Significance of Soil Properties in the Adsorption and Mobility of the Fungicide Metalaxyl in Vineyard Soils

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Adsorption and mobility of the fungicide metalaxyl were studied in 16 vineyard soils from the La Rioja region (Spain), with organic matter (OM) contents in the 0.31–1.37% range, and in 7 natural soils with OM contents in the 3.30–8.24% range. Adsorption isotherms were obtained using the batch equilibrium technique, and mobility was studied by soil thin-layer chromatography (soil-TLC). In all cases, the adsorption isotherms fit the Freundlich equation. The values of the K_f constants were low in the vineyard soils (0.01–0.64) and increased in the natural soils (1.05–2.83). The n_f values were in general lower than unity. K_f constants were significantly correlated ($p <$ 0.001) with the OM content when all of the soils were considered. According to the determination coefficient, r^2, OM would account for 88% of the variance in adsorption. When the vineyard soils alone were considered, a significant correlation was seen between K_f and the OM and clay contents; both parameters, varying simultaneously, explain 80% of the variance in adsorption. Study of the mobility of metalaxyl with soil-TLC indicated that in vineyard soils the fungicide has the potential for being highly mobile in 19% of the soils and mobile in 81% of them. In natural soils, the fungicide has the potential for being moderately mobile or mobile in 86 and 14% of the soils, respectively. This type of behavior of metalaxyl indicates that in vineyards soils of the La Rioja region (Spain) with low OM contents, where application of the compound is continuous, a leaching of the fungicide from the soil to groundwaters could potentially occur. These results should be borne in mind when metalaxyl is to be used in the soils of this region.

INTRODUCTION

Metalaxyl [methyl *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-DL-alaninate] is a fungicide with residual and systemic activity used to protect crops against diseases due to pathogens of the orders Peronosporales (*Peronospora*, *Pseudoperonospora*, *Plamopara*, and *Bremia*) and Pythiales (*Pythium* and *Phytophthora*) (*1–3*). It was introduced by Ciba-Geigy in 1977 and is used as a foliar fungicide and as a soil fungicide. It is a stable compound that is resistant to a broad range of pH, temperature, and light (*4*). Because of these properties and its broad-spectrum activity, metalaxyl is registered in many areas of the world such as the United States, Europe, Australia, and India, and its use in agriculture is very frequent in many types of fruits and vegetables, including vineyards (*5*).

In a recent review carried out on the behavior of metalaxyl in soils, Sukul and Spiteller (*5*) concluded that this compound could migrate to deeper soil horizons and reach underground waters especially in soils with low organic matter (OM) contents. However, other studies monitoring groundwater and drinking water included in this review (*6*) have reported that metalaxyl appears in groundwater only rarely and at levels well below 0.1 μg L^{-1}. According to these observations Sukul and

Spiteller (*5*) recommended that precautions be taken in the continued application of metalaxyl to crops and also indicate that if the use of metalaxyl is greatly increased, the risk of its occurrence in groundwater should be reassessed in the most vulnerable areas of the main regions of use.

In the La Rioja region (northeastern Spain), fungicides are extensively used in vineyards, which represent 10.5% of the total area cultivated (48288 ha) in the region, with metalaxyl one of the most widely used fungicides. Despite its extensive use, there are no studies on the behavior of this compound in the soils of the region or on the possible pollution of the groundwaters of the zone even though most municipalities use this as a source of drinking water.

Studies have been published on the adsorption and mobility of metalaxyl, but these have always been conducted in a small (three to five) number of soils and have indicated low adsorption and high mobility of the compound and the relationship of these processes to the organic matter content of the soils (*7–9*). However, more recently, Sukop and Cogger (*10*) and Sharma and Awasthi (*11*) highlighted the importance of the soil mineral fraction in metalaxyl adsorption. Studies monitoring the fungicide under field and laboratory conditions aimed at determining its degradation and leaching in the soil point to considerable variability in the persistence of metalaxyl in that medium (*12, 13*). Thus, the results of the studies carried out to date seem to show that the effects of soil properties on the behavior of metalaxyl remain in this system unclear.

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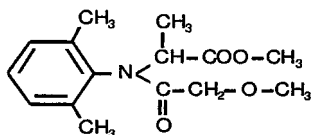
Figure 1. Chemical structure of metalaxyl.

