Effect of Organic Amendments on the Retention and Mobility of Imazaquin in Soils

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The influence of two organic amendments consisting of an urban waste compost (SUW) and a commercial amendment from olive mill wastes (OW) was assessed on the sorption properties and leaching of the ionizable herbicide imazaquin on four soils with different physicochemical characteristics. A loamy sand soil (CR), a loam soil (P44), a silt loam soil (AL), and a clay soil (TM), with low-medium organic matter contents, were chosen. Sorption−desorption experiments were performed on the original soils and on a mixture of these soils with the organic amendments at a rate of 6.25% (w/w). These mixtures were used just after preparation and after aging for 3 months. Imazaquin adsorption was higher on AL soil because of its high content of amorphous iron oxides, whereas it was related to the soils' organic matter (OM) contents on TM and CR soils and to acid pH on P44 soil. Addition of exogenous OM to soils caused a decrease in the adsorption of the herbicide with the only exception of CR soil, due to blocking of adsorptive surfaces and/or equilibrium pH rise. The extent of this decrease was dependent only on the nature of the added amendment on AL soil. The adsorbed amounts of imazaquin on aged organic fertilized soils were usually fairly close to that on original soils. Results of soil column experiments indicate that addition of exogenous organic matter cannot be considered as a regular practice for retarded movement of imazaquin.

KEYWORDS: Organic amendment; imazaquin; soil; adsorption−desorption; mobility

INTRODUCTION

Concerns about groundwater contamination by the use of pesticides have risen during recent years as a consequence of the increased pesticide application as well as the use of more mobile pesticides (*1*). In the United States, it was estimated that in 1990 92% of the nearly 300 million ha used for agricultural production received herbicide applications and 31% of the acreage received insecticide treatments (*2*). A survey on the occurrence of pesticides in groundwater tested across the United States during that year stated that 1.2% of community water system wells and 2.4% of rural domestic wells contained pesticides (*3*). Recent studies indicate that this trend is increasing. Troiano et al. (*4*) detected residues for 16 active ingredients and breakdown products in California groundwater as a result of legal agricultural use. Spalding et al. (*5*) reported detection of 14 pesticides and their transformation products in groundwater of the central Platte Valley of Nebraska. In a monitoring study, Barbash et al. (*6*) detected pesticides in groundwater within 1 year following application.

Several strategies have been considered for preventing herbicide leaching, such as adapting appropriate crop management practices, modifying application techniques, and develop-

ing slow-release formulations (*7, 8*). An important management strategy for reducing leaching is to manipulate the sorption potential of the soil by incorporating organic residues because a strong correlation is usually observed between soil organic C content and adsorption of pesticides (*9, 10*). Retarded movement by the application of organic amendments has been often described for widely used herbicides: clopyralid (*11*); diuron (*12*); linuron (*13*); metolachlor (*14*); etc.

Studies about the effect of addition of exogenous organic matter to soils on the adsorption and leaching of anionic herbicides are scarce. There are very few studies indicating an increase in the adsorption of some anionic herbicides when applied to amended soils (*15, 16*).

Imazaquin is a selective imidazolinone herbicide used for broad-spectrum weed control in soybean [*Glycine max* (L.) Merr.] and other legume crops. Imazaquin is an amphoteric molecule that has both an acidic carboxyl and a basic quinoline functional group with pK_a values of 3.8 and 2.0, respectively (*17*), and therefore it exists predominantly as an anion at typical soil suspension pH values. Several authors have reported it to be mobile (*18−20*), the time between its application and the first rainfall being a crucial factor in imazaquin leaching (*21*).

Because pH and organic matter are the soil properties that most significantly affect the sorption of imazaquin (*22−24*), the aim of the current study was to evaluate the application of

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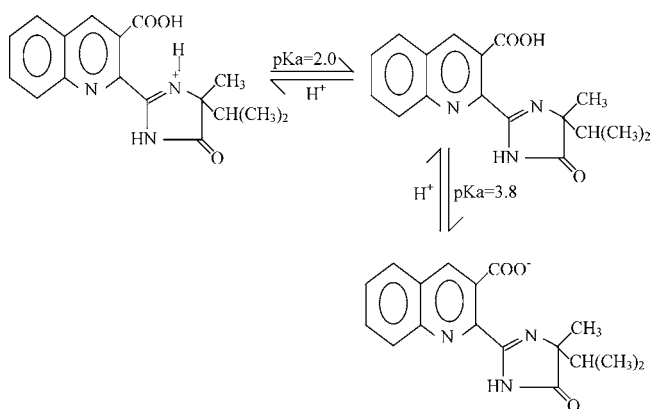
Scheme 1. Ionization of Imazaquin

Table 1. Some Characteristics of the Original Soils Used

	CR (loamy sand)	P44 (loam)	AL (silt loam)	TM (clay)
OM (g kg^{-1})	7.9	14.0	19.0	17.6
CEC (cmol$_c$ kg^{-1})	4.8	7.8	17.2	39.0
carbonates (g kg^{-1})	69.0	<0.1	<0.1	241.0
pH	8.0	5.5	7.6	8.0
sand (%)	87.6	49.8	16.4	2.7
silt (%)	4.0	34.5	61.2	31.5
clay (%)	8.4	15.7	22.6	65.9
total Fe$_2$O$_3$ (g kg^{-1})	11.4	46.1	241.7	43.9
amorphous Fe$_2$O$_3$ (g kg^{-1})	0.4	1.9	10.8	0.8
total Al$_2$O$_3$ (g kg^{-1})	53.2	111.8	161.0	116.4
amorphous Al$_2$O$_3$ (g kg^{-1})	0.2	1.0	9.4	3.5
total MnO (g kg^{-1})	<0.1	0.6	35.8	0.7
amorphous MnO (g kg^{-1})	<0.1	0.1	9.8	0.2

two organic waste amendments, consisting of a commercial product from olive mill wastewater and other plant residues and an urban waste compost, on the sorption and leaching of imazaquin by soils. In addition, the influence of aging of the exogenous organic matter added to the soil on imazaquin adsorption was also assessed because transformation of organic amendments applied to soils can modify the further interaction of xenobiotics with the amended soils (*10*).

