

Adsorption and Desorption Behavior of Metalaxyl in Intensively Cultivated Acid Soils

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S Supporting Information

ABSTRACT: Metalaxyl adsorption and desorption behavior in acid soils were evaluated via batch and stirred-flow chamber experiments. On the basis of batch experiments (adsorption curves of the Giles C-type), metalaxyl has a low affinity for acid soils. Also, as derived from batch and stirred-flow chamber tests, its adsorption in acid soils is dictated mainly by their organic matter and clay contents. The high correlation between these two variables makes it rather complicated to resolve their effects. Metalaxyl adsorption occurs largely (80–99%) via fast adsorption reactions. On the other hand, the pesticide is desorbed in variable proportions (30–100%). The desorption parameters obtained by fitting the results to a pseudo-first-order reaction were correlated with no edaphic variable; however, the q_0/q_{\max} ratio, which is a measure of reversibility in the adsorption–desorption process, exhibited significant negative correlation with the organic matter and clay contents.

KEYWORDS: metalaxyl, adsorption/desorption, kinetics, soil

INTRODUCTION

Agricultural productivity has increased markedly as a result of the development of new, high-yield cultivars, advances in machinery technology, and the widespread use of pesticides in general and herbicides and fungicides in particular.¹ These pesticides have provided undeniable benefits by effect of their dramatically reducing the adverse effects of plant diseases and pests on agricultural productivity. However, the excessive use of some pesticides has caused serious problems including environmental deterioration. In fact, the continual use of these polluting products has raised their concentrations in soils² to levels endangering sustainability in some agricultural systems.

Once they reach soil, pesticides undergo a series of mutually related physical, chemical, and biological processes. Although the significance of these processes depends on the chemical nature of the pesticide and properties of the soil, degradation and adsorption–desorption processes are usually the most consequential.³ In fact, adsorption–desorption processes govern the mobility of pesticides and influence their transport, persistence, transformations, and bioaccumulation in soil.⁴ For example, fairly irreversible adsorption of pesticides to soil colloids renders them less accessible to soil microorganisms, thereby reducing their persistence and restricting their transport in soil. Also, easy desorption of a pesticide from soil particles facilitates its leaching and drainage to subsurface or even surface waters.

Metalaxyl [methyl *N*-methoxyacetyl-*N*-(2,6-dimethyl)-DL-alaninate] is a major fungicide of systemic residual action⁵ and moderate toxicity.⁶ This pesticide is widely used to fight and prevent fungal diseases in a variety of crops worldwide. Metalaxyl is frequently applied directly to the aerial portion of plants, which inevitably causes part of the product to fall on the ground during spraying or to be swept off the plants by rain. The pesticide can also reach soil from plant debris remaining on soil after harvest or

from plant vestiges detached during treatment.⁷ As a result, metalaxyl adsorption is favored by a high content of organic matter;^{8,9} however, some soils containing large amounts of dissolved organic matter exhibit moderate to low adsorption of the pesticide by effect of its competition with organic matter for adsorption sites.^{10,11} Some authors have found metalaxyl adsorption to be favored by clay¹² and a low pH in the soil solution containing the pesticide to increase its adsorption in soil particles.¹³

Because the adsorption and desorption of contaminants in soil are not instantaneous, accurately studying these processes in metalaxyl required examining their kinetics for this pesticide. Most studies on metalaxyl adsorption kinetics have relied on batch^{8,14} or soil column tests.⁹ These techniques, however, are subject to some limitations such as the sluggishness of batch tests or the adverse effects of film diffusion in soil column tests. These shortcomings can be circumvented by using the stirred-flow chamber technique,¹⁵ which, however, has never previously been used to examine metalaxyl adsorption kinetics. In the stirred-flow technique, the sorbate is continuously circulated through a reaction chamber to avoid the potential problems resulting from the decrease in concentration in the liquid phase typically observed in batch processes; also, desorption of the pesticide is accelerated by removing the portion released into the liquid phase. This technique also avoids film diffusion caused by continuous agitation in column tests.¹⁶

The primary purpose of this work was to examine metalaxyl adsorption and desorption in acid soils. To this end, we used both

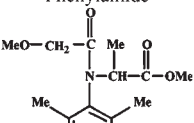
Received: March 14, 2011

Accepted: May 26, 2011

Revised: May 25, 2011

Published: May 26, 2011

Table 1. Structure and Chemical Properties of Metalaxyl^a

Common name	Metalaxyl
Name	Methyl <i>N</i> -methoxyacetyl- <i>N</i> -(2,6-dimethylphenyl)- <i>DL</i> -alaninate
CAS n°	57837-19-1
Chemical family	Phenylamide
Chemical structure	
p <i>K</i> _a ^a	1.41±0.50
MW ^b	279
<i>S</i> ^c (g L ⁻¹)	8.4
Log <i>P</i> _{ow} ^d	1.8
Koc ^e	30–300
Soil half-life ^f	10–40

^a Data from Tomlin³⁷ and Kamrin.³⁸ Key: (a) p*K*_a at 25 °C. (b) Molecular weight. (c) Solubility in water at 22 °C. (d) Octanol/water partition coefficient at 25 °C. (e) Partition coefficient normalized to organic carbon content (mL·goc⁻¹ or L·kgoc⁻¹). (f) Aerobic soil half-life (days).

batch and stirred-flow chamber tests to (a) obtain a detailed picture of metalaxyl adsorption/desorption in acid soils; (b) relate metalaxyl adsorption/desorption behavior to soil characteristics; (c) elucidate the adsorption/desorption kinetics of the pesticide; and (d) identify the principal factors responsible for its adsorption and desorption kinetics.