In light of the foregoing, and as a contribution to knowledge about the possible environmental impact of prolonged application of this fungicide to the soils of the La Rioja region, we decided to study the adsorption and mobility of metalaxyl as the main processes that govern the behavior of a pesticide in soils (*14*, *15*) in 23 soils from this region. The use of such a relatively large series of soils with different compositions should also allow us, through a statistical approach, to establish the soil parameters that mainly affect the adsorption and mobility of the compound and to broaden our knowledge of the effects of soil properties on both processes. Of the 23 soils studied, 16 were devoted to vineyard culture and in general had a sandy-loam or sandy-clay-loam texture, a low OM content (<2%), and a high or medium carbonate content. The other 7 soils were natural soils with a higher OM content (3.30−8.24%). The latter soils were included in the study in view of the importance of this parameter (OM) in the adsorption and mobility of pesticides (*16*). We also studied the adsorption of the fungicide by modeling individual components of the soil, clay minerals, and humic acid because of the importance of the nature of the soil colloidal fractions in these processes (*17*, *18*).

MATERIALS AND METHODS

Pesticide. Unlabeled metalaxyl (>97% technical purity) and labeled metalaxyl (*phenyl*-^{14}C) with a specific activity of 1.37 MBq mg^{-1} (97.2% purity) were supplied by Novartis Crop Protection AG (Basel, Switzerland). Metalaxyl is a solid compound with a water solubility of 8.4 g L^{-1} at 22 °C and a log K_{ow} of 1.75 (*19*). Its chemical structure is shown in Figure 1.

Soils. Table 1 shows the types of soils used and certain selected characteristics. Soils 1−16 were from different vineyard areas of the La Rioja region, whereas soils 17−23 were

natural uncultivated soils from the same region. The vineyard soils are remarkably alkaline. The natural soils, with a higher OM content, were included in the study to shed further light on the influence of OM in the adsorption and mobility of the pesticide because the OM content of the vineyard soils was very low (0.31−1.37%). Soil samples (0−15 cm) were air-dried and sieved through 2 mm mesh. Their particle size distribution was determined using the pipet method (*20*). Organic carbon was determined according to a modified version of the Walkley−Black procedure (*21*), the results being multiplied by 1.72 for conversion into OM contents. Soil pH values were measured in slurries made up at a 1:1 soil/water ratio. Inorganic carbon (as CaCO$_3$) was determined using a Bernard calcimeter.

Samples of Tidinit montmorillonite (M) (Morocco) (*22*), Beni-Buxera vermiculite (V) (Morocco) (*23*), Illite-35 (I) (Fithian, Illinois) (*24*), and Cuenca kaolin (K) (Spain) (*25*) and a commercial humic acid from Fluka (HA) (Fluka AG, Buchs, Switzerland) were also used. The percent composition of the humic acid was as follows: C, 47.1%; H, 3.61%; N, 0.33%; ash, 5.28%. Samples saturated with Ca^{2+} cation were obtained according to the methods of González-García and González-García (*26*) and Khan (*27*).

Adsorption. Adsorption experiments were carried out by the batch equilibration technique with [14C]metalaxyl. Duplicate 5 g soil samples or 50 mg clay or humic acid samples were equilibrated with 10 mL of 0.01 N CaCl$_2$ aqueous solutions containing 20, 30, 40, 50, and 60 μg mL^{-1} of the pesticide and a solution activity of 75 Bq mL^{-1}. The suspensions were kept at 20 ± 2 °C for 24 h in a thermostated chamber with intermittent shaking (2 h every 4 h). Preliminary experiments revealed contact for 24 h to be long enough for equilibrium to be reached. Subsequently, the suspensions were centrifuged at 3300 rpm for 30 min. To determine metalaxyl concentration, a 1.0 mL aliquot of supernatant was then withdrawn from each tube and added to 4.5 mL of scintillation liquid and its activity was measured in disintegrations per minute (dpm) on a Beckman LS 1800 liquid scintillation counter. The dpm recorded for the supernatant aliquot was related to the dpm obtained for the aliquots of the respective standards of metalaxyl solutions, and the metalaxyl equilibrium concentration was determined. The amount of pesticide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil.

