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ORIGINAL PAPER

Metalaxyl mobility in acid soils: evaluation using different methods

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Abstract In the present work, different methods were tested to evaluate the adsorption and desorption of metalaxyl in two acid soils with different organic carbon and clay contents. The three methods (batch, stirred flow chamber and column) that were examined produced similar findings when the two soils were compared: (a) the metalaxyl adsorption capacity was higher in the soil with higher organic matter and clay content, and (b) the soil with the lower organic matter and clay contents provided higher adsorption rate constants. In the two soils tested, the metalaxyl adsorbed in the soil was highly reversible. When only one soil was considered, the different methods yielded different results. The metalaxyl adsorption and its rate were higher with the stirred flow chamber than in the column experiments, and in the column experiments, the total metalaxyl adsorption and the rate of adsorption were higher than in the batch experiments. The percentages of metalaxyl desorbed from the soil were similar in the stirred flow chamber and column experiments, but in the batch experiments, the percentages were significantly lower. In the stirred flow chamber experiments, the desorption processes were faster than the adsorption processes, while in the column experiments, the adsorption and desorption processes exhibited similar rates.

Keywords Metalaxyl · Adsorption–desorption · Batch · Stirred flow chamber · Column · Soil

Introduction

Metalaxyl (methyl *N*-methoxyacetyl-*N*-(2,6-dimethyl)-DL-alaninate) is a systemic pesticide with moderate toxicity (Cohen et al. 1979; Kamrin 1997) that is widely used to combat and prevent fungal diseases. The intensive use of this pesticide in intensive agricultures could lead to high accumulations in the soil that could present considerable risks to the environment and human health (EPA 2009). In the soil, metalaxyl is subjected to various physical, chemical and biological processes (Bermúdez-Couso et al. 2013), such as chemical and biological degradation, leaching, runoff, uptake by plants, transformation, persistence and bioaccumulation (Arias-Estévez et al. 2008). However, the most important processes are adsorption and desorption of the pesticide in the soil because the other processes mentioned previously are influenced by pesticide adsorption and desorption (De Jonge et al. 1996). Pesticides could be adsorbed by different soil components such as organic matter (Farahani et al. 2008), clays (Sharma and Awasthi 1997), carbonates and oxy-hydroxides (Stathi et al. 2011) and even rock fragments (Vischetti et al. 2010). Also adsorption and desorption processes could be

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influenced by other soil characteristics such as pH (Stathi et al. 2011) and temperature (Li et al. 2011). The adsorption and desorption of pesticides could have different effects on pesticide persistence in the soil. Adsorption avoids the movement of pesticides into the water system but also prevents the volatilization and biodegradation of pesticides (Krishna and Philip 2011). Desorption of pesticides from the soil facilitates runoff and leaching but makes the pesticide available to soil microorganisms, facilitating its biodegradation. Moreover, desorption facilitates volatilization.

The importance of adsorption–desorption and other processes on the metalaxyl concentration in the soil solution necessitates a thorough understanding of these mechanisms in the soil to prevent the potential adverse effects of metalaxyl in the soil and to improve pesticide management in agriculture. The adsorption of metalaxyl in soils was studied previously. Most of these studies were performed at equilibrium using a batch technique (Arias et al. 2006; Baglieri et al. 2011; Marín-Benito et al. 2009a, 2012; Monkiedje and Spiteller 2002; Sharma and Awasthi 1997; Sukul and Spiteller 2001), leaching experiments using soil columns (Marín-Benito et al. 2009b) or a combination of both techniques (Andrades et al. 2001; Fernandes et al. 2003). However, studies on the characteristics of the kinetic of metalaxyl adsorption–desorption process are scarce (Bermúdez-Couso et al. 2011a). More detailed studies on the kinetic characteristics of the adsorption and desorption processes of pesticides in the soil are important as they are not an instantaneous processes. Therefore, it becomes necessary to study the rates of adsorption and desorption of metalaxyl in the soil to fill a gap that exists in the knowledge of the pesticide's behavior in the soil.