MATERIALS AND METHODS

Chemicals. Metalaxyl [methyl *N*-methoxyacetyl-*N*-(2,6-dimethyl)-*DL*-alaninate] was obtained in purity higher than 99.5% from Sigma–Aldrich (Steinheim, Germany). Table 1 shows its chemical structure and selected properties. All organic solvents used for sample preparation were residue analysis grade and supplied by Panreac (Barcelona, Spain). HPLC grade solvents for HPLC work were also supplied by Panreac. A stock standard solution containing a 1 mg·mL⁻¹ concentration of metalaxyl in methanol was used to make working-strength solutions by appropriate dilution as required. All solutions were stored in amber glass flasks under refrigeration in order to prevent degradation.

Soil Samples. The study area is located in “A Limia” (Galicia, northwest Spain). In this area, in the last 50 years, the soils were intensively managed, with potatoes and wheat being the main products cultivated in crop rotation. Sixteen samples obtained from the topmost layer (0–20 cm) of acid soils were collected. Once in the laboratory, the samples were air-dried, sieved through a 2 mm sieve, and stored in polyethylene bottles until analysis. The particle-size distribution was determined in the <2 mm fraction by the internationally recognized pipet method. Mineralogical clay composition was determined by X-ray diffraction with the use of Cu Kα radiation with a Philips PM8203 diffractometer (Philips, Wavre, Belgium). The soil pH was measured in water (ratio of soil:solution 1:2.5); the total nitrogen (N_T) was determined in finely milled samples in an agate mortar (Retsch RM100; Retsch GmbH, Hann, Germany), with a soil analyzer (Thermo Finnigan 1112 Series NC). The effective cation-exchange capacity (eCEC) was estimated as the sum of base cations (Na, K, Ca, and Mg) displaced with 1 M NH₄Ac at

pH 7 and the Al extracted with 1 M KCl. The total soil organic carbon (C_T) was determined by dichromate oxidation. The soil organic fractions were extracted according to conventional procedures based on changes in pH and determined by dichromate oxidation.

The soils were mainly loam or sandy loam in texture. Clay mineralogy is similar to those reported from soils developed from granitic materials; thus, 1:1 dioctahedral phyllosilicates such as kaolinite and halloysite dominated the mineralogical composition of clay fraction, whereas vermiculites (mainly interlayered aluminum hydroxide) are also frequent. Traces of gibbsite are also recorded in the soil samples with lowest carbon content. Total organic carbon (C_T) ranged from 1.1% to 16.6%. Humic substances (fulvic and humic acids) represents on average 62% of total organic carbon (range 38–93%). All samples were acidic (pH 4.3–5.7) and possessed a low cation-exchange capacity [1.92–10.24 cmol_(c)·kg⁻¹]. Their physicochemical properties are summarized in Table 2.

Metalaxyl Adsorption/Desorption As Measured in Batch Tests. Metalaxyl adsorption in the soils was measured via batch experiments as follows: an amount of 1 g of soil was mixed with 10 mL of aqueous solutions containing variable metalaxyl concentrations from 3 to 100 μmol·L⁻¹ in addition to 0.005 M CaCl₂ as background electrolyte. After 24 h of shaking, the soil suspensions obtained were centrifuged at 700g (15 min) and passed through a filter of 0.45 μm pore size, the supernatant being used to determine the pesticide by HPLC with UV detection.

Experimental data were modeled by fitting to the Freundlich equation

$$X = K_F C^n \quad (1)$$

and Langmuir equation

$$X = \frac{K_L X_m C}{1 + K_L C} \quad (2)$$

where *X* (*q*_s) is the amount of metalaxyl retained by weight (micromoles per kilogram), *C* is its concentration in solution after 24 h of equilibration (micromoles per liter), *K*_F and *n* are coefficients of the Freundlich equation, *K*_L (liters per micromole) is a constant dependent on the energy of adsorption, and *X*_m (micromoles per kilogram) is the maximum adsorption capacity of each sample.

In the desorption tests, adsorption of metalaxyl by the soil samples was immediately followed by weighing of the centrifuged residues to determine the amount of occluded solution. This was followed by resuspension in 10 mL of a 0.005 M CaCl₂ solution containing no metalaxyl and equilibration for 24 h. Finally, the samples were centrifuged at 700g (15 min) and the supernatant was used to determine the pesticide by HPLC-UV.

Metalaxyl Adsorption/Desorption As Measured in Stirred-Flow Chamber Tests. Nine soil samples (1, 2, 4, 5, 8, 10, 13, 14, and 15) were used for metalaxyl adsorption/desorption tests in an SFC-based reactor. The 1.5 cm³ propylene stirred-flow reactor used (Figure 1) was a slightly modified version of one previously reported by López-Periago et al.¹⁶ The reactor had a side inlet at the bottom and an outlet in the lid, the two being connected to a Minipuls 3 peristaltic pump from Gilson SAS (Villiers le Bel, France) by 0.5 mm i.d. poly(tetrafluoroethylene) (PTFE) tubing and covered with PTFE filters 10 mm in diameter and 0.45 μm in pore size to retain the samples in the reactor.