The adsorption data were fitted to the linearized form of the Freundlich equation: log C_s = log $K_f + n_f$ log C_e, where C_s (μg g^{-1}) is the amount of adsorbed fungicide, C_e (μg mL^{-1}) is the equilibrium concentration of fungicide in solution, and K_f

Table 1. Selected Characteristics of the Soils

soil	soil texture	soil type	pH	OM (%)	sand (%)	silt (%)	clay (%)	CaCO$_3$ (%)
			Vineyard Soils					
1		Calcixerollic Xerochrepts	8.8	0.31				35.5
2		Calcixerollic Xerochrepts	8.6	1.22				38.1
3		Calcixerollic Xerochrepts	8.6	1.27				31.8
4		Typic Xerochrepts	8.6	1.37				25.8
5	sandy clay loam	Typic Xerochrepts	8.7	0.66	63.9	11.6	24.5	12.2
6	loam	Fluventic Xerochrepts	8.5	0.61	36.0	40.5	23.5	18.0
7	sandy clay loam	Calcixerollic Xerochrepts	8.6	1.02	65.3	12.3	22.4	14.2
8	sandy loam	Fluventic Xerochrepts	8.1	0.51	80.0	7.8	12.2	4.3
9		Petrocalcic Palexeralfs	9.0	0.81				22.6
10	sandy clay loam	Calcixerollic Xerochrepts	8.6	1.17	48.6	17.5	33.9	19.5
11	sandy loam	Petrocalcic Xerochrepts	8.7	1.07	79.5	7.8	12.7	11.9
12	clayed loam	Calcixerollic Xerochrepts	8.6	0.66	44.4	22.3	33.3	10.1
13		Typic Xerochrepts	8.8	1.07				32.0
14		Calcixerollic Xerochrepts	8.7	1.17				40.0
15		Typic Xerofluvents	8.7	0.66				36.0
16	sandy clay loam	Calcic Haploxeralfs	8.4	0.81	52.4	22.3	25.3	4.5
			Natural Soils					
17		Typic Eutrochrepts	8.3	4.93				27.1
18	sandy clay loam	Typic Eutrochrepts	7.6	5.29	44.7	19.6	35.7	3.8
19	sandy clay loam	Dystric Eutrochrepts	6.8	3.30	63.4	11.4	25.2	0.0
20	loam	Typic Eutrochrepts	5.0	4.47	43.4	41.3	15.3	0.0
21		Typic Eutrochrepts	8.0	8.24				23.5
22	loam	Dystric Eutrochrepts	7.1	4.37	41.9	28.8	29.3	0.0
23	loam	Typic Dystrochrepts	5.3	4.83	50.4	32.0	17.7	0.0

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(μg^{1-n_f} mL^{n_f} g^{-1}) and n_f are two characteristic constants of the pesticide adsorption capacity. Distribution coefficients, K_d, and adsorption coefficients normalized to OM (K_{om}) were also calculated. K_d is the relationship between the amount of fungicide in the soil and in the equilibrium solution for a given equilibrium concentration, and K_{om} is the K_f value normalized to 100% organic matter ($K_{om} = 100 \times K_f$/% OM).

K_f and K_d values were subjected to analysis of variance, and the least significance difference (LSD) was determined to find significant differences among K_f values and among the K_d values of the different soils at the 5% significance level.

Soil Thin-Layer Chromatography (Soil-TLC). Soil plates for TLC were prepared by grinding the soil samples in a mortar followed by sieving through 160 μm mesh. Soil (7.5 g) and distilled water (15 g) were slurried and spread as a 0.5 mm thick layer over 20 × 5 cm² glass plates with the aid of a Desaga TLC spreading device. The three central plates in each set of five used for each type of soil were chosen for subsequent experiments. The selected plates were dried in a chamber at room temperature and subsequently stored in a desiccating chamber at a relative humidity of 70%. The plates were marked with two horizontal lines at distances of 2 and 12 cm, respectively, from the base. A 5 μL droplet of [^{14}C]-metalaxyl (380 Bq and 0.2 μg) was spotted onto the baseline of the three plates with the aid of a micropipet. The plates were placed in closed individual glass chromatography chambers 22 cm long and 5 cm wide, using distilled water as the developer. After the distilled water had migrated to a distance of 10 cm from the baseline, the plates were dried at room temperature. The movements of [^{14}C]metalaxyl were detected using a Berthold TLC Tracemaster 20 linear analyzer. The mobility factor, R_f, is given by $R_f = R_d/10$, where R_d is the frontal distance traveled by the fungicide.

RESULTS AND DISCUSSION

Soil Adsorption Studies. Figure 2 shows the adsorption isotherms of metalaxyl for all of the soils studied. These isotherms fit the Freundlich adsorption equation, with $r \geq 0.98$ values. The parameters K_f and n_f determined from that equation are shown in Table 2. K_f is the amount of fungicide adsorbed at an equilibrium concentration of 1 μg mL^{-1} and hence represents adsorption at low concentrations, and n_f reflects the variation in adsorption with the concentration.

