

Effect of Two Organic Amendments on Norflurazon Sorption and Release by Soils with Different Characteristics

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The influence of two organic amendments on norflurazon sorption–desorption processes in four soils with very different physicochemical characteristics was studied in laboratory experiments to evaluate the potential leaching of this pesticide through organic amended soils. Sorption–desorption experiments were performed on original soils and on a mixture of these soils with an urban waste compost (SUW) and a commercial amendment from olive-mill wastes (OW), at a rate of 6.25% (w/w). These mixtures were used immediately after preparation and after aging for 2 months. Norflurazon was analyzed by using a HPLC method. Norflurazon retention in original soils was related not only to the organic matter (OM) content but also to mineral surfaces present in soils. Norflurazon sorption increases largely after amendment in soils with low OM content, but the addition of exogenous OM to soils with medium OM content and/or other available adsorptive surfaces did not significantly affect norflurazon sorption. Even in some cases pesticide sorption decreases, due to the blocking of the mineral and organic soil surfaces with the amendment added. Transformation of exogenous OM during incubation depends both on the amendment added and on the type of soil and can affect sorption–desorption behavior of the soils surfaces in different manner, due to the modification of their hydrophobic–hydrophilic characteristics. Norflurazon desorption from original soils showed hysteresis in all cases, but it was not affected or even decreased in amended soils. It was a nonexpected behavior, especially in sandy soil, since it is generally assumed that a higher sorption always implies a lower mobility in soils. Norflurazon sorption must be taking place on very low affinity sites on exogenous OM through weak bindings, from which the pesticide can be easily desorbed. The application to soils of the organic amendments used in the present study could not be accepted to reduce norflurazon losses due to leaching processes.

Introduction

Contamination of aquifers and other water sources by agricultural pesticides has grown considerably in the past few years (1–3). The basic problem in most cases has been a lack of understanding of the processes affecting the behavior

and fate of pesticides in the environment (4). The fate of a pesticide in the soil is governed by the retention, transformation, and transport processes and the interaction of these processes between them. The retention processes, described as sorption, can retard or prevent the pesticide movement and affect its availability for plant or microbial uptake, being one of the main processes reducing the mobility of pesticides in soils (5).

Since organic matter (OM) is known to play an important role in pesticide sorption by soils, a possible management strategy for reducing leaching would be to manipulate the sorption potential (6). The incorporation of organic residues is generally accepted as a disposal practice that recycles beneficial plant nutrients and improves physical, chemical, and biochemical properties of soils (7, 8). Many studies have shown that organic amendments used to enrich soils of low organic matter content affect sorption, and therefore mobility, of pesticides in soils (9–12). The addition of organic amendments increases insoluble and soluble organic matter into the soil. While the insoluble organic matter enhances pesticide sorption, being a good method to reduce losses due to leaching processes, some researchers have reported that subsurface transporting of inorganic and organic contaminants may be related to the movement of endogenous and/or exogenous dissolved organic matter through the soil profile (13–15).

The herbicide norflurazon is a selective herbicide effective against many annual broad-leaved weeds. Its retention in soils is related to the organic matter, being subject to considerable leaching in sandy soils with low organic matter content (16, 17). Norflurazon has been detected in studies monitoring groundwater for pesticides (18). In the case of moderately soluble organic compounds such as norflurazon (solubility 28 mg L⁻¹), it has been postulated that interactions with the water soluble organic compounds in soil may play a role in their solubility and in their ultimate ability to leach to groundwater (19, 20).

In practice, both the original composition of the organic amendments and their transformation in soils due to environmental conditions may play a large role in the characteristics of the amended soil after an aging period (21). The dynamics of exogenous OM transformations may affect the accessibility of the sorption sites on the native soil (22). Therefore, it is also of great interest to know the effect of aging on the transformation of the exogenous OM added to soils and its behavior in sorption–desorption processes of pesticides.

The aim of this study was to assess the influence of 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–desorption processes of the herbicide norflurazon by soils. To study the effect of exogenous OM evolution in such processes, aged amended soils were also used. Four soils with very different characteristics were selected, as a step to evaluate norflurazon sorption behavior and its potential leaching through these soils under different amendments.

Experimental Section

Technical grade norflurazon (N) (97.8% purity) was kindly supplied by Novartis A.G. (Base, Switzerland).