Table 2. General Soil Characteristics^a

	sand, %	silt, %	clay, %	C _T , %	N _T , %	C _{HA} , %	C _{FA} , %	C _{HU} , %	pH	eCEC, cmol _(c) ·kg ⁻¹
1	48	20	32	5.21	0.48	1.74	0.59	2.88	4.3	4.38
2	56	22	22	3.49	0.26	1.75	0.43	1.31	5.0	4.29
3	58	23	19	1.59	0.15	0.68	0.22	0.69	5.4	3.17
4	77	11	12	1.28	0.01	0.67	0.11	0.50	5.4	1.92
5	72	15	13	1.07	0.13	0.72	0.06	0.29	4.8	2.49
6	74	13	13	2.07	0.12	0.62	0.16	1.29	5.0	2.35
7	67	20	13	1.44	0.13	0.58	0.26	0.60	4.9	2.40
8	59	25	16	1.53	0.13	0.82	0.32	0.39	4.7	3.04
9	71	17	12	1.38	0.17	0.78	0.48	0.12	4.8	3.26
10	58	26	16	1.44	0.13	0.64	0.08	0.72	4.3	2.84
11	48	30	22	2.98	0.23	2.44	0.33	0.20	5.5	6.96
12	58	20	22	2.55	0.27	1.14	0.43	0.97	4.9	4.81
13	77	8	15	5.78	0.48	2.68	0.40	2.70	5.7	6.18
14	21	35	44	16.61	1.18	6.82	0.98	8.81	5.4	10.24
15	42	31	27	3.87	0.31	1.39	0.71	1.77	4.9	4.95
16	54	20	26	3.00	0.28	1.65	0.38	0.97	5.0	3.35

^a C_T and N_T, total organic carbon and total nitrogen; C_{HA}, carbon of humic acids; C_{FA}, carbon of fulvic acids; C_{HU}, humin carbon; eCEC, effective cation exchange capacity.

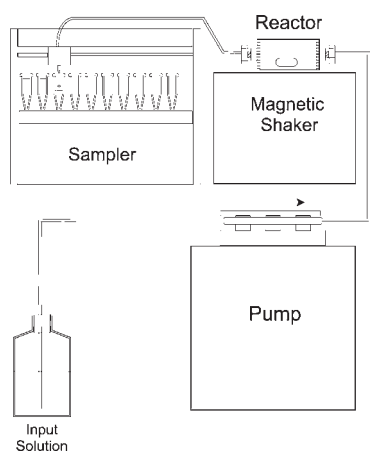


Figure 1. Schematic depiction of the stirred-flow reactor.

Stirring was provided by a PTFE-coated magnetic bar spun at 400 rpm, and output solution fractions were collected in 2 mL polypropylene Eppendorf vials by using a Gilson FC203G automatic fraction collector at a rate of 1 vial/min. Tests were performed in a cabinet thermostated at 25.0 ± 0.1 °C. The flow rate ($0.3 \text{ mL} \cdot \text{min}^{-1}$) was monitored throughout and found to oscillate by less than $\pm 3\%$.

An amount of ca. 0.2 g of soil (<2 mm) was placed together with a magnetic stirring bar in the reaction chamber and a $7.2 \mu\text{M}$ metalaxyl solution was then circulated at the selected flow rate with 0.005 M CaCl_2 as background electrolyte. In total, 60 subsamples of 0.2 mL each were collected in different vials that were filled for 1 min each. Immediately after metalaxyl was adsorbed, desorption tests were started by circulating the background electrolyte (0.005 M CaCl_2). The pesticide was determined by HPLC-UV in all subsamples from both the adsorption and desorption runs.

Metalaxyl Determination. High-performance liquid chromatography (HPLC) analyses were carried out on a liquid

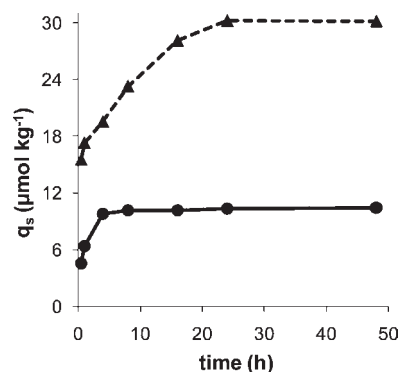


Figure 2. Kinetic adsorption curves obtained in batch tests on selected samples: (●) sample 2; (▲) sample 14.

chromatograph from Dionex Corporation (Sunnyvale, CA) equipped with a P680 quaternary pump, an ASI-100 autosampler, a TCC-100 thermostated column compartment, and a UVD170U detector connected to a PC computer running the software Chromeleon, also from Dionex Corporation. Chromatographic separations were done on a Symmetry C₁₈ column (150 mm long \times 4.60 mm i.d., $5 \mu\text{m}$ particle size) from Waters (Milford, MA) and a guard column (50 mm long \times 4.60 mm i.d., $5 \mu\text{m}$ particle size) packed with the same material. The mobile phases were methanol (A) and water (B), and the gradient program was as follows: 60% A + 40% B for 7 min, change to 95% A + 5% B in 3 min, hold 5 min, change to 60% A + 40% B in 0.1 min, and hold 10 min. The total analysis time was 25 min. The injected volume was set to $50 \mu\text{L}$ and the flow rate to $0.7 \text{ mL} \cdot \text{min}^{-1}$. Metalaxyl was detected at $\lambda = 200 \text{ nm}$.