In general, the n_f values are lower than unity, in agreement with the L shape of the isotherms (initial curvature concave) according to the classification of Giles et al. (*28*). These isotherms indicate high affinity of the adsorbent for the adsorbate, it being increasingly harder to find sites vacant for adsorption as the concentration increases. In some soils with low OM contents, the n_f values are higher than unity, the isotherms obtained being of the S-type (initial curvature convex). This indicates a strong competition by water molecules for adsorption sites at low fungicide concentrations. Nonlinear isotherms are frequently found in the literature addressing studies of the adsorption of organic compounds with polar groups by soils and their components (*29, 30*). According to Spurlock and Biggar (*31*), this lack of linearity must be due to the specific interactions that can exist between these compounds with polar groups and the OM or the mineral fraction of the soil.

The K_f values ranged between 0.01 ± 0.00 and 2.83 ± 0.10, the lowest values corresponding to soils with the lowest OM or clay contents (soils 1 and 8) and the highest ones to soils 18 and 21, with the highest OM and clay contents. The K_f values for all of the vineyard soils were lower than those found for the natural soils.

The coefficients of distribution, K_d, were determined for a $C_e = 20$ μg mL^{-1} (Table 2). These coefficients are often determined in adsorption studies when the n_f values depart from unity (*32*) in order to know the adsorption of the pesticide by the soils at an equilibrium concentration other than the unity and reached in all of the isotherms. The K_d values generally decreased in all soils compared to the values of K_f and ranged between 0.04 and 0.35 in the vineyard soils and between 0.61 and 1.34 in the natural soils.

With a view to determining, by means of a statistical approach, the effect of soil properties on the adsorption of metalaxyl, the simple and multiple correlations between the K_f and K_d adsorption constants and the characteristics of the soils were calculated using the Statgraphic Statistical Graphic System. The study was conducted considering all of the soils together and also considering the group of vineyard soils with an OM content <2% and the group of natural soils with an OM content >2%.

The results obtained (Table 3) point to the existence of a highly significant correlation ($r = 0.94$; $p < 0.001$) between the K_f and K_d constants and the OM content of the soils when all of the soils were considered together. There was also a significant negative correlation with pH, which is likely due to the correlation between OM and pH ($r = -0.60$; $p < 0.01$). On the basis of the determination coefficient, r^2, OM would account for 88% of the variance in adsorption. These results indicate that the OM content is an important parameter in the adsorption of metalaxyl by the soils of different compositions studied.

A significant correlation was also found between both K_f and K_d constants and the OM content when the group of vineyard soils was considered. The determination coefficient, r^2, explained 26% of the variance in adsorption for the correlation between K_f and OM and 54% for the correlation between K_d and OM. In addition, the correlation between K_f and clay was also significant in these soils ($r = 0.72$, $p < 0.05$).

When the natural soils were considered, a significant correlation was observed only between the adsorption constants and OM content; the determination coefficient r^2 for the correlation between K_d and OM content accounted for 59% of the adsorption.

The results obtained were also subjected to multiple linear regression analysis by combining two or more variables with a view to knowing the relative importance of the soil parameters when they vary simultaneously. Table 4 shows the equations obtained with the t values and significance levels for the related variables. When all of the soils are considered, the t values show that the variability in K_d can mainly be attributed to the OM content, and the multiple determination coefficient, R^2, obtained provided no further explanation for the adsorption variability as compared with the single determination coefficient, r^2. However, when we consider the vineyard soils, the t values indicate that the contributions of the OM and clay contents to the variance in adsorption are similar. The determination coefficient, R^2, obtained in this case affords a higher explanation of the variance in adsorption (80%) than the single coefficient obtained when the OM or clay content was considered individually (Table 3). These findings show that both clay and OM are important parameters in the adsorption of metalaxyl by the vineyard soils with low OM contents.