The soils used were sampled from the surface horizon (0–20 cm) and were classified as Hydromorphic Regosol (soil SR), Ultic Haploxeralf (soil P48), Typic Eutrochrept (soil AL), and Entic Pelloxerert (soil TM). The soils were dried and crushed to pass a 2 mm sieve and were analyzed for pH in

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TABLE 1. Some Characteristics of the Original Soils Used

	SR	P48	AL	TM
organic matter (g kg ⁻¹)	5.1	24.8	16.0	17.6
CEC (cmol _c kg ⁻¹)	3.5	9.5	17.2	39.0
carbonates (g kg ⁻¹)	<0.1	<0.1	<0.1	241.0
pH	6.5	5.8	7.6	8.0
coarse sand (%)	88.4	31.0	12.5	0.8
fine sand (%)	4.4	3.2	3.9	1.9
silt (%)	4.4	48.2	61.2	31.5
clay (%)	2.5	17.6	22.6	65.9
total Fe ₂ O ₃ (g kg ⁻¹)	8.3	64.2	241.7	43.9
amorphous Fe ₂ O ₃ (g kg ⁻¹)	0.3	2.7	10.8	0.8
total Al ₂ O ₃ (g kg ⁻¹)	23.7	165.1	161.0	116.4
amorphous Al ₂ O ₃ (g kg ⁻¹)	0.3	1.1	9.4	3.5
total MnO (g kg ⁻¹)	0.1	1.0	35.8	0.7
amorphous MnO (g kg ⁻¹)	<0.1	0.1	9.8	0.2

TABLE 2. Some Chemical Characteristics of the Organic Amendments^a

	OW	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	190.0	189.0
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

^a OW: olive mill wastewater; SUW: solid urban wastes.

saturated paste, total carbonate content, cationic exchange capacity (CEC), and particle size distribution. Organic matter content (OM) was determined by the dichromate oxidation method and organic carbon content (OC) was calculated as follows (23): $OC(\%) = 0.58 \times OM(\%)$.

The total metal contents of the soils were determined by dissolving the samples using a three-acid method (24), and amorphous Fe, Mn and Al oxides were determined according to McKeague et al. (25). The above indicated characteristics of the original soils used are given in Table 1.

The mineralogical composition of the soil clay fraction was determined by X-ray diffraction (XRD) using Cu K α radiation. Semiquantitative estimation of the minerals was performed using characteristic XRD reflections and their relative intensities were determined according to Schultze (26).

Two organic amendments were used: a commercial product manufactured from olive mill wastewater and other plant residues (OW) and an urban waste compost from Vilarrasa (SW Spain) (SUW). The organic amendments were dried at 70 °C for 48 h, homogenized, and crushed to pass a 1 mm sieve. The composition of the amendments is given in Table 2.

The organic carbon amendment of the soils was carried out by mixing thoroughly, during 24 h, 300 g of the original soils with 20 g of the three amendments (6.25% of the total) (from now on fresh amended soils). After preparation, fresh amended soils were autoclaved for 3 days at 120 °C (90 min per day), to avoid transformations of the organic matter added.

To study the exogenous OM evolution, incubation experiments under controlled conditions were also performed. Although it is difficult to extrapolate such experiments to

TABLE 3. Organic Matter Content (OM, g kg⁻¹) and pH of the Original and Amended Soils^a

	SR		P48		AL		TM	
	OM	pH	OM	pH	OM	pH	OM	pH
original soil	5.1	6.5	24.8	5.1	16.0	7.6	17.6	8.0
OW-F	20.7	8.1	42.8	6.7	35.9	7.5	32.1	7.6
OW-A	16.9	8.7	31.0	8.0	28.4	8.1	26.4	7.8
SUW-F	31.0	7.0	49.7	6.3	56.2	7.1	47.6	7.4
SUW-A	18.8	8.1	34.0	7.5	30.2	8.2	26.7	7.6

^a SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.

field conditions, they may help to understand the effects that aging can produce on exogenous OM. The amended soils were maintained under constant humidity at field capacity during 2 months at 30 °C (from now on aged amended soils). Aged amended soils were autoclaved for 3 days at 120 °C (90 min per day) in order to stop the organic matter transformation. The pH and organic matter content of the amended soils were measured before and after aging (Table 3).

Quadruplicate sorption experiments were done by mixing 10 g of the soils with 20 mL of 0.01 M Ca(NO₃)₂ solutions, containing various concentrations (4, 8, 12, 16, 20 mg L⁻¹) of norflurazon, in 50 mL polypropylene centrifuge tubes. The samples were shaken for 24 h at 20 ± 1 °C. This time of reaction was chosen from preliminary kinetic studies (not shown). After shaking, the suspensions were centrifuged, and the concentration of norflurazon in the supernatant was determined by using a HPLC equipped with fluorescence detector, by the method described by Willian and Mueller (27). The difference in pesticide concentration between the initial and final equilibrium solutions was assumed to be due to sorption, and the amount of norflurazon retained by the soils was calculated.