RESULTS AND DISCUSSION

Metalaxyl Adsorption. Prior to adsorption tests, two selected samples with low (sample 2) and high (sample 14) carbon content were subjected to a batch kinetic test. As can be seen

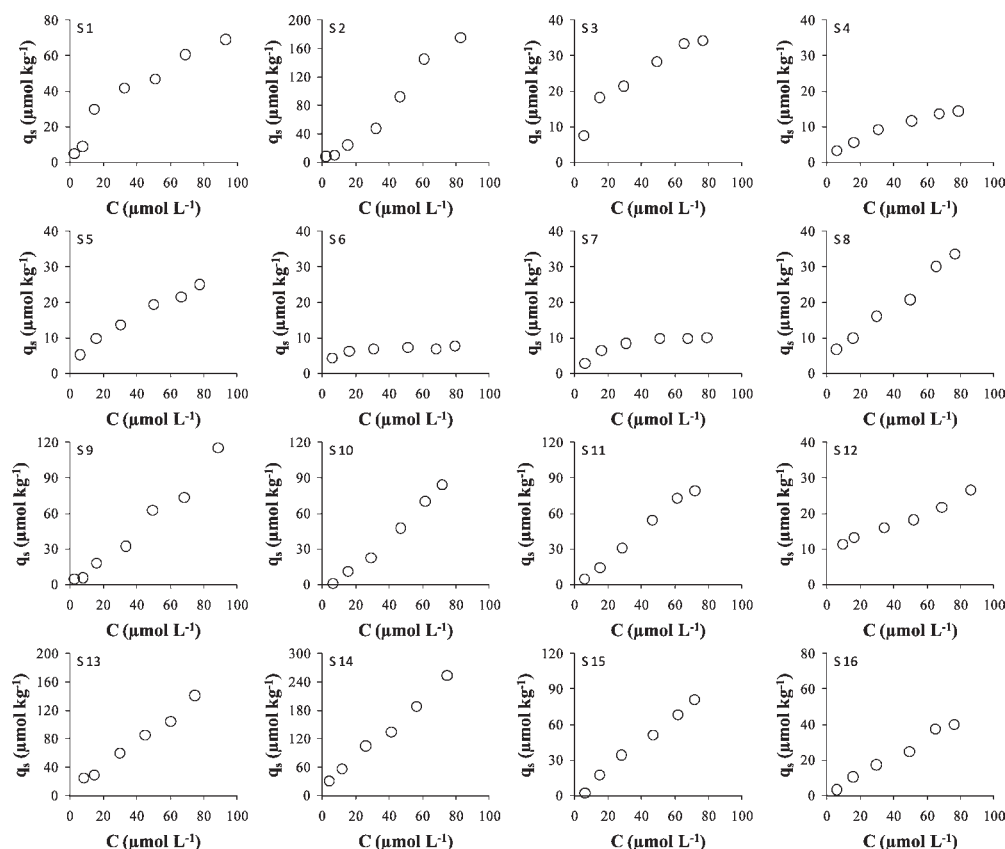


Figure 3. Metalaxyl adsorption equilibria in the 16 studied soils as determined in the batch tests.

from Figure 2, equilibrium was reached within 24 h of metalaxyl–soil contact. This led us to use an equilibration time of 24 h in all batch adsorption/desorption runs.

Overall, metalaxyl adsorption was low, which is consistent with its high mobility.^{17,18} Plotting the amount of pesticide adsorbed (q_s , micromoles of metalaxyl per kilogram of soil) against its equilibrium concentration (C , micromoles per liter) gave near-linear (i.e., C-type, according to Giles et al.¹⁹) curves (Figure 3). This suggests that soil particles had little affinity for metalaxyl. All adsorption curves except those for two samples fitted a linear equation with $R^2 > 0.900$ (Table 3). This reflected constant partitioning between adsorbing surfaces and the soil solution and allowed the coefficient of distribution, K_d , to be calculated from the slopes of the curves. The K_d values thus obtained ranged from 0.03 to 3.08 $L \cdot kg^{-1}$ and averaged 0.91 $L \cdot kg^{-1}$; also, they were significantly correlated with total soil organic matter (C_T and N_T), organic matter fractions (C_{HA} , C_{FA} , and C_{HU}) and eCEC ($p < 0.01$), as well as with sand and clay contents ($p < 0.05$) (Table S1, Supporting Information).