The aim of this work was to evaluate the adsorption–desorption kinetics and transport of metalaxyl in two acid soils with different organic matter concentrations assessing three different experimental methods: batch, stirred flow chamber and soil column experiments. This research was conducted at the laboratories of soil science of the University of Vigo (Spain) during 2012.

Materials and methods

Chemicals

Metalaxyl [methyl *N*-methoxyacetyl-*N*-(2,6-dimethyl)-DL-alaninate] was obtained in purity >99.5 % from Sigma-Aldrich (Steinheim, Germany). The chemical structure and selected properties of metalaxyl are showed in ESM Table 1. All of the organic solvents used for sample preparation were residue analysis grade and supplied by Panreac (Barcelona, Spain). The high-performance liquid chromatograph (HPLC) grade solvents for HPLC measurements were also supplied by Panreac.

Soil samples

Two plots devoted to intensive farming were selected in the region called A Limia (Galicia, NW Spain), and the samples were collected from the topmost soil layer (0–20 cm). In the laboratory, the samples were air-dried, sieved (<2 mm) and stored in polyethylene jars until analysis. The soil samples' characteristics were analyzed using the same methods employed in a previous study (Bermúdez-Couso et al. 2011a, 2012) in which the methods used for the general characterization are described in detail. The general characteristics of the soils used in the experiments are shown in ESM Table 2. Both soils presented similar pH and effective cation exchange capacity (ECEC). However, the soil 1 (S1) presented higher amounts of clay and organic matter than soil 2 (S2). The main difference among the two soils is the organic carbon content, 22.7 % in the soil 1 and 2.7 % in the soil 2.

Metalaxyl adsorption and desorption

The processes by which pesticides are retained by and released from soils can be studied by different methods (Aharoni and Sparks 1991). We choose for this work three methods frequently used: batch experiments, stirred flow chamber and column experiments. Batch reactors are closed systems where the soil and the pesticides are in contact during a specific time; stirred flow chamber experiments are continuous flow methods under stirring; and column experiments are continuous flow methods without stirring.

Metalaxyl adsorption and desorption using batch experiments

Batch methods were widely used to obtain adsorption kinetic data in soils because its low cost and relative easy use related to other methods. In this system, the film diffusion is eliminated, but generally not the intraparticle diffusion. In this system, the equilibrium concentration diminishes during the adsorption processes and increased in desorption processes over time, and hence, both adsorption and desorption can be underestimated.

Two different experiments were performed using the batch technique: metalaxyl adsorption kinetics and metalaxyl adsorption at equilibrium. All these experiments were carried out at 25 °C and under dark conditions.

The kinetic experiments were conducted as follows: 1 g of soil was placed in a 40-mL glass centrifuge tube with 10 mL of a 7.2-μM metalaxyl and 0.005 M $CaCl_2$ solution.

After that, the suspension was mixed in an end-over-end shaker at 50 rpm for different lengths of time (0.5, 1, 4, 8, 16, 24 and 48 h). Preliminary experiments showed that 7.2 μM is an adequate concentration to perform the three kinetic experiments (bath, stirred flow chamber and column). After incubation, the soil suspensions were centrifuged at 2,000 rpm for 15 min and passed through a polyester filter with pore sizes of 0.45 μm (Macherey–Nagel, Düren, Germany). Previously, several tests were run to be verified that these filters do not adsorb metalaxyl. The resulting supernatant was used to determine the pesticide concentration using HPLC–UV. The amount of metalaxyl adsorbed on the soil was calculated by subtracting the amount of metalaxyl in solution from the amount of metalaxyl that was previously added. All tests were performed in duplicate.

Equilibrium experiments were conducted as follows: A 1 g amount of soil was mixed with 10 mL of aqueous solutions containing variable metalaxyl concentrations (9–90 μM) and 0.005 M $CaCl_2$ as a background electrolyte. After 24 h of shaking, the soil suspensions were centrifuged at 2,000 rpm for 15 min and passed through a filter with a 0.45-μm pore size. The supernatant was used to determine the metalaxyl concentrations by HPLC using a UV detector. The amount of pesticide adsorbed was calculated as the difference between the amount added and the amount measured in the solution.