MATERIALS AND METHODS

Herbicide. Technical grade imazaquin (97% purity) was obtained from AGAN Chemical Manufacturers (Ashdod, Israel). Its molecular structure and ionization are shown in **Scheme 1**.

Soils. The soils used were sampled from the surface horizon (0−20 cm) and were classified as Typic Xeropsamment (CR soil), Aquic Haploxeralf (P44 soil), Typic Eutrochrept (AL soil), and Entic Pelloxerert (TM soil). The soils were dried and crushed to pass a 2 mm sieve and were analyzed for pH in saturated paste, total carbonate content, and particle size distribution. Organic carbon content (OC) was determined according to the dichromate oxidation method, and organic matter content (OM) was calculated as follows: OM (%) = 1.724 × OC (%).

The chemical composition of the soils was determined by dissolving the samples using a three-acid method (*25*); amorphous and organically bound iron, manganese, and aluminum oxides were determined according to the ammonium oxalate−oxalic acid method (*26*).

The mineralogical composition of the soil clay fraction was determined by X-ray diffraction (XRD) using Cu Kα radiation. Semiquantitative estimation of the minerals was performed using characteristic XRD reflections and their relative intensities according to the method of Schultz (*27*).

The determined physicochemical properties of the original soils are listed in **Table 1**.

Table 2. Some Chemical Characteristics of the Organic Amendments

	olive mill wastewater (OW)	solid urban wastes (SUW)
pH	8.6	8.0
organic matter (g kg^{-1})	315.0	441.0
Kjeldahl N (g kg^{-1})	9.6	13.5
C/N	19.0	18.9
P (g kg^{-1}, P$_2$O$_5$)	8.7	10.3
K (g kg^{-1}, K$_2$O)	32.3	5.1
Ca (g kg^{-1})	65.0	60.4
Mg (g kg^{-1})	13.0	3.7
Na (g kg^{-1})	2.0	2.6
Cu (mg kg^{-1})	70.0	283
Pb (mg kg^{-1})	19.0	134
Mn (mg kg^{-1})	240	217
Zn (mg kg^{-1})	67.0	373

Amended Soils. Two organic amendments were used: a commercial product manufactured from olive mill wastewater and other plant residues (OW) and an urban waste compost from Villarasa (south-western Spain) (SUW). The organic amendments were dried at 70 °C for 48 h, homogenized, and crushed to pass a 4 mm sieve. The composition of the amendments is given in **Table 2**.

The organic amendment of the soils was carried out by mixing thoroughly, during 24 h, 300 g of the original soils with 20 g of the two amendments (6.25% of the total) (hereafter fresh amended soils).

To study the exogenous OM evolution, incubation experiments under controlled conditions were also performed. The amended soils were maintained under constant humidity at field capacity during 3 months in darkness at 30 °C (hereafter aged amended soils).

Sorption−Desorption Experiments. Triplicate sorption experiments were done by mixing 10 g of the soils with 10 mL of 0.01 M Ca-(NO$_3$)$_2$ solutions, containing various concentrations (0.16, 0.32, 0.96, 1.60, 2.60, and 3.20 μM) of imazaquin, in 30 mL polypropylene centrifuge tubes. The samples were shaken for 3 days at 20 ± 1 °C. Preliminary experiments showed that equilibration was completed within 3 days. After shaking, the suspensions were centrifuged and the concentration of the herbicide in the supernatant was determined. The difference in pesticide concentration between the initial and final equilibrium solutions was assumed to be due to sorption.

Additional adsorption experiments of imazaquin at 1.60 and 3.20 μM were performed on the soils by determining the adsorbed amount at 24 h for an estimation of the percent adsorbed with respect to the total amount after 3 days.

Imazaquin analysis was performed by using a Shimadzu HPLC equipped with a PDA detector set at a wavelength of 240 nm. The reverse phase column was a 15 cm Kromasil 100 C18. The mobile phase was a mixture of 65% water and 35% methanol containing 2% acetic acid. The flow rate was 1.2 mL min^{-1}. The retention time was 18.2 min.

Desorption experiments were performed on original and amended soils after sorption equilibrium was reached for the points corresponding to imazaquin initial concentrations of 0.96 and 2.60 μM, by removing half of the supernatant after centrifugation, replacing it by 5 mL of 0.01 M Ca(NO$_3$)$_2$ solution, allowing equilibration for an additional 3 days period, and after that operating as in the sorption experiment. This process was repeated twice more.