Desorption experiments were performed on original and aged amended soils after sorption equilibrium was reached for the points corresponding to norflurazon initial concentrations of 4, 12, and 20 mg L⁻¹, by removing half of the supernatant after centrifugation, replacing it by 10 mL of 0.01 M Ca(NO₃)₂ solution, allowing equilibration for an additional 24-h 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 ($\mu\text{mol kg}^{-1}$) is the amount of herbicide sorbed at the equilibrium concentration C_e ($\mu\text{mol L}^{-1}$), 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 (10 $\mu\text{mol L}^{-1}$) and also organic carbon (OC) normalized distribution coefficient (K_{oc}). K_{oc} is often used in the discussion of sorption of nonpolar hydrophobic compounds, being the concept compatible with the idea of OC having the same affinity for a nonpolar compound, independent of the source of OC.

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

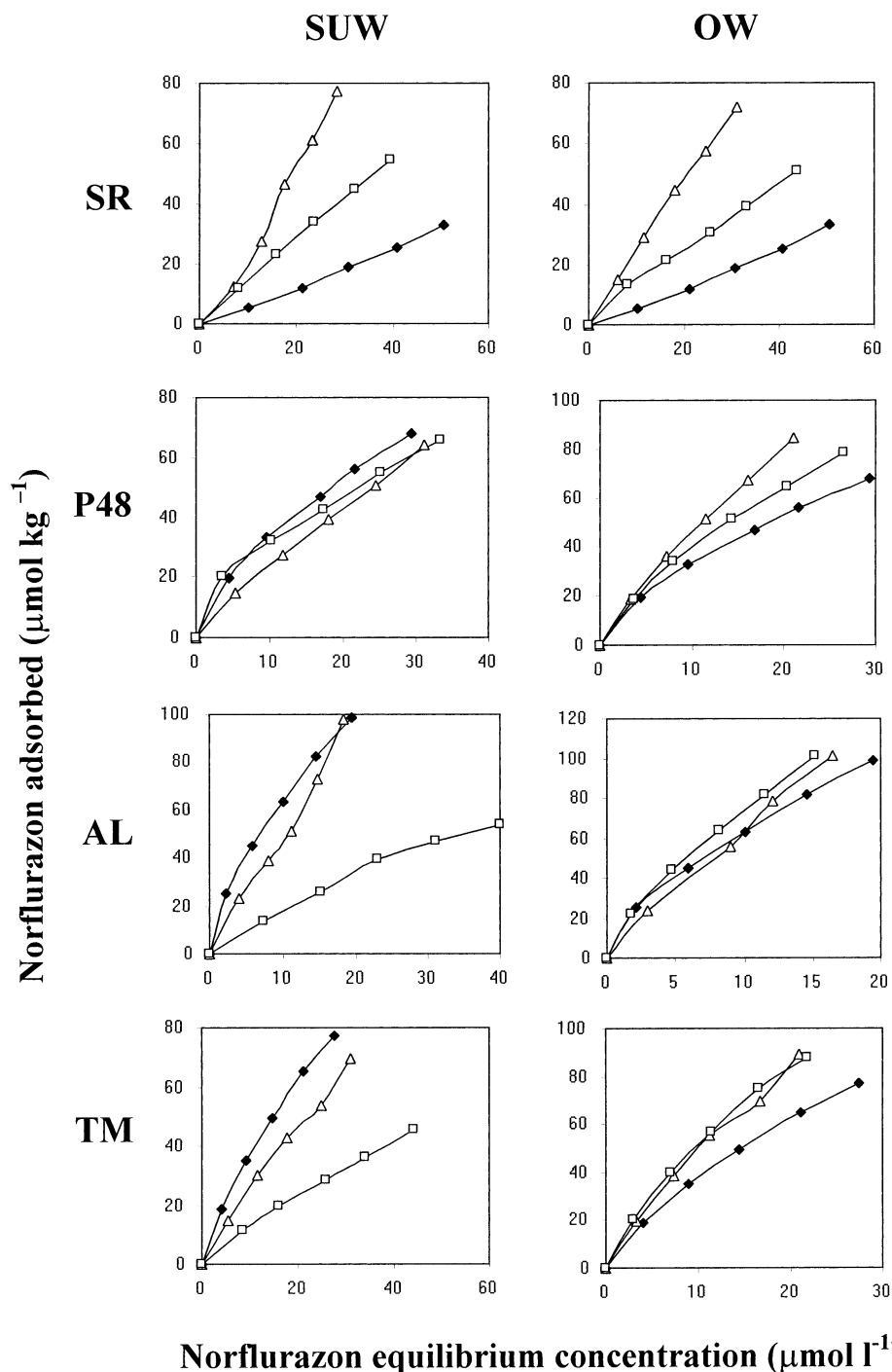


FIGURE 1. Norflurazon adsorption isotherms on original (◆), fresh amended (□), and aged amended (△) soils with SUW and OW.