In both the kinetic and equilibrium experiments, desorption experiments were performed immediately after adsorption, weighing the samples to quantify the amount of occluded solution. To each tube, 10 mL of 0.005 M $CaCl_2$ was added. After 24 h of shaking following the equilibrium adsorption experiments and variable times after the kinetic experiments, the samples were centrifuged at 2,000 rpm for 15 min, and the supernatant was filtered through a 0.45-μm filter and was used to determine the metalaxyl concentrations using HPLC–UV.

Metalaxyl adsorption and desorption using stirred flow chamber experiments

In order to avoid the problems associated with the batch method, flow methods have been developed and used to obtain soil adsorption and desorption kinetics. The main difference among flow and batch methods is that flow methods are inherently open systems. In the stirred flow chamber method, the flow through the reactor is maintained constant by a pump, and a fraction collector is used to collect the rector effluent. In the adsorption processes, the equilibrium is achieved at inflow concentration and during the desorption experiments; the products released to the solution are continually removed. Moreover, the stirring eliminate the film diffusion. The main difference with other flow methods is the reactor, where a suspension of soil and solution is continuously stirred.

The reactor used was similar to that used by López-Periago et al. (2008) with minor modifications (ESM Fig. 1). The micro-reactor used in this study was made of polypropylene (1.5 cm^3) with two polytetrafluoroethylene (PTFE) filters, measuring 10 mm in diameter and 0.45 μm in pore size, fitted in the outlet port and over the inlet port to retain the soil inside the chamber. The input was connected to a peristaltic pump, Gilson Minipuls 3. The flow rate was fixed at 0.2 mL min^{-1}, and the outlet port was connected to a fraction collector, Gilson FC 203 B, in which the effluent fractions were collected into 2 mL polypropylene Eppendorf vials. The reactor was located inside a cabin at a temperature of 25 ± 0.1 °C during the adsorption and desorption experiments. Stirring was provided by a PTFE-coated magnetic bar (3 mm × 1 mm) that spun at 400 rpm.

The adsorption experiments were performed as follows: A 0.2 g amount of soil was placed inside the micro-reactor, and a solution with 7.2 μM of metalaxyl and 0.005 M $CaCl_2$ as a background electrolyte was subsequently passed through the reactor. In total, 60 0.2-mL subsamples were collected in different vials (all of which were filled in 1 min). After the adsorption experiments, the metalaxyl solution was replaced by another solution with only 0.005 M $CaCl_2$ to perform the desorption experiments. The same number of samples (in the same time period) as used in the adsorption experiments were collected. The determination of metalaxyl was performed by HPLC–UV in all samples.

Metalaxyl adsorption and desorption using column experiments

Column experiments are one type of flow methods in which the reactor are full filled of soil and the soil solution flow among the soil particles. In this case, the conditions have more similarity to the real conditions in the soil than other methods. In this case, the film diffusion is not avoided, and its limitations can be studied. Like in the case of stirred flow chamber, the flow through the reactor is maintained constant by a pump, and a fraction collector is used to collect the rector effluent. Therefore, the equilibrium is achieved at inflow concentration in the adsorption experiments, and the desorbed products are continually removed.

The columns used were glass tubes 8 cm in length and 1.5 cm in diameter. The soil (<2 mm) was added in increments of 0.5 cm depth followed by gentle tapping of the column to consolidate the soil and remove any air bubbles (Chotpantarat et al. 2011). At the end, columns of soil 1 and 2 were filled with 9.1 and 15.0 g, respectively.

The input was connected to a peristaltic pump, namely the Gilson Minipuls 3. The output was connected to a fraction collector, the Gilson FC 203 B. The column experiments were conducted at 25 ± 0.1 °C, and the flow rate was 0.3 mL min^{-1}. The experiments were conducted as follows: The soil columns were initially saturated from the bottom with 0.005 M $CaCl_2$ during 24 h. After the saturation procedure, different experiments were performed on the two studied soils: (a) a solution of 0.005 M $CaCl_2$ containing 10 mg L^{-1} of bromide (Br^-) was injected from the bottom. Next, 40 samples of 3 mL each were collected in glass vials. A solution of 0.005 M $CaCl_2$ was subsequently injected, and another 40 samples were collected. The bromide concentration in each sample was measured in a segmented flow analyzer, Bran Luebbe Autoanalyzer 3; (b) a solution with 7.2 µM metalaxyl with 0.005 M $CaCl_2$ as a background electrolyte was injected from the bottom. Next, 40 samples of 3 mL each, filled in 10 min, were collected in glass vials. Afterward, the metalaxyl solution was replaced by 0.005 M $CaCl_2$, and the procedure was repeated. The determination of metalaxyl was performed by HPLC–UV in all samples.