Studies carried out by Sharom and Edgington (*8*) on the adsorption of metalaxyl by four soils with OM
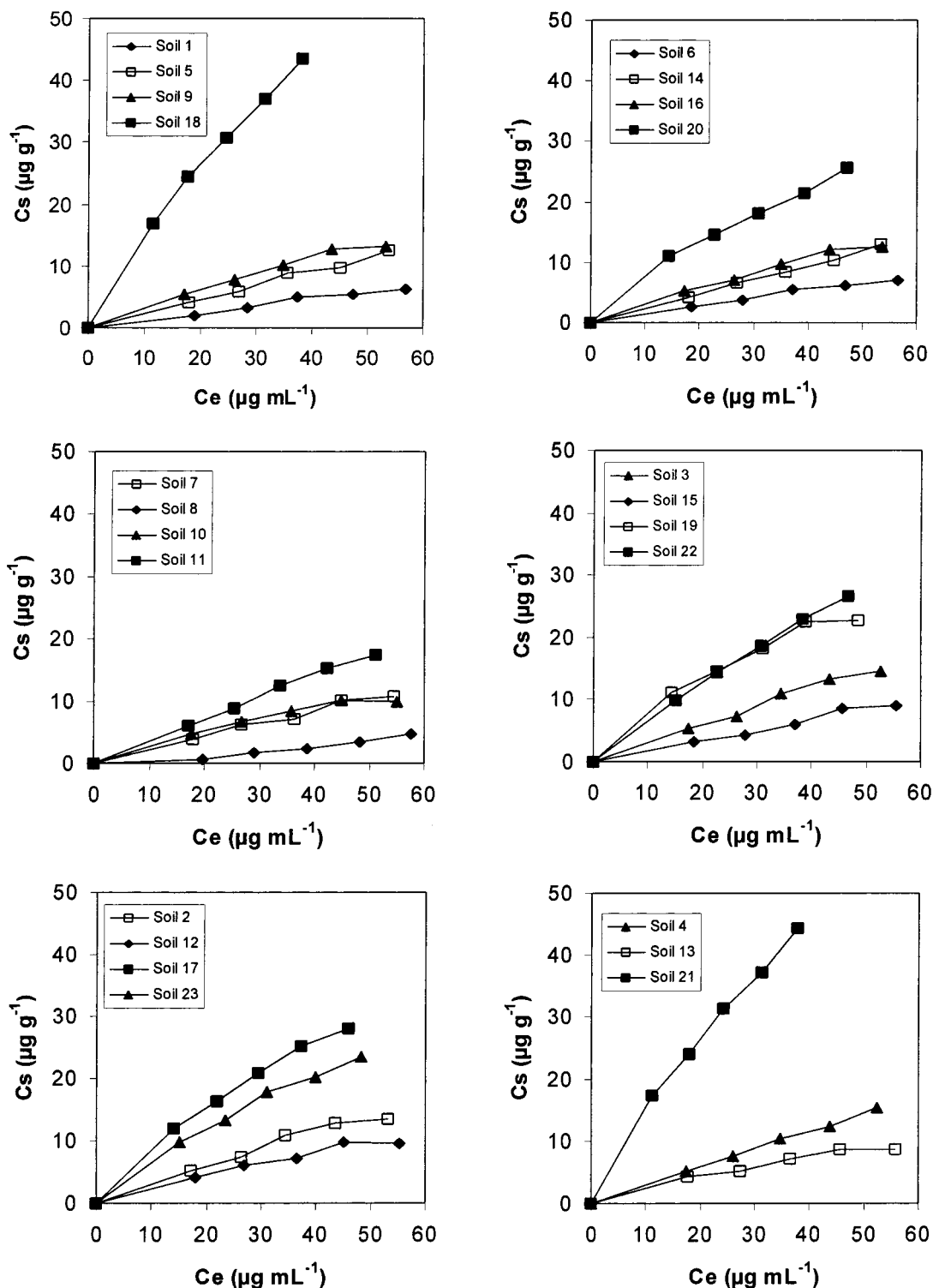
Figure 2. Adsorption isotherms of metalaxyl by soils.

contents in the 1.7−62.8% range and by Musumeci et al. (*7*) on the adsorption by three soils with OM contents between 2.0 and 4.3% have also highlighted the importance of the OM content in this process. However, Sukop and Cogger (*10*) indicated the importance of the mineral surfaces in the adsorption of metalaxyl by samples corresponding to two soil profiles with OM contents between 0.12 and 2.58%. A correlation with the clay content was also reported by Sharma and Awasthi (*11*) in a study of the metalaxyl adsorption by three soils with OM contents between 0.62 and 13.9%, even though

maximum adsorption took place in the soil with the highest OM content.