(28). This ratio n_a/n_d has been also used by other authors to describe the hysteretic behavior of desorption from soils (29, 30).

Results and Discussion

Sorption Experiments on Original Soils. Figure 1 shows the sorption isotherms of norflurazon on the original soils SR, AL, P48, and TM and on these soils after amendment, both used just after mixing and after incubation for 2 months. In all cases norflurazon sorption isotherms were well described by the linearized Freundlich relationship. The sorption isotherms were compared using the K_f parameter of the Freundlich equation (Table 4). The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1

$\mu\text{mol L}^{-1}$. Sorption of norflurazon on the original soils increased in the following order:

$$\text{SR} < \text{P48} < \text{TM} < \text{AL}$$

K_f values ranged largely from 0.35 to 15.54 $\mu\text{mol kg}^{-1}$, indicating that they were probably influenced by soil properties, because of differences in organic matter, soil pH, cation exchange capacity, and textural fractions (Table 1).

Although norflurazon sorption has been previously related to the OM content of soils (17), the higher sorption was obtained in AL soil, despite soil P48 being that of higher OM content in our study. The herbicide sorption on TM soil is even slightly higher than on P48, despite its lower OM content.

TABLE 4. Freundlich Adsorption Isotherms Parameters (K_f and n Values) for Norflurazon Sorption on the Soils Used^a

	SR		P48		AL		TM	
	K_f	n	K_f	n	K_f	n	K_f	n
original soil	0.35 (±0.02)	1.15 (±0.02)	6.56 (±0.18)	0.65 (±0.01)	15.54 (±0.54)	0.61 (±0.02)	7.34 (±0.25)	0.75 (±0.01)
OW-F	2.83 (±0.14)	0.94 (±0.02)	7.12 (±0.15)	0.81 (±0.01)	9.32 (±0.83)	0.84 (±0.04)	7.70 (±0.53)	0.80 (±0.03)
OW-A	2.52 (±0.29)	0.78 (±0.04)	7.14 (±0.26)	0.73 (±0.01)	14.78 (±0.22)	0.70 (±0.01)	9.25 (±0.40)	0.74 (±0.02)
SUW-F	1.99 (±0.16)	1.31 (±0.06)	5.64 (±0.20)	0.82 (±0.02)	5.91 (±1.06)	0.93 (±0.08)	3.36 (±0.31)	0.88 (±0.03)
SUW-A	1.57 (±0.02)	0.97 (±0.01)	6.79 (±0.85)	0.53 (±0.03)	2.64 (±0.41)	0.83 (±0.05)	2.01 (±0.08)	0.82 (±0.01)

^a Numbers in parentheses are standard errors. The coefficients of determination (R^2) were higher than 0.994 in all cases. SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.

TABLE 5. Distribution (K_d) and Organic Carbon Normalized Distribution Coefficients (K_{oc}) for Norflurazon Sorption on the Original and Amended Soils^a

	SR		P48		AL		TM	
	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
original soil	0.51 (± 0.05)	174 (± 19)	3.35 (± 0.14)	233 (± 9)	6.43 (± 0.43)	691 (± 46)	3.70 (± 0.27)	363 (± 26)
OW-F	2.49 (± 0.22)	207 (± 18)	4.60 (± 0.18)	185 (± 8)	6.51 (± 0.50)	313 (± 24)	5.29 (± 0.39)	285 (± 20)
OW-A	1.53 (± 0.14)	157 (± 15)	3.88 (± 0.27)	216 (± 16)	7.46 (± 0.23)	452 (± 14)	5.09 (± 0.44)	333 (± 28)
SUW-F	2.05 (± 0.16)	114 (± 9)	2.44 (± 0.25)	85 (± 9)	5.69 (± 0.61)	174 (± 19)	2.55 (± 0.15)	92 (± 6)
SUW-A	1.46 (± 0.03)	134 (± 3)	2.20 (± 0.37)	111 (± 19)	1.81 (± 0.26)	103 (± 15)	1.33 (± 0.09)	86 (± 6)

^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.

It indicates that OM content may not be the only factor determining norflurazon sorption in these soils (16).