Overall, the adsorption curves fitted the Freundlich equation better ($R^2 = 0.865$ – 0.998 versus 0.682 – 0.995 for the linear fit) than the Langmuir equation, which exhibited nonsignificant R^2 values or large errors in the calculated parameters (Table 3). Freundlich fitting parameters are shown in Table 3. This equation, which is applicable to soils with nonuniform surface properties,²⁰ is an empirical function where K_F can be interpreted as the amount of sorbate adsorbed at $C = 1$ and n is a measure of heterogeneity in adsorption sites. Surface heterogeneity increased as n approached 0 and decreases as n approached 1. Constant K_F , which ranged from 0.2 to 6.3, was significantly

Table 3. Fitting of Adsorption Results to the Freundlich Equation and a Straight Line^a

	Straight line		Freundlich equation		
	K_d	R^2	K_F	n	R^2
1	0.69 ± 0.09	0.914	4.7 ± 1.5	0.60 ± 0.08	0.963
2	2.24 ± 0.16	0.975	1.0 ± 0.5	1.18 ± 0.13	0.980
3	0.35 ± 0.05	0.927	4.1 ± 0.8	0.50 ± 0.05	0.974
4	0.15 ± 0.01	0.961	1.2 ± 0.2	0.57 ± 0.03	0.992
5	0.26 ± 0.02	0.981	1.9 ± 0.2	0.59 ± 0.03	0.995
6	0.03 ± 0.01	0.682	3.5 ± 0.5	0.18 ± 0.04	0.865
7	0.08 ± 0.02	0.756	2.1 ± 0.6	0.37 ± 0.08	0.895
8	0.38 ± 0.02	0.987	1.3 ± 0.4	0.75 ± 0.08	0.974
9	1.26 ± 0.08	0.978	0.6 ± 0.3	1.17 ± 0.11	0.984
10	1.29 ± 0.06	0.991	0.2 ± 0.0	1.42 ± 0.05	0.998
11	1.18 ± 0.04	0.995	1.0 ± 0.3	1.04 ± 0.07	0.993
12	0.19 ± 0.01	0.983	4.1 ± 1.0	0.40 ± 0.06	0.936
13	1.73 ± 0.08	0.991	2.8 ± 0.8	0.90 ± 0.07	0.988
14	3.08 ± 0.12	0.994	6.3 ± 1.8	0.85 ± 0.07	0.988
15	1.15 ± 0.05	0.993	1.1 ± 0.3	1.01 ± 0.07	0.992
16	0.52 ± 0.03	0.987	0.7 ± 0.2	0.92 ± 0.08	0.987

^a Amount adsorbed in micromoles per kilogram; equilibrium concentration in micromoles per liter.

correlated with soil organic matter, with $r = 0.652$ for the C_T content and $r = 0.668$ for the N_T content. The highest correlation coefficient ($r = 0.710$) was found with C_{HU} fraction.

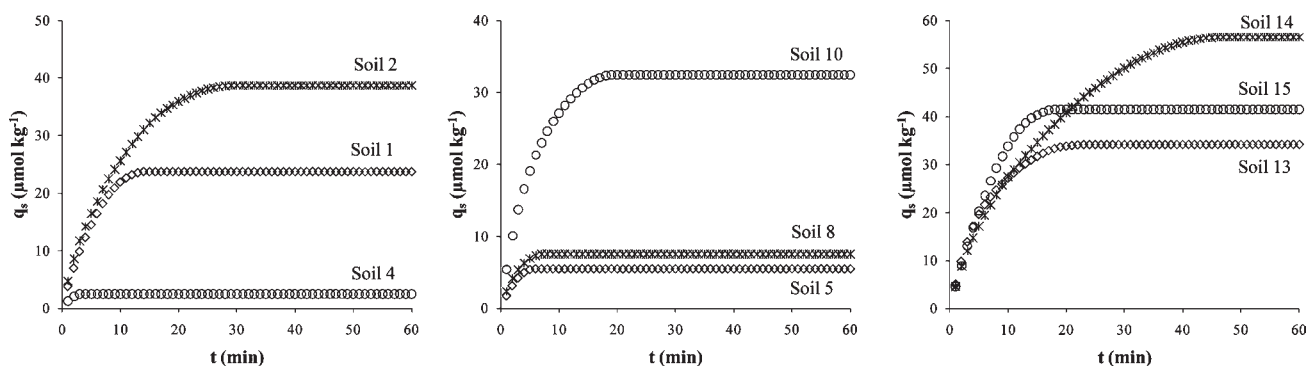


Figure 4. Cumulative metalaxyl adsorption (q_s) as function of time in the nine soil samples used in the stirred-flow chamber tests.

Table 4. Fitting of Kinetic Adsorption Data for Metalaxyl

sample	q_{\max} , $\mu\text{mol} \cdot \text{kg}^{-1}$	k_s , min^{-1}	R^2
1	26.4 ± 0.7	0.152 ± 0.012	0.961
2	40.4 ± 0.6	0.112 ± 0.004	0.960
4	2.6 ± 0.3	0.609 ± 0.217	0.941
5	5.9 ± 0.3	0.365 ± 0.045	0.953
8	8.0 ± 0.2	0.319 ± 0.024	0.980
10	33.6 ± 0.3	0.154 ± 0.004	0.988
13	34.7 ± 0.4	0.152 ± 0.005	0.979
14	60.4 ± 1.0	0.057 ± 0.002	0.940
15	47.1 ± 1.4	0.114 ± 0.007	0.938

The constant was also significantly correlated with eCEC ($r = 0.498$) and clay ($r = 0.561$) (Table S1, Supporting Information). These results are very similar to those for K_d , which suggests that metalaxyl adsorption at low concentrations (K_F) occurs via similar mechanisms to those prevailing at low to medium concentrations of the pesticide (K_d). On the other hand, n varied over a wide range (0.18–1.42) and was not significantly correlated with the edaphic variables.