Sorption−desorption isotherms were fitted to the logarithmic form of the Freundlich equation

$$\log C_s = \log K_f + n \log C_e$$

where C_s (μmol kg^{-1}) is the amount of herbicide sorbed at the equilibrium concentration C_e (μmol L^{-1}) and K_f and n are constants that characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicide. The fitted equation was used to calculate sorption distribution coefficients (K_d) at a selected C_e (2 μmol L^{-1}). The organic carbon (OC) normalized distribution coefficient (K_{oc}) was

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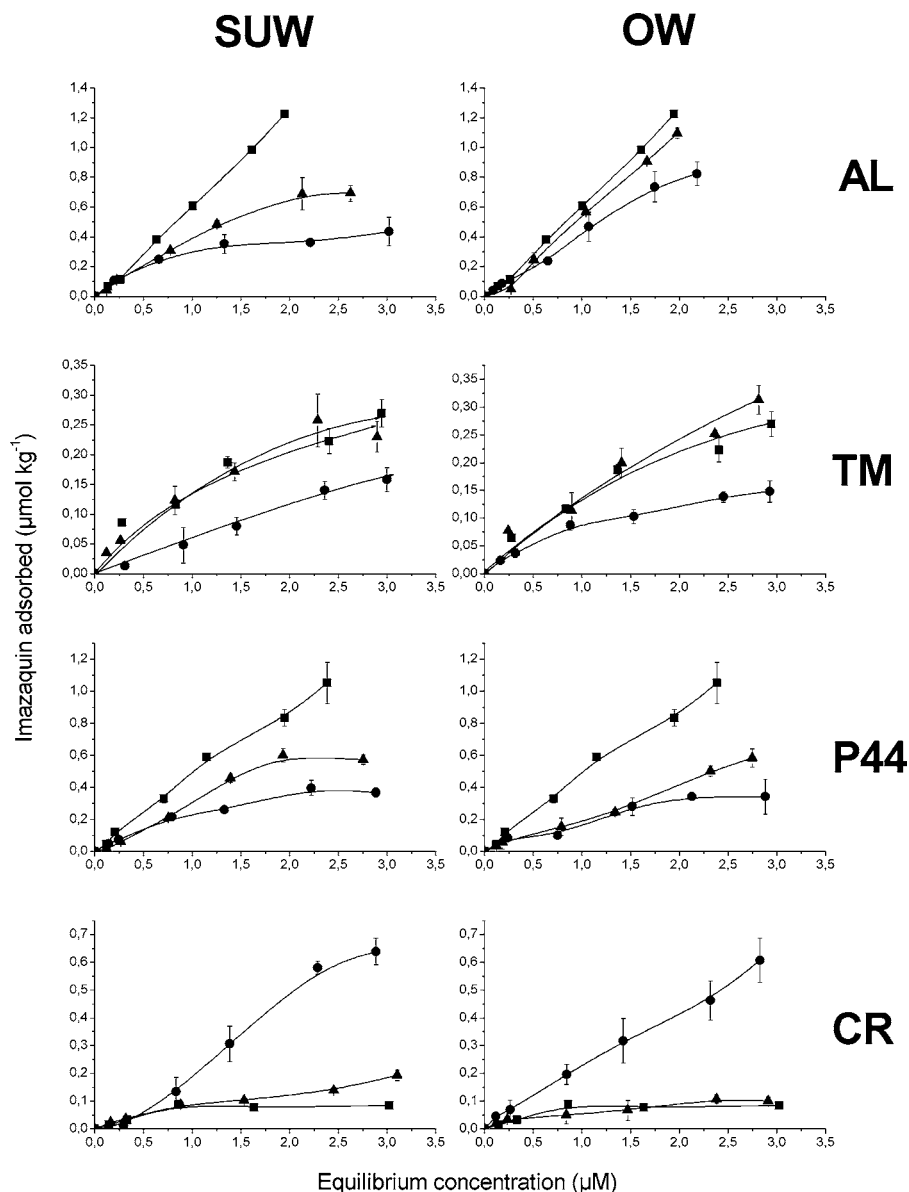
SUW   OW

Figure 1. Adsorption isotherms of imazaquin on original (■), fresh amended (●), and aged amended (▲) soils with SUW and OW.

calculated from K_d values. Hysteresis coefficients, H, for the sorption–desorption isotherms were calculated according to

$$H = n_a/n_d$$

where n_a and n_d are the Freundlich n constants obtained from the sorption and desorption isotherms, respectively. The ratio n_a/n_d has been used to describe the hysteretic behavior of desorption from soils (*10, 28*).

Leaching Experiments. Leaching experiments were performed in methacrylate tubes of 3.0 cm diameter cut into 4 and 8 cm sections, and 5 units of 4 cm were glued together with a 8 cm unit at one end to construct a 28 cm column. The column was covered at the end opposite to the 8 cm unit with a 1 mm nylon screen padded with a thin layer of glass wool (0.5 g) to hold the soil firmly in the column. Soil was packed from the top of the column (8 cm section), creating a 24 cm soil column that could be readily separated into 4 cm segments. A thin layer of glass wool was placed on top of each soil column to maintain the integrity of the surface during leaching.

The leaching experiments were carried out in triplicate in CR, P44, and AL soils, their amounts packed in the columns being 0.240, 0.246, and 0.190 kg, respectively. The pore volume of the soils was determined to be 57 mL in CR soil, 66 mL in P44 soil, and 88 mL in AL soil. These soil column experiments were also performed with fresh amended

soil by filling the first two upper rings of the columns with the equivalent amount of amended soil instead of the original soil.

The columns were treated with 5 pore volumes of a 0.01 M $Ca(NO_3)_2$ solution followed by 1 pore volume of distilled water before 10 mL of the herbicide was sprayed at a rate of 140 g of active ingredient (ai) ha^{-1}. Twenty-five milliliters of distilled water was added every 24 h at the top of the column, and the leachates were collected and analyzed for the herbicide.