The results obtained by the above authors and those offered in this work indicate that the OM is an important parameter in the adsorption of metalaxyl by soils, although the clay content is also involved in this process. The influence of both soil fractions may be due to the structure of the metalaxyl molecule, with a hydrophobic part (dimethylphenyl) and another polar part (methoxyacetyl). The influence of the colloidal fractions, OM and clay, is frequent in the adsorption of pesticides with

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Table 2. Freundlich Constants (K_f, n_f), Distribution Coefficients (K_d), log K_{om}, and R_f Values

soil	K_f	n_f	$K_d{}^a$	log K_{om}	R_f
			Vineyard Soils		
1	0.09 ± 0.04^b	1.06 ± 0.12	0.11 ± 0.01^b	1.48	0.94 ± 0.03^b
2	0.43 ± 0.03	0.89 ± 0.02	0.31 ± 0.00	1.55	0.72 ± 0.05
3	0.32 ± 0.02	0.98 ± 0.01	0.30 ± 0.02	1.40	0.67 ± 0.06
4	0.33 ± 0.05	0.97 ± 0.05	0.30 ± 0.00	1.38	0.71 ± 0.04
5	0.22 ± 0.04	1.01 ± 0.05	0.23 ± 0.00	1.52	0.66 ± 0.06
6	0.21 ± 0.06	0.88 ± 0.06	0.14 ± 0.01	1.53	0.81 ± 0.01
7	0.30 ± 0.02	0.90 ± 0.01	0.22 ± 0.01	1.47	0.69 ± 0.04
8	0.01 ± 0.00	1.75 ± 0.07	0.04 ± 0.02	0.29	0.91 ± 0.03
9	0.53 ± 0.07	0.83 ± 0.04	0.32 ± 0.02	1.82	0.69 ± 0.05
10	0.63 ± 0.00	0.71 ± 0.00	0.26 ± 0.01	1.73	0.70 ± 0.03
11	0.36 ± 0.03	0.99 ± 0.03	0.35 ± 0.00	1.53	0.70 ± 0.06
12	0.44 ± 0.11	0.79 ± 0.07	0.23 ± 0.01	1.83	0.66 ± 0.05
13	0.64 ± 0.02	0.66 ± 0.00	0.23 ± 0.01	1.78	0.72 ± 0.05
14	0.19 ± 0.01	1.06 ± 0.00	0.23 ± 0.00	1.21	0.82 ± 0.05
15	0.14 ± 0.01	1.05 ± 0.02	0.16 ± 0.00	1.47	0.90 ± 0.06
16	0.48 ± 0.12	0.84 ± 0.07	0.29 ± 0.01	1.77	0.79 ± 0.02
			Natural Soils		
17	1.69 ± 0.00	0.74 ± 0.00	0.78 ± 0.01	1.54	0.46 ± 0.03
18	2.31 ± 0.22	0.79 ± 0.03	1.31 ± 0.02	1.67	0.40 ± 0.03
19	1.96 ± 0.10	0.64 ± 0.01	0.68 ± 0.01	1.79	0.53 ± 0.02
20	1.76 ± 0.16	0.70 ± 0.03	0.68 ± 0.01	1.57	0.63 ± 0.05
21	2.83 ± 0.10	0.77 ± 0.01	1.34 ± 0.00	1.51	0.34 ± 0.02
22	1.05 ± 0.19	0.88 ± 0.06	0.64 ± 0.01	1.32	0.59 ± 0.06
23	1.30 ± 0.06	0.76 ± 0.01	0.61 ± 0.01	1.41	0.59 ± 0.04
LSD	0.23		0.02		

^{a} K_d values were estimated at $C_e = 20$ μg mL^{-1}. ^{b} Mean values $\pm$ standard deviation of two replicates. ^{c} Mean values $\pm$ standard deviation of three replicates

Table 3. Simple Correlation Coefficients (r) between Freundlich Constants (K_f) and Distribution Coefficients (K_d) and Soil Characteristics

| soils	constant	pH	OM	clay	silt	silt + clay	CaCO$_3$
all	K_f	-0.57^b	0.94^a	0.26	0.26	0.31	-0.37^d
	K_d	-0.47^c	0.94^a	0.33	0.20	0.29	-0.31
vineyard	K_f	0.37	0.51^c	0.72^c	0.15	0.46	-0.03
	K_d	0.44^d	0.73^b	0.24	-0.14	0.02	-0.07
natural	K_f	0.44	0.68^d	0.36	-0.47	-0.23	0.48
	K_d	0.59	0.77^c	0.73	-0.36	-0.28	0.46

^{a} Significant at <0.001 level. ^{b} Significant at 0.01−0.001 level. ^{c} Significant at 0.05−0.01 level. ^{d} Significant at 0.1−0.05

Table 4. Multiple Regression Equations of Adsorption Constants with Soil Properties

	OM		clay		
regression eq	t value	signif level	t value	signif level	R^2
all soils					
$K_d = -0.15 + 0.16$ OM $+ 0.01$ clay	7.015	0.000	1.848	0.095	0.82
vineyard soils					
$K_f = -0.39 + 0.47$ OM $+ 0.01$ clay	3.410	0.019	3.513	0.017	0.80

hydrophobic and polar groups in their molecular structure (*33−35*).