Figure 4 shows the results of the metalaxyl adsorption tests in the stirred-flow chamber. The amount of metalaxyl retained ranged from 2.5 to $56.5 \mu\text{mol kg}^{-1}$. The curves of Figure 4 were fitted to a mathematical model considering a single adsorption site and based on the pseudo-first-order equation of Aharoni and Sparks:²¹ $dq_s/dt = k_s(q_{\max} - q_s)$, where dq_s/dt (micromoles per kilogram per minute) is the metalaxyl adsorption rate, k_s (per minute) is a kinetic constant, q_{\max} (micromoles per kilogram) is the maximum metalaxyl adsorption capacity of the soil under experimental conditions, and q_s (micromoles per kilogram) is the amount of pesticide retained by the soil. This model is among the most widely used on account of its simplicity and the fact that many reaction kinetics are similarly described by various methods.²² The experimental data fitted the pseudo-first-order equation very closely, with $R^2 > 0.93$ in all cases (Table 4). The maximum adsorption capacity of the soil, q_{\max} , ranged from 2.6 to $60.4 \mu\text{mol} \cdot \text{kg}^{-1}$; its greatest value was for sample 14, which had the highest organic carbon content (16.6%), and the smallest was for sample 4, which had one of the lowest C_T contents and the lowest clay (12%). q_{\max} was significantly correlated with soil texture (sand and clay), organic matter (C_T and N_T), organic matter fractions (C_{HA} , C_{FA} , and C_{HU}), and eCEC (Table S2, Supporting Information), which were the same variables influencing K_d and K_F in the batch tests. This confirms the importance

of these variables to the adsorption of metalaxyl by soil. The results are consistent with those of other authors who found metalaxyl adsorption in soil to be especially marked in soils containing abundant organic matter and clay.^{8,9,23} The high correlation between q_{\max} and eCEC may have resulted from these variables being strongly dependent on clay and organic matter; in fact, eCEC was positively correlated with the contents in both organic C_T ($r = 0.877$, $p < 0.05$) and clay ($r = 0.825$, $p < 0.05$).

The high organic matter content of the soil may have adversely affected its ability to adsorb the pesticide since high contents of organic matter in solution can reduce the soil retention capacity through competition of dissolved organic matter for adsorption sites¹¹ or the formation of easily leached complexes with metalaxyl in solution.^{24–27} However, these mechanisms are unlikely in acid soils, where organic matter is very scarcely dissolved.²⁸ In fact, absorbance measurements at 400 nm showed all 16 samples to contain very little organic matter (less than 0.3% of total OM) in the soil solution.

Resolving the effect of organic matter and clay is very difficult²³ since the two are usually closely associated in soil aggregates. In fact, the organic matter and clay contents were closely related in our samples ($n = 16$, $r = 0.834$, $p < 0.05$). As a rule, soil organic matter is highly influential on pesticide retention (particularly with low-water-soluble pesticides such as penconazole). By contrast, organic matter has little effect on high-water-soluble pesticides such as metalaxyl.²⁹ Marín-Benito et al.²³ found metalaxyl adsorption to be slightly increased by organic amendments and little or no adsorption to occur under the very low hydrophobicity observed in the presence of this pesticide. As a rule, humic acids, which constitute the major fraction of soil organic matter, have a higher metalaxyl adsorption capacity than most soil minerals (montmorillonite excluded). Thus, Andrades et al.⁸ found the following sequence of adsorption capacity for this pesticide: montmorillonite > humic acids \approx illite > vermiculite \gg kaolinite. Because the clay fraction of the soils was dominated by low-activity clay materials such as halloysite and kaolinite, differences in adsorption capacity between samples were probably a result of differences in organic matter content. This hypothesis is supported by the previous finding of Pose-Juan et al.³⁰ that metalaxyl adsorption on pure kaolinite was 3 times lower than it was on sandy loam soils with an organic C content between 3% and 4%. Also, adsorption has been found to be dictated by inorganic compounds in soils with a low organic matter content and by organic matter in those with a high organic matter content¹⁸ such as those studied here. Other

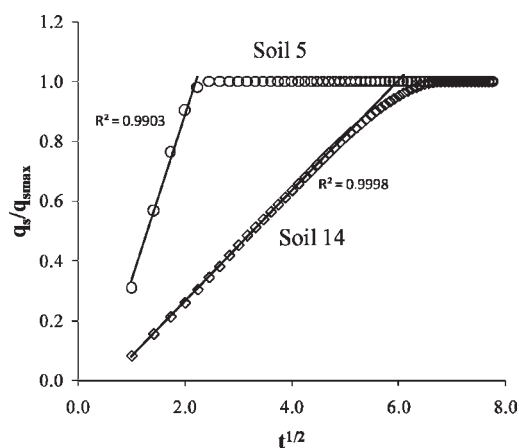


Figure 5. Plot of fractional cumulative adsorption (q_s/q_{\max}) vs $t^{1/2}$ in two of the soil samples as determined in stirred-flow chamber tests.

studies involving the addition of various surfactants to clay showed the presence of a cationic surfactant to strongly increase the sorption capacity of the soil³¹ and metalaxyl adsorption to be related to organic C in organoclays.³²