The role of hydrophobic bonds on nonpolar hydrophobic herbicides sorption on organic matter of soils can be compared by normalizing the distribution coefficient, K_d , to the percentage of organic C of the different samples (from now on K_{oc}). K_{oc} can be used as a measure of the probability for partition from the aqueous phase to the organic phase in soils and it is independent of other soil properties. When hydrophobic bonds are responsible for the adsorption of a herbicide, K_{oc} values must be more or less constant among different soils.

The estimated distribution coefficients, K_d and K_{oc} , are shown in Table 5. K_d values for herbicide sorption on original soils ranged between 0.51 for SR and 6.43 for AL soil. Such a wide range of K_d values suggest weak to moderate binding capacity of these soils for norflurazon. K_d and K_{oc} values found in this study were similar to those reported by other authors. Reddy et al. (16) found K_d values between 0.63 and 2.2. Similar results were obtained by Hubbs and Lavy (31), with K_d values ranging from 0.54 to 2.75. Alva and Singh (32) observed a K_d value of 16 in the case of norflurazon sorption on a soil with an OM content of 3.4%; however, K_d presented values between 0.4 and 2.3 in soils with OM content below 1.4%. Suba and Essington (33) obtained K_d values between 2.04 and 12.15.

Although the K_{oc} mean value given for norflurazon is 248 L kg⁻¹ (34), the values obtained in this study for original soils ranged from 174 to 691 L kg⁻¹. Lower values were observed by Reddy et al. (16) (K_{oc} from 144 to 373), Hubbs and Lavy (31), with an average K_{oc} of 78, and Alva and Singh (32) (average K_{oc} of 122). Suba and Essington (33) reported higher K_{oc} values (ranging from 456 to 551) which did not vary greatly with soil OC content, illustrating the influence of this parameter on norflurazon sorption. In our case, K_{oc} values are not so similar among them, indicating that sorption mechanism is perhaps related to some soil properties other than hydrophobic bounds to OM, although it is important to take into account that the quality, rather than the quantity, of the organic matter is one of the most important sources of variability in the sorptive interactions.

Soil AL presented the higher K_{oc} value (691), even higher than those found in the literature. This soil presents very

high oxides content and also a high amount of amorphous oxides (Table 1), which have a large surface area, and they can be good sorptive surfaces for norflurazon.

In relation to the size particle distribution, soils AL and TM, which show the highest K_d values, also have a high percentage of silt and clay fractions (83.8 and 97.4%, respectively), presenting high surfaces for herbicide sorption. Moreover, soil TM presents a high clay minerals content, including illite, kaolinite, and, in a higher proportion, smectite, and according to Reddy et al. (16) and Hubbs and Lavy (31), clay minerals content was also correlated with norflurazon sorption in soils. On the other hand, in the case of soil P48, although the percentage of clay fraction was much lower in this soil than in TM soil, its colloidal fraction is composed primarily of phyllosilicates, especially illite and kaolinite (35), which could contribute together with the OM content in P48 to norflurazon sorption.

We have determined the influence of the different soil properties (OM, CEC, carbonates, pH, and amorphous oxide contents of Fe, Al, and Mn) and the textural soil fractions on norflurazon sorption by using 17 different soils, to apply a statistical approach. Multiple linear regression analysis was used to identify predictive equations for norflurazon adsorption affinity (expressed as its distribution coefficient, K_d) as a function of the properties of the soils used (data not shown). The significant variables for prediction of K_d values were organic matter and the iron and aluminum oxides content. Among these soil properties, the organic matter content was the most significant variable accounting for 85% of the variability. By including iron and aluminum oxide contents, resulting multiple regression equations gave an 11% increase in evaluation accuracy compared with evaluation on organic matter alone.

Sorption on Fresh and Aged Amended Soils. Table 3 shows the changes of OM content and pH of the soils just after amendment with SUW and OW and after incubation. The pH values of the fresh amended soils were higher than the unamended soils due to the basic pH of the amendments added. After incubation for 2 months, the OM content decreases in all soils, due to the increase of microbial activity of the soil as a consequence of the incubation conditions,

although it is higher than in original soils. The pH increases slightly practically in all the cases.

Norflurazon sorption isotherms on fresh and aged amended soils are also shown in Figure 1. Amendment addition to the different soils give as a result different behaviors depending on the type of amendment and on the soil.