Each soil column was separated into six 4 cm segments, and the soil was dried at 40 °C. A bioassay was used to calculate the residual activity of the herbicide throughout the rings of the soil column by measuring the inhibition of shoot weight of sorghum seedlings. Ten grams of soil in triplicate from each segment was mixed with 10 g of the original soil, and four seeds were planted. The weight of the shoots was measured after 9 days, and the inhibition percentage was determined by comparison with a control of the untreated soil.

RESULTS AND DISCUSSION

Sorption on the Original Soils. Figure 1 shows the adsorption isotherms of imazaquin on the original soils CR, P44, AL, and TM and on these soils after amendment, both used just after mixing and after incubation for 3 months. The sorption

Table 3. Freundlich Adsorption Isotherm Parameters (K_f and n Values) for Imazaquin Sorption on the Soils Used[a]

	CR		P44		AL		TM	
	K_f	n	K_f	n	K_f	n	K_f	n
original soil	0.06 (± 0.02)	0.56 (± 0.14)	0.46 (± 0.03)	1.00 (± 0.06)	0.59 (± 0.02)	1.14 (± 0.03)	0.15 (± 0.02)	0.49 (± 0.06)
OW-F	0.24 (± 0.02)	0.83 (± 0.04)	0.18 (± 0.05)	0.66 (± 0.14)	0.41 (± 0.02)	0.96 (± 0.03)	0.08 (± 0.02)	0.65 (± 0.03)
OW-A	0.06 (± 0.02)	0.48 (± 0.04)	0.22 (± 0.03)	0.88 (± 0.05)	0.46 (± 0.06)	1.52 (± 0.20)	0.16 (± 0.03)	0.57 (± 0.09)
SUW-F	0.13 (± 0.04)	1.79 (± 0.19)	0.21 (± 0.03)	0.71 (± 0.05)	0.27 (± 0.02)	0.50 (± 0.06)	0.10 (± 0.02)	0.55 (± 0.03)
SUW-A	0.08 (± 0.02)	0.69 (± 0.04)	0.25 (± 0.05)	1.20 (± 0.11)	0.35 (± 0.03)	0.91 (± 0.07)	0.14 (± 0.02)	0.63 (± 0.03)

[a] The numbers in parentheses are standard errors. The coefficients of determination (R^2) were >0.952 in all cases. SUW, soils amended with SUW; OW, soils amended with OW; F, fresh amended soils; A, aged amended soils.

Table 4. Organic Matter Content (Grams per Kilogram) and Equilibrium pH of the Original and Amended Soils after Treatment with the Initial Solutions of Imazaquin in the Adsorption Experiments[a]

	CR		P44		AL		TM	
	OM	pH	OM	pH	OM	pH	OM	pH
original soil	7.9	7.83 (± 0.29)	14.0	5.42 (± 0.36)	19.0	7.69 (± 0.11)	17.6	7.83 (± 0.17)
OW-F	18.6	8.10 (± 0.35)	32.8	8.04 (± 0.26)	35.9	7.57 (± 0.25)	32.1	7.65 (± 0.15)
OW-A	12.1	8.11 (± 0.35)	23.3	8.49 (± 0.22)	28.4	7.98 (± 0.30)	26.4	8.08 (± 0.21)
SUW-F	24.3	7.71 (± 0.24)	37.1	7.95 (± 0.32)	56.2	7.65 (± 0.31)	47.6	7.51 (± 0.31)
SUW-A	16.4	7.96 (± 0.21)	25.5	8.01 (± 0.24)	30.2	8.03 (± 0.25)	26.9	7.91 (± 0.27)

[a] SUW, soils amended with SUW; OW, soils amended with OW; F, fresh amended soils; A, aged amended soils.

of the herbicide is well described by fitting the experimental data to the linearized Freundlich relationship (**Table 3**).

As can be inferred from **Figure 1**, the sequence of sorption of imazaquin on the original soils was AL > P44 > TM > CR.

The soil properties found to be better correlated with imazaquin sorption are the organic matter content and the soil solution pH (*19*, *24*, *29*). However, positively charged iron and aluminum oxyhydroxides contribute to sorption of the herbicide on soils with low organic matter content (*23*, *30*). Gennari et al. (*31*) found a positive correlation between K_f values of imazaquin and extractable amorphous iron oxides in addition to organic matter content. The high affinity of imazaquin for oxyhydroxides was the basis for the development of slow-release formulations of this herbicide (*32*). The highest adsorption of the herbicide on AL soil can be explained on the basis of its high iron oxides content, especially of amorphous oxides (**Table 1**). This is illustrated by comparing imazaquin adsorption on AL and TM soils, where the content of the iron amorphous oxides is ~13-fold higher on AL soil than on TM soil, but the differences between the organic matter contents and equilibrium pH are negligible (**Table 4**). At the equilibrium pH, the iron oxides will exhibit partially positive charge because their zero point charge values are around pH 8.5 (*33*), and therefore these surfaces will interact with the anionic molecules of the herbicide.