The kinetic constant, k_s , ranged from 0.057 to 0.609 min^{-1} (Table 4) and was greatest for sample 4 and smallest for sample 14. This suggests that the decrease in metalaxyl adsorption rate is a function of the soil adsorption capacity for the pesticide. In fact, q_{\max} and k_s were significantly correlated ($r = 0.878$, $p < 0.05$) and the metalaxyl adsorption rate was inversely proportional to the soil adsorption capacity. On the other hand, k_s was significantly and negatively correlated only with eCEC and C_{FA} (Table S2, Supporting Information). The relatively high values of k_s (0.226 min^{-1} on average, Table 4) reflected in very fast adsorption of metalaxyl. Thus, more than 50% of the amount of pesticide adsorbed throughout the experiment (5 min on average) was adsorbed within 12 min; also, more than 95% of the maximum adsorption (15 min on average) was reached within 38 min. Fast adsorption processes are usually diffusion-controlled.³³ The linear relationship observed between the metalaxyl relative adsorption (q/q_{\max}) and the square root of time ($t^{1/2}$) is in fact typical of diffusion-controlled processes. By way of example, Figure 5 shows two q/q_{\max} versus $t^{1/2}$ plots, based on which 80–99% of all metalaxyl was adsorbed via fast reactions.

Metalaxyl Desorption. The results of the batch metalaxyl desorption tests are shown in Table 5. The amount of metalaxyl adsorbed ranged from not detected ($<0.05 \mu\text{mol kg}^{-1}$) to $74.9 \mu\text{mol} \cdot \text{kg}^{-1}$ and was dependent on the particular soil and amount of metalaxyl added. Thus, the amount of pesticide desorbed increased with increasing amount added, which suggests that metalaxyl tended to bind increasingly, and via increasingly weaker bonds, to nonspecific adsorption sites as saturation was approached. Also, metalaxyl adsorption at low rates fell below the limit of quantitation ($0.05 \mu\text{mol} \cdot \text{kg}^{-1}$) in nine of the 16 samples (Table 5). The amount of metalaxyl desorbed, in micromoles per kilogram, was significantly correlated with that previously adsorbed ($r = 0.951$, $n = 99$). Expressed as a percentage of metalaxyl previously adsorbed, desorption averaged $20\% \pm 12\%$ and was unrelated to the soil characteristics.

Figure 6 shows the metalaxyl desorption results obtained in the stirred-flow chamber tests as the amounts of metalaxyl remaining in the soil following adsorption of the pesticide. As can be seen, metalaxyl desorption was very fast. Thus, after 3 min,

Table 5. Metalaxyl Concentration Desorbed in Batch Tests and Percent Desorption^a Relative to the Initially Added Concentration

	initial concn, $\mu\text{mol} \cdot \text{L}^{-1}$				
	18	36	54	72	89
1	6.3 (21.1)	7.9 (18.9)	11.3 (24.2)	19.4 (32.0)	21.0 (30.4)
2	16.3 (66.8)	16.5 (34.7)	24.4 (26.4)	43.1 (29.7)	48.5 (27.7)
3		2.5 (11.6)	3.8 (13.5)	8.4 (25.2)	10.1 (29.4)
4			2.5 (21.6)	3.1 (22.8)	2.8 (19.7)
5		0.9 (6.8)	1.1 (5.5)	1.3 (5.8)	1.4 (5.6)
6		0.4 (5.1)	0.4 (5.3)	0.5 (7.4)	0.6 (8.2)
7		0.9 (11.0)	1.2 (12.1)	2.1 (20.9)	2.3 (23.1)
8		0.4 (2.3)	0.8 (3.7)	1.1 (3.7)	1.7 (5.0)
9	6.0 (32.9)	11.1 (34.2)	13.7 (21.9)	13.5 (18.4)	19.2 (16.6)
10		6.0 (26.5)	7.3 (15.3)	9.5 (13.5)	10.3 (12.3)
11	2.5 (17.1)	5.4 (17.6)	9.1 (16.7)	10.9 (14.9)	14.8 (18.7)
12	0.2 (1.3)	0.6 (3.5)	3.6 (19.8)	5.1 (23.3)	11.4 (43.1)
13	7.9 (27.0)	19.5 (32.4)	28.2 (33.1)	39.3 (37.7)	53.8 (38.2)
14	21.4 (38.3)	33.9 (32.4)	37.8 (28.1)	47.3 (25.2)	74.9 (29.5)
15		7.1 (20.8)	11.2 (22.0)	17.2 (25.2)	21.3 (26.3)
16		4.1 (23.7)	5.7 (22.9)	7.6 (20.3)	8.8 (21.9)

^a Percent desorption is shown in parentheses.

82% (sample 14) to only 1% (sample 5) remained in the soil, the nine samples averaging at 44%. These proportions are higher than those obtained in the batch tests, possibly because desorption in the stirred-flow chamber was accelerated by the continuous removal of desorbed metalaxyl, whereas desorption of the pesticide in the batch tests was limited by the amount present in solution.

The metalaxyl desorption results fitted the first-order kinetic equation $dq_d/dt = k_d(q_0 - q_d)$, where dq_d/dt (micromoles per kilogram per minute) is the metalaxyl desorption rate, k_d (per minute) is the kinetic desorption constant, q_0 (micromoles per kilogram) is the amount of pesticide that can be desorbed under the experimental conditions, and q_d (micromoles per kilogram) is the amount that desorbed in practice. The estimated q_0 values ranged from 2.6 to $37.9 \mu\text{mol} \cdot \text{kg}^{-1}$ (Table 6), which amounted to 30–100% (78% on average) of the maximum metalaxyl retention capacity, q_{\max} .