The correlations obtained are in agreement with the log K_{om} values found (Table 2), which vary over a relatively broad range (0.29−1.83). A narrow variation between the K_{om} values of soils with different OM contents often shows that adsorption is governed by the OM content of the soil, whereas a broad range can indicate that other soil properties may be affecting adsorption (*36*). The mean log K_{om} value was 1.50, which lies within the range reported by Hosang (*37*) (1.07−2.07), with a typical value of 1.46. It is also close to the theoretical value (1.55) determined with the Briggs
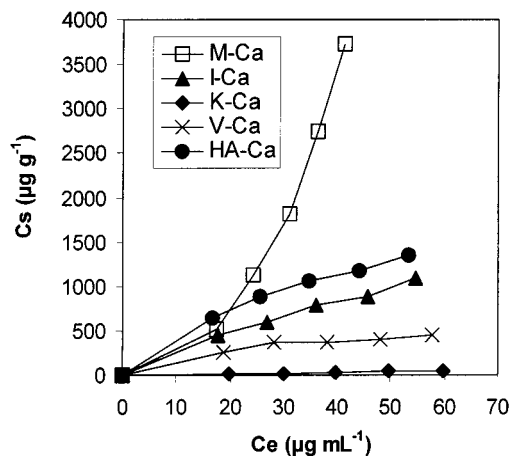
Figure 3. Adsorption isotherms of metalaxyl by clay minerals and humic acid.

Table 5. Freundlich Adsorption Constants (K_f, n_f) and Distribution Coefficients (K_d) for the Adsorption of Metalaxyl by Model Soil Components

sample	K_f	n_f	$K_d{}^a$
Ca-M	0.74 ± 0.21^b	2.29 ± 0.02^b	85.1 ± 1.86^b
Ca-I	50.2 ± 3.63	0.76 ± 0.02	20.8 ± 0.76
Ca-V	73.1 ± 10.5	0.45 ± 0.02	9.63 ± 1.02
Ca-K	0.13 ± 0.06	1.48 ± 0.52	0.78 ± 0.07
Ca-HA	108 ± 2.07	0.64 ± 0.01	28.3 ± 0.01

^{a} K_d values were estimated at $C_e = 40$ μg mL^{-1}. ^{b} Mean values $\pm$ standard deviation of two replicates.

equation (*38*) (log $K_{om} = 0.52$ log $K_{ow} + 0.64$), considering the K_{ow} value reported by Tomlin (*19*).

Adsorption by Soil Components. With a view to gaining further insight into the effect of the soil components on the adsorption of metalaxyl, the adsorption isotherms of the fungicide by type clay minerals of different natures and by humic acid were obtained. Figure 3 shows the adsorption isotherms of metalaxyl by Ca samples of the clay minerals montmorillonite, illite, vermiculite, kaolin, and humic acid. The isotherms obtained were of the L type according to the classification of Giles et al. (*28*), like those found in adsorption by soils except those corresponding to Ca-M and K-M. In these samples the isotherms were of the S type, indicating that adsorption increases with the increase in the fungicide concentration in solution.

The Freundlich adsorption constants K_f and n_f and the K_d distribution coefficients determined for a $C_e = 40$ μg mL^{-1} for all of the samples are shown in Table 5. The K_f value of the Ca-HA sample is higher than the values corresponding to the clay samples. However, the highest K_d value corresponds to the Ca-M sample. According to the n_f values, adsorption by the Ca-M samples strongly depends on the metalaxyl concentration in the solution, the K_d coefficient being 115-fold higher than the K_f constant. The results obtained indicate that at low concentrations of the compound in solution adsorption is greatest by the humic acid sample. However, the adsorption by the clay mineral montmorillonite increases significantly with the concentration of the compound in solution. The K_d value of the Ca-M sample is 3-fold higher than the K_d value for the Ca-HA sample. These results confirm those obtained for the effect of OM and clay on the adsorption of metalaxyl by soils indicated above.