The high adsorption of imazaquin on P44 soil is related to the low pH of this soil during the adsorption experiments, which amounts to >2 units lower than in the rest of soils (**Table 4**). Although >99% of the imazaquin molecules are predicted to be ionized at the lowest solution pH found in this study (pH 5.42), according to Stougaard et al. (*19*), the effective acidity at soil colloid surfaces can be 2 or 3 units lower than solution pH due to cation distribution in the diffuse double layer and higher hydrogen concentrations near weakly ionized organic functional groups and mineral edges. Imazaquin affinity for the soil surface will increase with a pH decrease because of a larger decrease in the percentage of herbicide molecules remaining as anion, and there will be a decrease in the electrostatic repulsion of herbicide molecules from negatively charged soil surfaces. At the effective pH of the colloidal surfaces of P44 soil,

imazaquin adsorption will be favored because of strong interactions with the humic substances (*22*). In addition, a semi-quantitative estimation of the clay minerals present in the clay fraction of P44 soil indicated the presence of clay minerals such as kaolinite and illite, the percentages of which with respect to the total layer silicate content were 42 and 58%, respectively. These clay minerals are able to develop a small amount of positive charge on the edges under acidic conditions (*34*), with a subsequent enhancement on imazaquin adsorption.

No influence of pH is expected on the sorption of the herbicide on the original TM and CR soils because of identical equilibrium pH (**Table 4**). Adsorption of the herbicide on TM soil is higher than on CR soil (**Figure 1**), which is related to the organic matter content. K_f values are 2.5-fold higher on TM than on CR soil (**Table 3**). When the K_f values are normalized to the organic carbon content (K_{oc} values), there is no statistical difference between the calculated values for both soils (**Table 5**), indicating the organic matter as the main soil property controlling the sorption of the herbicide on these soils. These K_{oc} values are within the range of the calculated values (8.1– 30.6) from the data in the work by Loux et al. (*29*) for soils with a pH of ~7.8, at which imazaquin adsorption was stated to be correlated with the organic matter content. A few deviations from that range in that work may arise from the fact that additional sites can be affecting the adsorption, probably amorphous iron oxides, the influence of which was not examined.

Sorption on Amended Soils. The adsorption of imazaquin on fresh and aged amended soils shows different patterns depending on the type of amendment and the soil (**Figure 1**). As commented above, the pH of the soil solution and the content of organic matter have been reported as the most important factors for determining the adsorption of imazaquin on soils, in addition to their amorphous iron oxides content. The supply of amendments to the soil will influence both the pH and the organic matter content. The pH of the adsorption experiments on amended soils is shown in **Table 4**, where there is almost no difference between the equilibrium pH of fresh and aged amended soils. These values are also identical to those of equilibrium of the herbicide on the original soils because of

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Table 5. Distribution (K_d, Liters per Kilogram) and Organic Carbon Normalized Distribution Coefficients (K_{oc}) for Imazaquin Sorption on the Original and Amended Soils[a]

	CR		P44		AL		TM	
	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
original soil	0.044 (± 0.009)	9.6 (± 1.8)	0.463 (± 0.041)	57.1 (± 4.4)	0.646 (± 0.025)	58.6 (± 2.7)	0.105 (± 0.011)	10.3 (± 1.1)
OW-F	0.213 (± 0.011)	19.7 (± 1.0)	0.142 (± 0.034)	7.5 (± 1.7)	0.396 (± 0.019)	19.0 (± 1.0)	0.062 (± 0.008)	3.3 (± 0.5)
OW-A	0.043 (± 0.009)	6.1 (± 1.3)	0.202 (± 0.016)	14.9 (± 1.1)	0.650 (± 0.101)	39.5 (± 5.5)	0.116 (± 0.018)	7.6 (± 1.3)
SUW-F	0.228 (± 0.048)	16.2 (± 3.4)	0.171 (± 0.014)	8.0 (± 0.7)	0.188 (±0.023)	5.8 (± 0.6)	0.073 (± 0.023)	2.6 (± 0.2)
SUW-A	0.066 (± 0.004)	6.9 (± 0.4)	0.285 (± 0.035)	19.3 (± 2.4)	0.326 (± 0.031)	34.9 (± 1.5)	0.104 (± 0.006)	6.6 (± 0.4)

[a] Numbers in parentheses are standard errors. SUW, soils amended with SUW; OW, soils amended with OW; F, fresh amended soils; A, aged amended soils.

the buffer effect of the soil, except on P44 soil because of its quite initial low pH value. As a consequence, adsorption of the herbicide on the amended soils, with the exception of P44 soil, will be mainly determined by the content and the properties of their organic matter (original and from amendment). The organic matter contents of the original and amended soils are also listed in **Table 4**. A decrease in the percent of the organic matter content is notorious after incubation of the amended soils for 3 months due to the increase in the microbial activity of the soil with a subsequent decomposition of the organic matter, but the final values are always higher than those of the original soils.

In general, the addition of fresh amendments on the soil decreases the adsorption of the herbicide because much of the mineral and organic soil surfaces become blocked, with the exception of the sandy soil, which has originally very few adsorptive surfaces. Moreover, except for AL soil, the type of amendment did not influence the adsorption of the herbicide on the amended soils.

In AL soil, the addition of fresh exogenous organic matter causes a decrease in the adsorption of the herbicide because of covering by the added organic matter of the iron oxide surfaces, which are mainly responsible for the high adsorption of the herbicide on this soil. The contribution of the sorptive surfaces supplied by the amendments is negligible compared with that of blocked iron oxide surfaces, and the overall adsorption of imazaquin is decreased. A similar pattern was observed by Leone et al. (*35*) in their study on imazaquin adsorption on ferrihydrite and ferrihydrite−humic acid associations.