In the case of SR soil, both amendments added increased norflurazon retention, both in fresh and aged amended soil. Amendments effects were especially prominent in this soil used just after amending, increasing K_f values from 0.35 to 1.57 and 2.83 for SUW and OW treated soils, respectively. This is due to the increase in its OM content of SR soil after amendment (Table 3), which was 4-fold and 6-fold higher after the addition of OW and SUW, respectively. K_f values decreased a little for aged amended soils, in which OM content has decreased too (Table 3). The n values obtained for SR soil are close to one, suggesting linear sorption. An n value near 1 is indicative of compounds retained by partitioning into the organic fraction of the soil (36). K_{oc} values in this soil SR did not vary greatly before and after amendment with OW, and also after aging, (Table 5), corroborating that sorption of the herbicide on this soil depends on the OM content. However, when the amendment used was SUW, K_{oc} values are lower, and it seems to indicate that the exogenous OM added with SUW has a lower sorption capacity than OW for norflurazon, that is, the nature of the organic amendment used has to be taken into account, since not all OM has the same effectiveness for herbicide sorption. This behavior was also observed in the other three soils after amendment with SUW, since K_{oc} values obtained were always lower than those obtained when OW is used (Table 5).

In the case of P48 soil, Figure 1 shows that, in general, norflurazon sorption is very similar for original, fresh, and aged amended soils with SUW, despite the increased OM content of the amended soil (Table 3). It indicates that the addition of SUW does not give new sorption sites for norflurazon on P48 soil, and it is reflected also in the lower K_{oc} values obtained. However, when OW is used, norflurazon sorption increases in fresh and aged amended soil, and K_{oc} values did not vary greatly with that of original soil, suggesting that OM content of these OW amended soils is controlling the herbicide sorption.

The sorption of norflurazon on AL soil amended with OW and SUW (Figure 1) is not different from that of the original soil, except in the SUW aged amended soil, which will be discussed latter. It indicates that the addition of both amendments does not affect the norflurazon sorption, and the adsorptive surface of this soil continues to be available for the herbicide, despite the presence of the amendments.

However, norflurazon sorption behavior observed in aged amended AL soil was very different, since there was a reduction of about 50% of herbicide sorption. The same behavior was also observed in SUW aged amended TM soil. Among different possible reasons that could explain this behavior, one of them is the different degradation rate and different qualitative transformation of the OM added depending on the type of soil. It is probable that the OM obtained after incubation with soils AL and TM has a different hydrophobicity than that obtained from soils SR and P48. This OM degraded can be sorbed on certain soil components which were acting previously as surfaces available for norflurazon sorption. It could modify the hydrophobic–hydrophilic characteristics of the soil surfaces, decreasing the number of adsorption sites for the herbicide and giving as a result a lower herbicide sorption.

Norflurazon sorption on TM soil was very different depending on the amendment added. When SUW was used, the herbicide sorption was lower than in original soil, both in fresh and in the aged amended soil. But when the soil was

amended with OW, the sorption was higher than in the original soil in all cases, and K_{oc} values obtained were also similar among them (Table 5), indicating that OM was the principal factor responsible for norflurazon sorption in TM soil. However, K_{oc} values in fresh and aged TM amended soil with SUW were very low, indicating that the addition of such amendment on this soil impeded in part the herbicide sorption, due to the covering of the soil highly adsorptive surfaces, and therefore, K_{oc} values are not correct, since sorption is not correlated with the higher OM content of the amended TM soil.

In general, SUW supplied to the four soils gave an OM with a lower available surface for norflurazon sorption than OW amendment. SUW addition decreased the herbicide sorption, since much of the mineral and organic soil surfaces were blocked, with the exception of the sandy soil which had originally very low adsorptive surfaces.

Desorption Experiments. Figure 2 shows the sorption–desorption isotherms of norflurazon corresponding to original soils and aged amended soils. Desorption isotherms were also described by the Freundlich equation, and hysteresis coefficients were calculated using “ n ” Freundlich constant. In Table 6 the percentage of norflurazon desorbed (%D) and hysteresis coefficients (H) are shown.

Norflurazon desorption from original soils was hysteretic in all cases but especially in TM soil, which presents the higher H values (Table 6). In general, norflurazon sorption on original soils is more irreversible (lower %D) at low concentrations adsorbed (desorption from an initial concentration of 4 mg L⁻¹), showing high hysteresis coefficients (Table 6). That is, norflurazon molecules are more strongly sorbed at low surface coverage, and, consequently, it is more difficult to desorb them. This behavior is not observed when the soils have been amended with SUW and OW, indicating that when a low amount of norflurazon is sorbed on the soils, it is easier to release it from soils previously amended than from the original ones.

