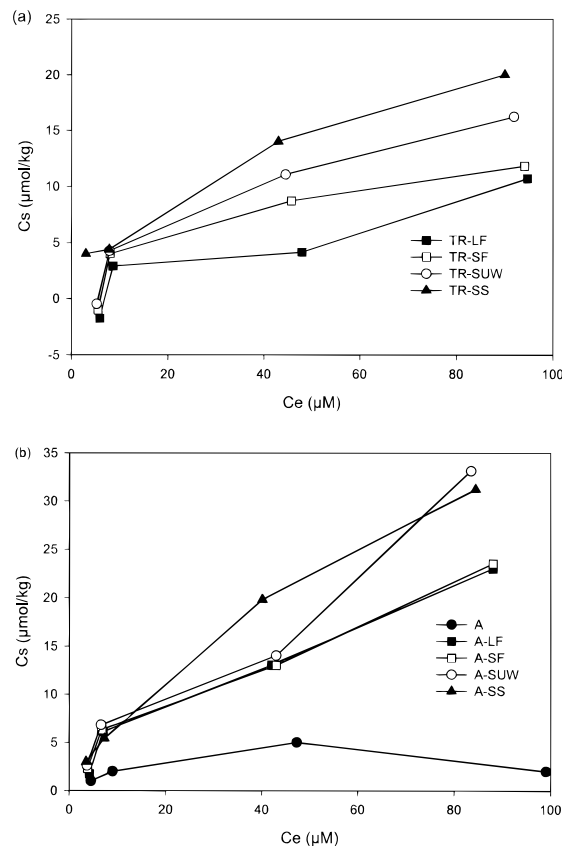


FIGURE 5. 2,4-D sorption isotherms amended TR soils (a) and in A soil and amended A soils (b).

The different behavior of 2,4-D in the amended A+LF soil compared to simazine should be noted. In this case, LF does not decrease 2,4-D sorption, and this can be explained by considering the different sorption mechanisms of simazine and 2,4-D. Previous studies by the authors have shown that 2,4-D does not sorb on montmorillonite (20). Consequently, 2,4-D species do not compete with the DOM molecules of LF for sorption sites as it does simazine, which sorbs on montmorillonite (32).

**Environmental Implications.** Our results indicate that the effect of soil organic matter addition on sorption and, consequently, on leaching of pesticides is highly dependent not only on the nature of the organic amendment and pesticide but also on the soil to which exogenous organic matter is applied. Thoroughly characterization of DOM (in absence and presence of the soil) and mineral soil components allow pesticide-soil interaction to be interpreted on the basis of the chemical character of the pesticide and the interassociation of exogenous OM and original soil com-

ponents. Limitations on the role of organic matter in reducing leaching potential of contaminants such as pesticides should be taken into account, since dissolved organic matter can favor leaching not only by interactions with the pesticide (facilitated transport) but also by interactions with the soil surfaces (competitive sorption).

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