In addition, there is a notorious difference in the reduction of the amount sorbed of the herbicide depending on the source of the amendment. SUW produces a 2-fold decrease in the amount of adsorbed imazaquin when compared to the use of OW. Similar K_{oc} values are expected if the organic matter is controlling its adsorption on the fresh amended soils. However, K_{oc} values are ∼3-fold higher in AL soil amended with OW than with SUW (**Table 5**), and therefore the nature of the exogenous organic matter is an important factor determining the extension of adsorption of herbicides on soils with a high content of iron oxides. The protonated iron oxide surfaces will interact with the carboxylate groups of the exogenous organic matter, resulting in the formation of inner-sphere complexes according to the scheme in ref *35*. Cox et al. (*16*) obtained a lower humification index by fluorescence measurements for SUW than for OW. As a consequence, SUW amendment with a higher content of carboxylic groups will block in a larger extension the iron oxide surfaces responsible for imazaquin adsorption on this soil.

The adsorption of imazaquin on TM soil freshly amended with SUW and OW decreases considerably with respect to the original soil (**Figure 1**). K_{oc} values of the OW- and SUW-amended soils are 3- and 4-fold lower, respectively, than that of the original soil (**Table 5**). It seems that the exogenous

organic matter has a lower adsorption capacity than the original, and the addition of the amendments impedes in part the herbicide sorption due to the covering and blocking of the more reactive soil adsorptive surfaces in TM soil, mainly the endogenous organic matter.

Adsorption of imazaquin on fresh amended P44 soils also resulted in a high decrease in comparison to the original soil because of their higher pH values (**Figure 1**), although it could be also due to a blockage of the sorptive sites operating at these solution pH values on the original soil by the added organic matter.

The incubation of the soils with the organic amendments for 3 months produced a modification of the exogenous organic matter by modifying its hydrophilic−hydrophobic balance (*10*). The highest degradation occurred on AL and TM soils amended with OW, accounting for ∼45% of the OM content of the freshly amended. The sorption behavior of imazaquin on the aged amended soils shows a clear pattern for TM and CR soils where imazaquin tends to be sorbed to the same extent as on the original soil (**Figure 1**). In **Table 5**, the K_{oc} values for the original CR and TM soils, for which the organic matter was the key parameter governing the adsorption of imazaquin, are quite close to those of the aged amended soils, which may indicate a more related nature of the degraded and humified organic amendment to that of the original soils.

Desorption Experiments. No general trend of desorption of imazaquin on the original and amended soils is followed from the desorption percentages and hysteresis coefficients in **Table 6**.

In AL soil, the use of both fresh amendments decreased its hysteresis. The addition of fresh amendment blocks the sorptive sites on the original soil and gives additional sites that may be considered of lower affinity, therefore enhancing the desorption of the herbicide as shown by the lower *H* values as compared with those of the original soil. On AL aged soils, the hysteresis was dependent on the type of the added amendment. Unlike the soil treated with SUW, the use of OW increased the hysteretic behavior of the herbicide on the aged soil in addition to highly promoting its adsorption with respect to the use of fresh amendment (**Figure 1**). This indicates that the transformed organic matter from OW on AL soil provides more active sites than those of the fresh amendment and/or a release of adsorption sites on the amorphous iron oxides previously blocked.

The CR soil presents in general the highest desorption percentages. In the original soil and after amendment with SUW, *H* values are fairly close to unity, indicating that the adsorption of the herbicide on these soils is almost completely reversible.

In P44 soil, the hysteresis coefficients are very low for the original soil, unlike the amended soils. The pH in the desorption steps were acid on the original soil, whereas on the amended soils they were as those in the adsorption steps (data not shown). On the original soil, imazaquin is adsorbed not only on the

Table 6. Percentage of Imazaquin Desorbed (%D) and Hysteresis Coefficients (*H*) for Original, Fresh, and Aged Amended Soils When Treated with the Initial Concentrations of the Herbicide of 0.96 and 2.6 μM[a]