Desorption behavior is different depending not only on the soil but also on the amendment used. Norflurazon desorption from SR soil reveals a nonexpected behavior, since the amount of herbicide desorbed increases in the presence of both amendments (Figure 2). That is, the higher the OM content the higher the amount of norflurazon desorbed. %D is higher in amended than in original soil, and, consequently, there is less hysteresis, as it is demonstrated by the lower H values (Table 6). Even in this soil amended with OW norflurazon sorption was almost completely reversible, since desorption points fall on or near the line estimated from the sorption points. Sandy soils are frequently treated with organic amendments to enrich them in OM and to promote herbicide sorption for reducing pesticide contamination of groundwater (7–10), and it is assumed that a higher sorption always implies a lower mobility. In the current work we demonstrated that it is not always true, but it is dependent on the type of surface of the soil interacting with the pesticide. It can be explained by considering the nonionic nature of norflurazon which would bind to the organic matter by means of a hydrophobic mechanism. Although the amount of norflurazon adsorbed is higher than in the original soil, if sorption on amended soil takes place on the external coatings of OM through weak hydrophobic interactions, the desorption process can easily remove the pesticide.

The amendment with SUW and OW of soil P48 does not affect to the desorption behavior of norflurazon (Figure 2), being the values %D and H very similar between the original and the amended soils. It is in agreement to the sorption behavior previously observed, which practically was not affected by the presence of organic amendments.

Soils AL and TM amended with SUW showed a special behavior, since norflurazon sorption is highly reversible, even

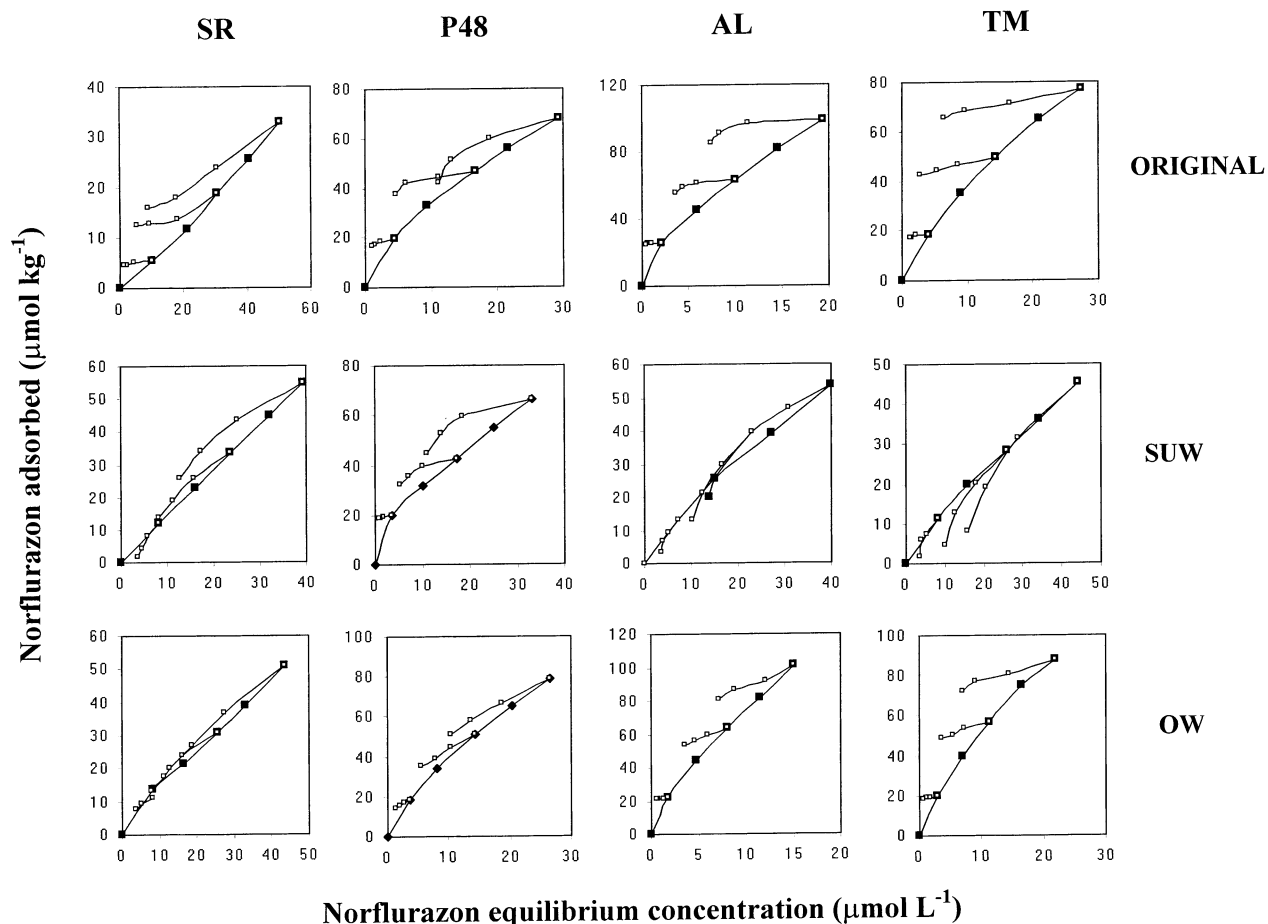


FIGURE 2. Norflurazon adsorption–desorption isotherms on original and aged amended soils with SUW and OW.