Metalaxyl determination

The determination of metalaxyl was performed using a HPLC with a UV–Visible detector (Dionex Corporation, Sunnyvale, EE.UU.), equipped with a P680 quaternary pump, an ASI-100 autosampler, a TCC-10 thermostated column compartment and a UVD170U detector. Chromatographic separation was done on a Symmetry C18 column (4.6 × 150 mm, 5 µm) obtained from Waters (Milford, MA, USA) and a C18 guard column (4.6 × 50 mm, 5 µm) packet with the same material. The elution conditions for metalaxyl were as follows: The mobile phases were methanol (A) and water (B), and the gradient program was 60 % A + 40 % B for 7 min, changing to 95 % A + 5 % B for 3 min, holding for 5 min, changing to 60 % A + 40 % B for 0.1 min and holding for 10 min. The total analysis time was 25 min. The injected volume was 50 µL, and the flow rate was 0.7 mL min^{-1}. Metalaxyl was detected to $\lambda = 200$ nm.

Data analysis

Analysis of the equilibrium data from batch tests

The results from the equilibrium experiments performed via batch tests were fitted to Freundlich (1), Langmuir (2) and Straight Line (3) equations.

$$X = K_F C^n \tag{1}$$

$$X = \frac{K_L X_m C}{1 + K_L C} \tag{2}$$

$$X = K_D C \tag{3}$$

where X is the concentration of metalaxyl adsorbed in the soil (µmol kg^{-1}); C is the concentration of metalaxyl in the aqueous phase after equilibrium (µM); K_F (L^n kg^{-1} $\mu\text{mol}^{(1-n)}$) and n (dimensionless) are coefficients of the Freundlich equation; K_L (L μmol^{-1}) and X_m (µmol kg^{-1}) are the coefficients of Langmuir equation; and K_D (L μmol^{-1}) is the partitioning coefficient.

The Freundlich equation is an empirical function, where K_F can be interpreted as the amount of sorbate adsorbed at $C = 1$, i.e., a measure of metalaxyl adsorption at low concentrations, whereas the n parameter is a measure of the adsorption site's heterogeneity. This heterogeneity increased as n approached 0 and decreased as n approached 1 (Vidal et al. 2009). The parameters of Langmuir equation have the next physical meaning: K_L is dependent on the energy of adsorption bounds, and X_m is the maximum capacity of the soil the adsorb metalaxyl. On the other hand, the partitioning coefficient (K_D) is the ratio of the metalaxyl concentration in the soil to the concentration of metalaxyl in the soil solution.

Analysis of the kinetic data

In order to describe the kinetics of the pollutants sorption, the use of kinetics models is normally helpful. An important number of kinetics models can be employed. In this work, the kinetic data were fitted to the pseudo-first-order equation. This equation is widely used because its a simple model, which generally fit the kinetic data adequately, and when rate functions are used, the simplest models with good fits are the most desirables (Amacher 1991). For the adsorption processes, the equation can be expressed as the Eqs. (4) or (5), whereas for the desorption processes can be expressed as the Eqs. (6) and (7). For adsorption:

$$\mathrm{d}q_s/\mathrm{d}t = k_s(q_{\max} - q_s), \tag{4}$$

where $\mathrm{d}q_s/\mathrm{d}t$ (µmol kg^{-1} min^{-1}) is the metalaxyl adsorption rate; k_s (min^{-1}) is the metalaxyl adsorption rate constant; $q_{\max}$ (µmol kg^{-1}) is the amount of metalaxyl adsorbed at equilibrium; and q_s (µmol kg^{-1}) is the amount of metalaxyl adsorbed in the soil. The aforementioned Eq. (4) can be expressed in its integrated form (5), where t is the time.