		original soil		SUW-F		SUW-A		OW-F		OW-A	
		0.96 μM	2.60 μM	0.96 μM	2.60 μM	0.96 μM	2.60 μM	0.96 μM	2.60 μM	0.96 μM	2.60 μM
CR	%D	50.7 ($\pm$ 10.3)	73.2 ($\pm$ 8.1)	68.5 ($\pm$ 3.5)	74.5 ($\pm$ 6.7)	69.6 ($\pm$ 1.2)	71.4 ($\pm$ 1.0)	58.7 ($\pm$ 1.8)	65.2 ($\pm$ 0.4)	56.2 ($\pm$ 2.7)	67.5 ($\pm$ 5.7)
	H	1.05 ($\pm$ 0.18)	0.95 ($\pm$ 0.10)	0.94 ($\pm$ 0.27)	1.05 ($\pm$ 0.08)	1.14 ($\pm$ 0.23)	1.15 ($\pm$ 0.18)	1.46 ($\pm$ 0.10)	1.48 ($\pm$ 0.14)	1.24 ($\pm$ 0.11)	1.32 ($\pm$ 0.08)
P44	%D	51.6 ($\pm$ 4.4)	40.2 ($\pm$ 8.8)	40.3 ($\pm$ 3.6)	38.6 ($\pm$ 2.8)	45.4 ($\pm$ 4.3)	41.6 ($\pm$ 3.7)	33.5 ($\pm$ 1.4)	30.4 ($\pm$ 3.4)	58.2 ($\pm$ 3.8)	47.1 ($\pm$ 7.2)
	H	1.00 ($\pm$ 0.13)	2.09 ($\pm$ 0.09)	3.25 ($\pm$ 0.13)	3.56 ($\pm$ 0.09)	2.48 ($\pm$ 0.13)	2.71 ($\pm$ 0.09)	3.03 ($\pm$ 0.16)	3.29 ($\pm$ 0.22)	1.28 ($\pm$ 0.09)	2.47 ($\pm$ 0.06)
AL	%D	44.0 ($\pm$ 1.0)	38.8 ($\pm$ 1.8)	40.5 ($\pm$ 2.3)	52.3 ($\pm$ 6.5)	64.0 ($\pm$ 4.4)	56.4 ($\pm$ 2.1)	44.3 ($\pm$ 9.2)	57.1 ($\pm$ 0.5)	47.5 ($\pm$ 4.2)	42.8 ($\pm$ 5.6)
	H	3.35 ($\pm$ 0.01)	5.26 ($\pm$ 0.04)	1.07 ($\pm$ 0.02)	1.87 ($\pm$ 0.20)	0.98 ($\pm$ 0.30)	1.29 ($\pm$ 0.12)	2.15 ($\pm$ 0.03)	2.25 ($\pm$ 0.06)	2.81 ($\pm$ 0.04)	3.30 ($\pm$ 0.04)
TM	%D	43.5 ($\pm$ 8.5)	35.5 ($\pm$ 3.2)	40.6 ($\pm$ 2.7)	31.4 ($\pm$ 4.5)	45.6 ($\pm$ 2.3)	58.8 ($\pm$ 5.0)	50.7 ($\pm$ 0.4)	47.1 ($\pm$ 6.5)	41.4 ($\pm$ 10.2)	59.6 ($\pm$ 5.6)
	H	4.25 ($\pm$ 0.05)	7.05 ($\pm$ 0.06)	1.66 ($\pm$ 0.06)	3.05 ($\pm$ 0.09)	1.98 ($\pm$ 0.07)	3.02 ($\pm$ 0.11)	1.64 ($\pm$ 0.18)	3.00 ($\pm$ 0.11)	2.04 ($\pm$ 0.07)	2.96 ($\pm$ 0.19)

[a] Numbers in parentheses are standard errors. SUW, soils amended with SUW; OW, soils amended with OW; F, fresh amended soils; A, aged amended soils.

organic matter but also on surfaces exhibiting pH-dependent charges, on which the herbicide is easily desorbed, and therefore *H* values will be lower than those on the amended soils. This is in agreement with the study by Che et al. (*22*), who observed that under acidic conditions imazaquin adsorbed on pH-dependent surfaces from clay minerals was completely desorbed after two desorption cycles, whereas an important fraction remained adsorbed on humic acids. These pH-dependent surfaces on P44 soil are of lower affinity for the retention of the herbicide than those of the amorphous iron oxides operating on AL soil (*31*).

The original TM soil has a very small amount of amorphous iron oxides and a higher fine fraction (clay + silt) than P44 soil, and as a consequence a higher reversibility of the adsorbed imazaquin would be expected. However, this soil has the highest *H* values, showing that the adsorption of the herbicide is not occurring on pH-dependent surfaces such as those of P44 soil but mainly on the original organic matter. Molecular modeling of adsorption data of imazaquin on humic acids by Nègre et al. (*36*) showed that in addition to binding to specific sites of the humic acids, the herbicide was strongly trapped by steric hindrance, which would be the reason for the high values of *H* obtained.

The desorption pattern of imazaquin from TM soil is completely different from that on CR soil despite the adsorption of the herbicide in both soils being mainly determined by the organic matter content, but the hysteresis coefficients show a hysteretic behavior in imazaquin desorption from TM soil, unlike CR soil, indicating a higher affinity of the herbicide for the original organic matter present in TM soil than that in CR soil. This higher affinity for the original organic matter in TM soil is also clearly deduced when *H* values of the original soil and those of this soil treated with both fresh amendments are compared. *H* values decrease in fresh amended soils because adsorption of the herbicide is also occurring on sites of the added organic matter from which imazaquin molecules are more easily detached than those from the original organic matter. *H* values indicate that the aging of the added OW in this soil produces either a degraded material with a higher affinity for the herbicide than that of the freshly amended soil or a release of adsorption sites blocked just after amendment.

Leaching Experiments. Leaching experiments were performed on CR, P44, and AL soils but not on TM soil because it has an important fine fraction containing swelling clay minerals that impeded the flow of water through the column.

The shapes of the elution curves of imazaquin on original and fresh amended CR and those on P44 and AL soils are completely different (**Figure 2**). The curves are highly symmetric for CR soils, whereas for P44 and AL soils the elution curves present a very sharp ascendant part and a longer extended tail.
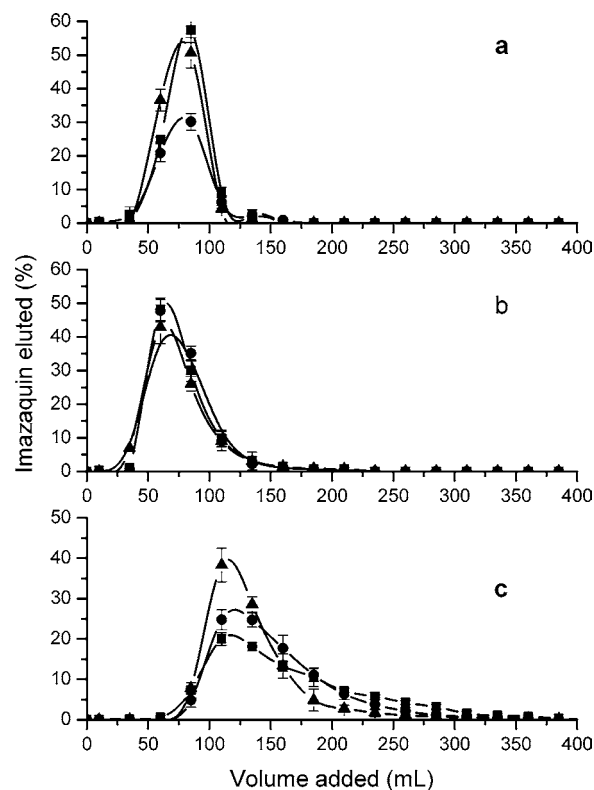

Figure 2. Breakthrough curves of imazaquin on CR (**a**), P44 (**b**), and AL (**c**) soils. The soils used were original (■) and freshly amended with OW (●) and SUW (▲).