These desorption results are consistent with those of Monkiedje and Spiteller,³⁴ who concluded that soil–metalaxyl interactions were weak and the pesticide adsorption in the soil was highly reversible as a result. The high desorption of metalaxyl was a consequence of its low hydrophobicity. Thus, Marín-Benito et al.²⁶ found this highly water-soluble pesticide to be more readily leached and biodegradable than low-water-soluble pesticides such as penconazole.

One other especially interesting variable for adsorption/desorption studies is the ratio of the amount of pesticide potentially desorbed to the soil adsorption capacity, q_0/q_{\max} . This variable is a measure of irreversibility in soil adsorption processes. As a rule, metalaxyl adsorption in soil is highly reversible.³² The q_0/q_{\max} ratio varied from 0.3 to 1.0 and exhibited significant positive correlation with the sand content and negative correlation with the clay, silt, and C_{T} , C_{FA} , C_{HU} , and N_{T} contents, in addition to the effective cation-exchange capacity (Table S3, Supporting Information). In previous work, metalaxyl was found

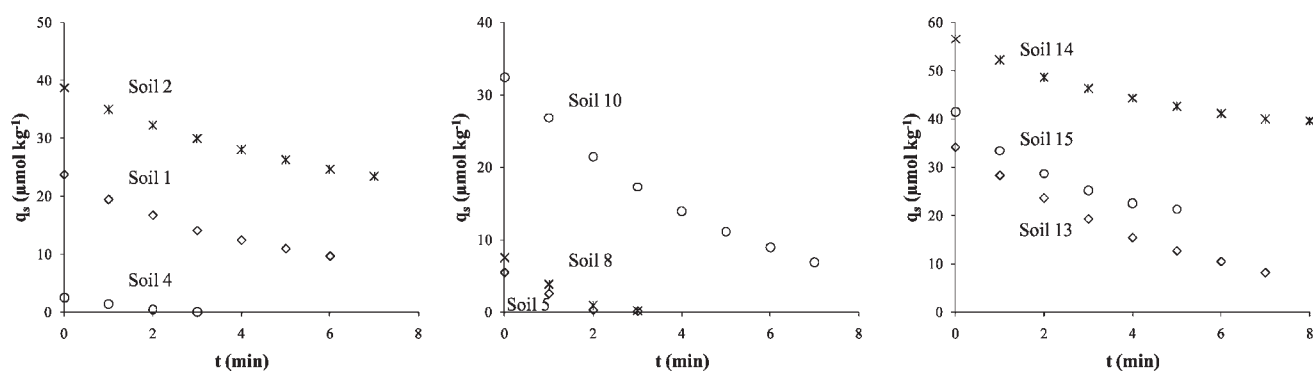


Figure 6. Cumulative metalaxyl remaining in the soil (q_s) as a function of time during desorption in nine soil samples as measured in the stirred-flow chamber tests.

Table 6. Fitting of Kinetic Desorption Results for Metalaxyl

	$q_0, \mu\text{mol} \cdot \text{kg}^{-1}$	k_d, min^{-1}	R^2
1	19.0 ± 1.4	0.196 ± 0.028	0.940
2	23.9 ± 0.6	0.132 ± 0.005	0.994
4	2.6 ± 0.1	0.661 ± 0.091	0.973
5	5.3 ± 0.0	0.956 ± 0.006	0.998
8	7.4 ± 0.1	0.782 ± 0.030	0.997
10	33.3 ± 1.1	0.190 ± 0.011	0.986
13	37.9 ± 2.9	0.153 ± 0.020	0.940
14	18.4 ± 0.6	0.248 ± 0.022	0.947
15	23.8 ± 1.3	0.307 ± 0.035	0.975

to be almost completely desorbed from soils with a low content of organic matter,³⁵ and raising its content by addition of a surfactant caused strong retention of the pesticide. Similarly, column tests conducted by Marín-Benito et al.²⁶ revealed that the addition of insoluble organic matter to soil decreased the extent and rate of metalaxyl leaching. Also, some authors have found peat and organic waste amendments to decrease metalaxyl mobility in soils.^{11,24,36}

The kinetic desorption constant, k_d , ranged from 0.132 to 0.956 min^{-1} and clearly exceeded its adsorption counterpart, k_s , (paired $t = 2.5$, $p < 0.05$). Therefore, metalaxyl was more rapidly released than it was adsorbed, twice as fast on average. Also, the kinetic desorption constant was not significantly correlated with any edaphic variable (Table S3, Supporting Information). On the other hand, Rodríguez-Cruz et al.³⁵ found metalaxyl to be rapidly leached from soils with a low organic matter content (<2%), and the addition of a cationic surfactant substantially increased the content to make leaching of the pesticide slower.

■ ASSOCIATED CONTENT

Supporting Information. Three tables showing details of correlation coefficients and signification of metalaxyl adsorption/desorption parameters with general soil characteristics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was funded by INCITE Programme 08PXIB38-3190PR of the Galician Council of Innovation and Industry. D.F.-C. additionally acknowledges award of an Ángeles Alvariño contract by the Council.

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