The increase in the adsorption of metalaxyl by the Ca-M sample with the increase in the solution concen-

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Table 6. Simple Correlation Coefficients (r) between R_f and Soil Characteristics

parameter	all soils	vineyard soils	natural soils
K	−0.88[a]	−0.67[b]	−0.83[c]
K_d	−0.90[a]	−0.76[a]	−0.91[b]
pH	0.38[d]	−0.29	−0.81[c]
OM	−0.85[a]	−0.59[c]	−0.73[d]
clay	−0.48[d]	−0.52	−0.83[d]
silt	−0.08	0.14	0.68
silt + clay	−0.29	−0.17	0.06
$CaCO_3$	0.34	0.20	−0.70[d]

[a] Significant at <0.001 level. [b] Significant at 0.01−0.001 level. [c] Significant at 0.05−0.01 level. [d] Significant at 0.1−0.05 level.

tration could be due to the possible intercalation of the fungicide molecule into the interlayer space of this silicate, which can expand. Compounds with a structure similar to that of metalaxyl, such as metolachlor or alachlor, are adsorbed into the interlayer space of homoionic samples of montmorillonite, becoming coordinated with exchange cations through the C=O and C−N groups of the organic compound (*39*, *40*). As is known, clay minerals have a strong capacity to adsorb organic compounds (*41*); in particular, montmorillonite permits the intercalation of polar organic molecules in its interlayer space (*42*). However, the water molecules present in the hydration sphere of the exchange cations present in this mineral hinder the adsorption of organic compounds when they are present at very low concentrations.

Soil-TLC Mobility Studies. Table 2 shows the R_f values obtained in the study of the mobility of metalaxyl from soil-TLC (averages of three determinations) under saturated flow conditions, as occurs in the leaching of the fungicide with this technique. In the soils studied, the R_f values range between 0.34 and 0.94 (mean = 0.68). For the vineyard soils these values range between 0.66 and 0.94 (mean = 0.76) and in the natural soils between 0.34 and 0.63 (mean = 0.51). The lowest value corresponds to soil 21, with the highest OM content, and the highest values correspond to soils with low OM and clay contents.

According to the mobility scale based on soil-TLC proposed by Helling and Turner (*43*), in vineyard soils metalaxyl behaves as a very mobile (85%) and a mobile (14%) compound. A high mobility for metalaxyl has also been reported by Zaviezo et al. (*44*) in studies on the effectiveness of the fungicide and by Horst et al. (*12*) and Kookana et al. (*45*) in studies on the leaching and degradation of a group of pesticides, including metalaxyl, in a sandy soil and on golf courses.

The simple correlation coefficients between the R_f values and K_f and K_d constants and soil parameters are shown in Table 6. Negative correlations are observed between R_f and K_f and K_d, with a higher or lower significance level, when considering all of the soils together and when the groups of vineyard soils or natural soils are considered separately. A significant negative correlation is also seen with OM in the three groups of soils, and a negative correlation with clay is also found that is not very significant or does not reach significance.

The results obtained are consistent with those reported by Petrovic et al. (*46*), who observed a decrease in the leaching of metalaxyl in sand amended with peat, and with those studies conducted by the U.S. EPA (*47*), indicating a rapid leaching of [^{14}C]metalaxyl in a sandy soil, with a recovery of 92% of the radioactivity in the leachate, whereas <0.6% of the radioactivity was recovered in the leachate from sandy clay loam and silty loam soils.

Conclusions. The adsorption of metalaxyl by the soils from the region of La Rioja (Spain) with OM and clay contents ranging from 0.31 to 1.37% and between 12.2 and 33.3%, respectively, devoted to vineyard culture and receiving a continued contribution of the fungicide is low. The values of the Freundlich constant K_f range from 0.01 to 0.64. Both OM and clay contents affect the adsorption of the fungicide by these soils; when both parameters are considered simultaneously, they account for 80% of the variability in adsorption. According to the R_f values found in the study of the mobility of the metalaxyl (0.66−0.94), the compound is mobile in 81% of the vineyard soils considered and highly mobile in 19% of them. In natural soils from the region, included in the work for comparative purposes, with OM and clay contents ranging from 3.3 to 8.24% and from 15.3 to 35.7%, respectively, the adsorption of metalaxyl increases (K_f = 1.05−2.83) and mobility decreases (R_f = 0.34−0.63). According to the results obtained, intensive application of metalaxyl to the vineyard soils of the region studied implies a potential risk for groundwaters. Additionally, the results on the adsorption of the fungicide in natural soils, in which the K_f value of the soil with an OM content of 8.24% reaches 283-fold the value corresponding to that the vineyard soil with a 0.51% OM content, suggest the possibility of decreasing the leaching of metalaxyl, when necessary in selected locations, via the application of organic amendments.

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