TABLE 6. Percentage of Norflurazon Desorbed (%D) and Hysteresis Coefficients (*H*) for Original and Aged Amended Soils^a

desorptions		original			SUW			OW		
		4	12	20	4	12	20	4	12	20
SR	%D	12.3 (±0.6)	34.0 (±1.2)	48.5 (±1.1)	77.5 (±6.6)	59.1 (±5.0)	52.8 (±1.4)	44.5 (±1.5)	56.3 (±2.8)	60.2 (±2.1)
	<i>H</i>	17.3 (±0.03)	5.3 (±0.03)	2.8 (±0.10)	0.4 (±0.02)	1.1 (±0.14)	1.5 (±0.15)	1.5 (±0.13)	1.1 (±0.12)	1.0 (±0.05)
P48	%D	14.4 (±0.5)	20.5 (±0.5)	38.5 (±2.6)	7.2 (±1.4)	24.5 (±1.7)	32.2 (±2.2)	21.4 (±1.1)	29.8 (±1.5)	34.5 (±1.9)
	<i>H</i>	1.0 (±0.02)	2.6 (±0.01)	1.4 (±0.08)	2.3 (±0.04)	2.3 (±0.07)	1.6 (±0.10)	1.4 (±0.05)	1.0 (±0.05)	0.9 (±0.02)
AL	%D	2.0 (±0.4)	11.7 (±1.4)	13.7 (±1.1)	73.2 (±9.3)	66.9 (±2.7)	75.6 (±8.3)	6.5 (±0.9)	15.2 (±1.5)	20.2 (±1.1)
	<i>H</i>	18.9 (±0.03)	3.3 (±0.04)	2.2 (±0.07)	0.8 (±0.09)	0.6 (±0.08)	0.5 (±0.08)	0.2 (±0.01)	3.4 (±0.01)	2.5 (±0.04)
TM	%D	8.2 (±0.3)	13.8 (±0.9)	15.3 (±1.0)	83.8 (±1.8)	98.4 (±5.7)	82.0 (±8.8)	7.5 (±0.8)	14.7 (±1.6)	17.6 (±1.7)
	<i>H</i>	19.5 (±0.02)	8.2 (±0.01)	6.9 (±0.02)	0.9 (±0.07)	0.5 (±0.06)	0.5 (±0.04)	10.2 (±0.03)	5.3 (±0.04)	4.6 (±0.04)

^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.

more than expected from the sorption isotherm, giving as a result a negative hysteresis ($H < 1$) (Table 6). This table also shows a high increment of percent desorbed (%D): in original soils, the maximum amount desorbed was 13.7% and 15.3% for AL and TM soils, respectively; but in SUW amended soils the percent desorbed increases until 75.6% and 98.4% for AL and TM soils, respectively. It is in agreement and corroborates our previous observation in norflurazon sorption process on AL and TM aged amended soils, which decreased very much due to the transformation of the OM from SUW during

incubation period. The surfaces where norflurazon was sorbed in these aged amended soils have a lower amount of adsorption sites, as it was observed before, but also these new surfaces have hydrophobic–hydrophilic characteristics different to those of the pesticide norflurazon, taking place its sorption on very low affinity sites through weaker bindings, so norflurazon can be easily desorbed.

Norflurazon desorption from AL and TM soils amended with OW is totally different, since practically it is not affected by the amendment. It can be clearly observed in Table 6

where both %D and H have similar values in original and RF amended soils. This behavior is similar to that observed for P48 soil with and without amendment, and it is in relation to the sorption behavior observed in AL and TM soils before and after treatment with OW, in which almost no variations in sorption was observed.

From results obtained from P48, AL, and TM soils it can be concluded that, in these soils with medium-high OM content and/or significant amounts of other available surfaces for pesticides sorption, the addition of exogenous OM scarcely affects their sorption-desorption behavior (unless a degradation of the exogenous OM and covering of the adsorptive surfaces can take place, as probably occurs in AL and TM soils after amendment and incubation with SUW).

Thus it is not possible to generalize, as is often the case, by considering the content in organic matter as the parameter responsible for the sorption of pesticides by soils from an aqueous medium. The application to soils of the organic amendments used in the present study could not be accepted to reduce norflurazon losses due to leaching processes, since the amounts desorbed are higher in amended than in nonamended soils.

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