The herbicide is almost completely eluted from the original CR soil, and when the SUW amendment is applied, the recovery percentages are 97.2 $\pm$ 0.5 and 92.8 $\pm$ 0.6%, respectively. In contrast, the total recovery of the soil where the upper layers were amended with OW was 61.0 $\pm$ 4.9%, amounting to a one-third reduction in leaching. The lower recovery of the herbicide in CR soil amended with OW may be due to some microbial degradation. Addition of compost to soils has been reported to enhance microbial degradation of the herbicides (*9*, *37*). The possibility that some amount of the herbicide was degraded instead of remaining adsorbed was checked by applying the sterilization method of the soil as in ref *38*. No statistical difference was observed in the eluted amounts of the herbicide when compared to those of the nonsterilized soil. The retained herbicide in nonsterilized OW-amended CR soil was available for plants because bioassays performed along the rings of the soil columns showed in the first and second upper layers of the soil column, respectively, 18.2 $\pm$ 1.1 and 11.0 $\pm$ 0.7% inhibitions expressed as a percent of the control.

Table 7. Percent of Imazaquin Adsorbed of the Total Amount Adsorbed after 3 Days in Batch Experiments, as a Function of Time

soil	time (h)	1.60 μM[a]	3.20 μM[a]
CR	0–24	77.8	95.0
	24–72	22.3	5.0
CR + OW	0–24	76.6	94.7
	24–72	23.4	5.3
CR + SUW	0–24	35.0	26.9
	24–72	65.0	73.1
P44	0–24	88.9	100
	24–72	11.1	0
P44 + OW	0–24	16.0	26.5
	24–72	83.0	73.5
P44 + SUW	0–24	10.0	13.9
	24–72	90.0	86.1
AL	0–24	87.5	94.4
	24–72	12.5	5.6
AL + SUW	0–24	72.8	82.1
	24–72	27.2	17.9
AL + F	0–24	67.3	81.2
	24–72	32.7	18.8

[a] Initial concentrations of the herbicide were 1.60 and 3.20 μM.

A different trend is noted in P44 soil, where there is no statistical difference between the elution percentages of imazaquin in the amended and the original soil. The elution percentages were 95.3 ± 7.6% for the original soil and 96.5 ± 0.3 and 81.8 ± 6.7% for SUW- and OW-amended soils, respectively. In the case of both amended soils, these results are again in agreement with those from the adsorption experiments, by which similar values of K_{oc} and K_d were obtained by the use of fresh amendments (**Table 5**). However, the retention of the herbicide in the columns filled with only the original soil is too low and comparable to those by using amendments, despite of its much higher adsorption (**Figure 1**). This trend, opposite to the batch adsorption data, may be explained because of a slower kinetics for the retention of the herbicide in the leaching experiments. Similar results were obtained by Worrall et al. (*39*) on their adsorption study of the herbicide isoproturon on soils and subsoils, showing that different methodologies such as batch and column techniques will reflect different kinetic processes. To assess the influence of the kinetics on imazaquin adsorption, the amount of herbicide adsorbed after 24 and 72 h was determined in batch experiments. As seen in **Table 7**, only a very small fraction of the total adsorbed amount occurred during the first 24 h on the amended P44 soils, and despite the adsorption on the original soil occurring practically within the first 24 h, the hysteresis coefficients in **Table 6** are very low, indicating almost total reversibility in the desorption of the herbicide on this soil. As a consequence, the elution pattern of the herbicide on P44 soils is well-explained by the high reversibility of imazaquin from the original soil, and that on the amended soils is explained by the low amount adsorbed in the layers filled with amended soil during the lapsed time between every elution event.

In AL soil, the elution peak is shifted to a higher elution volume, indicating a higher retention on AL soil when compared to CR and P44 soils. At the top of the elution peaks, the cumulative amounts of imazaquin eluted were 43.0 ± 2.4% for the original soil and 87.9 ± 1.0 and 54.2 ± 3.0% for the SUW- and OW-amended soils, respectively, amounting to a significant reduction in leaching in the case of the original soil and after OW amendment when compared to SUW. This sequence in the elution pattern agrees with the sorption data of the herbicide (**Figure 1**) on these soils and their H values (**Table 6**), where a higher retention is expected on the original soil and after OW

amendment because of its higher adsorption and hysteretic behavior than after SUW amendment. After 400 mL, the total leaching percentages were 85.4 ± 2.6, 100.6 ± 4.8, and 97.9 ± 4.2% for the original and SUW- and OW-amended soils, respectively.

Leaching experiments indicate that the application of organic amendments for retarded movement of the herbicide is limited to sandy soils such as CR because of their originally very low adsorptive surfaces. Consequently, the application to soils of the organic amendments used in the present study cannot be accepted as a general practice to reduce herbicide losses due to leaching processes.

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