$$\text{Ln}\ (q_s) = \text{Ln}\ (q_{\max} - q_s) + k_s t \tag{5}$$

For desorption:

$$\mathrm{d}q_d/\mathrm{d}t = k_d\ (q_0 - q_d) \tag{6}$$

where dq_d/dt (µmol kg^{-1} min^{-1}) is the metalaxyl desorption rate; k_d (min^{-1}) is the metalaxyl desorption rate constant; q_0 (µmol kg^{-1}) is the amount of metalaxyl that could be desorbed under experimental conditions; and q_d (µmol kg^{-1}) is the amount of metalaxyl desorbed from the soil. The aforementioned Eq. (6) can be expressed in its integrated form (7), where t is the time.

$$\text{Ln}\ (q_d) = \text{Ln}\ (q_0 - q_d) + k_d t. \qquad (7)$$

The $q_{\max}$ values expressed the maximum amount of metalaxyl that the soil can adsorb under the experimental conditions, i.e., flow rate, temperature and inflow concentration. The metalaxyl adsorption rate constant (k_s) is related with the adsorption process rate. The adsorption processes became faster as high the values of k_s are. The explanation of the desorption parameters is similar. The q_0 values expressed the maximum amount of metalaxyl that can be desorbed from the soil the experimental conditions, i.e., flow rate, temperature and the amount of metalaxyl previously adsorbed. The metalaxyl desorption rate constant (k_d) is related with the desorption process rate, and this became faster as higher are the values of k_d.

Statistics

Summary statistics were used to obtain the mean and standard deviation of the studied parameters. Student's t test and a paired two-sample test were used to compare the results from the soils studied. For all these analyses, the results were considered significant at a probability level of $P < 0.05$.

Results and discussion

Metalaxyl adsorption using batch experiments

Figure 1 shows the amount of metalaxyl adsorbed as a function of the incubation time. In both soils, equilibrium was reached at 24 h of incubation, although after 16 h, the amount of metalaxyl adsorbed was 95 and 98 % of the metalaxyl adsorbed at equilibrium in Soil 1 and Soil 2, respectively. Once at equilibrium, the amount of metalaxyl adsorbed was 32.8 ± 0.2 µmol kg^{-1} for Soils 1 and significantly lower ($t = 162.9$; $P < 0.05$) for soil 2 (6.4 ± 0.1 µmol kg^{-1}).

The data from the batch kinetic experiments were well fitted to the pseudo-first-order equation with R^2 of 0.92 and 0.99 for Soil 1 and Soil 2, respectively. The metalaxyl adsorption rate constants (k_s) were 0.0037 ± 0.0004 min^{-1} for Soil 1 and 0.0045 ± 0.0002 min^{-1} for Soil 2.

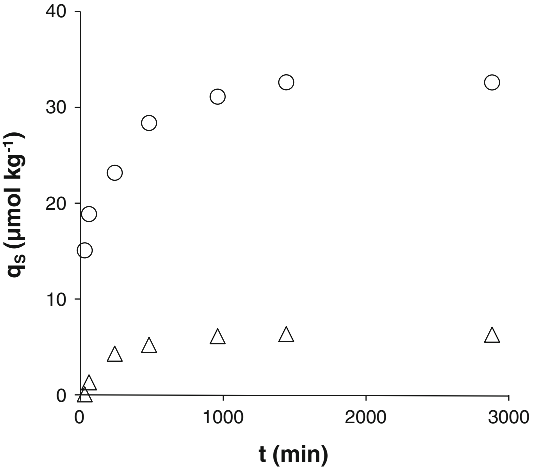

Fig. 1 Metalaxyl adsorption as a function of time in the batch experiments. The initial metalaxyl concentration was 7.2 µM. Soil 1 (*circles*); Soil 2 (*triangles*). The standard error was lower than 5 %, being smaller than the size of the symbols

Figure 2 shows the metalaxyl adsorption curves at equilibrium in the two studied samples. The metalaxyl adsorption curves were linear for both soils, i.e., Giles type C curves (Giles et al. 1974). This type of curve implies a constant partition between the amounts of metalaxyl adsorbed in the soil and the metalaxyl concentration in solution, i.e., a constant coefficient of distribution (K_D). This coefficient was calculated fitting the adsorption results obtained at equilibrium to a Straight Line Eq. (3). The data were well fitted to the lineal equation (Table 1), with R^2 values higher than 0.95 for the two studied soils. The K_D values were 5.94 ± 014 L kg^{-1} in Soil 1 and 0.58 ± 0.01 L kg^{-1} in Soil 2. This significant difference ($t = 48.5$; $P < 0.05$) could be attributed to differences in the organic matter concentration between the two studied soils. In fact, other authors showed that soil organic matter plays a key role in metalaxyl adsorption (Andrades et al. 2001; Marín-Benito et al. 2009b). The K_D value for Soil 2 was in the range previously reported (Andrades et al. 2001; Bermúdez-Couso et al. 2011a; Fernandes et al. 2003; Marín-Benito et al. 2009b; Monkiedje and Spiteller 2002). However, Soil 1 had a K_D value higher than all previously reported soils with one exception, specifically, a soil with 0.5 % organic carbon content, 68 % in clay and 32 % in silt and K_D 9.17 L kg^{-1} (Fernandes et al. 2003).

The adsorption data obtained at equilibrium were also fitted to the Freundlich (1) and Langmuir (2) equations. Fitting to the Langmuir equation was discarded because of the high level of error associated with the fitted parameters. However, fitting the metalaxyl adsorption data to the Freundlich equation was satisfactory with R^2 values higher than 0.95 for the two studied soils (Table 1). The fitted values of the Freundlich constant (K_F) were 12.15 L^n kg^{-1} µmol$^{(1-n)}$ for Soil 1 and 0.88 L^n kg^{-1} µmol$^{(1-n)}$ for Soil 2, whereas the

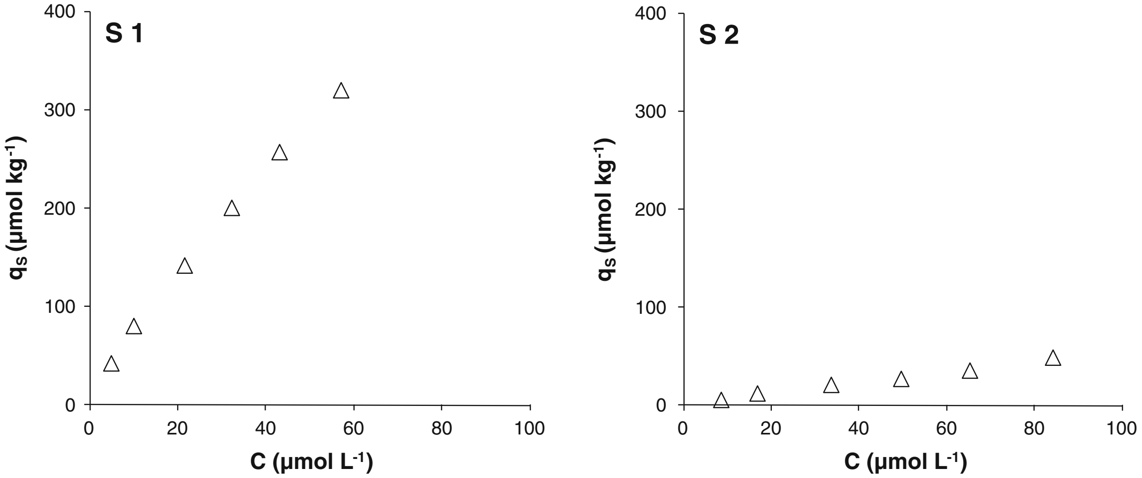

Fig. 2 Adsorption of metalaxyl in the two studied soils, as determined in the batch experiments performed at equilibrium. The standard error was smaller than the size of the symbols

n parameter (dimensionless) was 0.82 for Soil 1 and 0.90 for Soil 2. The *n* parameter values of the present work were in the range previously reported (Sharma and Awasthi 1997; Andrades et al. 2001; Fernandes et al. 2003; Bermúdez-Couso et al. 2011a), showing a notably low heterogeneity in the metalaxyl adsorption sites. The K_F values followed the same pattern as the K_D values with higher values in Soil 1 than in Soil 2.

Metalaxyl desorption using batch experiments

The metalaxyl desorption after its adsorption in the kinetic batch experiments was negligible (<0.5 µmol kg^{-1}). However, after the metalaxyl adsorption experiments at equilibrium, the results of metalaxyl desorption were detectable above the 90 µmol kg^{-1} that was added (Table 2). In the two studied soils, the amount of metalaxyl desorbed increased as the amount of metalaxyl previously added increased, ranging from 4.0 to 121.1 µmol kg^{-1} in Soil 1 and from 1.3 to 19.4 µmol kg^{-1} in Soil 2. In general, the percentage of metalaxyl desorbed also increased as the amount of metalaxyl previously added increased, ranging between 9.2 and 37.8 % in Soil 1 and between 21.7 and 42.6 % in Soil 2. This behavior suggests that the strength of the metalaxyl's bond to the soil diminishes as the amount of metalaxyl adsorbed in the soil increased (Bermúdez-Couso et al. 2011a). Results also show a high irreversibility of adsorption processes because more than 50 % of the previously adsorbed metalaxyl remained in the soil after the desorption experiments in all cases. The percentage of metalaxyl desorbed was significantly lower in Soil 1 than in Soil 2 (paired $t = -4.2$; $P < 0.05$), suggesting that the irreversibility of metalaxyl adsorption was increased as the soil organic matter content increased, as was suggested previously by Marín-Benito et al. (2009a).

Metalaxyl adsorption using stirred flow chamber experiments

Figure 3 shows the amount of metalaxyl adsorbed in the soil as a function of time in the stirred flow chamber experiments. During the experiment, 49.4 ± 0.7 µmol kg^{-1} of metalaxyl was adsorbed in Soil 1, whereas in Soil 2, the amount of metalaxyl adsorbed was significantly lower ($t = 66.8$; $P < 0.05$), 10.1 ± 0.4 µmol kg^{-1}. The data shown in Fig. 3 were well fitted to the pseudo-first-order Eq. (4), with R^2 values of 0.87 and 0.98 being observed for Soil 1 and Soil 2, respectively. The amount of metalaxyl adsorbed at equilibrium ($q_{\max}$) was 54.7 ± 0.9 µmol kg^{-1} for Soil 1 and 10.1 ± 0.2 µmol kg^{-1} for Soil 2. These values were 68 and 58 % higher than those found in the batch kinetic experiments for Soil 1 and Soil 2, respectively. Moreover, the metalaxyl adsorption was faster than in the batch experiments. In Soil 1, equilibrium was not achieved during the experiment (60 min), but at 30 min, the metalaxyl adsorbed was 62 % of the metalaxyl that can be adsorbed at equilibrium, and at 60 min, this percentage increased to 90 %. In Soil 2, equilibrium was reached at 17 min into the experiment. This faster metalaxyl adsorption than in batch experiments was reflected in higher k_s values, 0.032 ± 0.004 min^{-1} in Soil 1 and 0.275 ± 0.013 min^{-1} in Soil 2, i.e., in Soil 1, k_s was 8.6 times higher than in the batch experiments, and in Soil 2, k_s was 61.1 times higher. These k_s results also showed that the adsorption of metalaxyl was faster in Soil 2 than in Soil 1 ($t = -16.1$; $P < 0.05$), suggesting that the

Table 1 Fitting of metalaxyl adsorption results using batch experiments at equilibrium to the Freundlich and Straight line equations

Sample	Freundlich equation			Straight line	
	K_F (L^n kg^{-1} $\mu mol^{(1-n)}$)	n	R^2	K_D (L kg^{-1})	R^2
S1	12.15 ± 0.94	0.82 ± 0.02	0.997	5.94 ± 0.14	0.973
S2	0.88 ± 0.19	0.90 ± 0.05	0.984	0.58 ± 0.01	0.978

Table 2 Metalaxyl desorbed (μmol kg^{-1}) after batch experiments at equilibrium and percentage of metalaxyl desorbed with respect to the amount of metalaxyl previously adsorbed (in brackets)

Metalaxyl added (μmol kg^{-1})						
	90	179	358	537	716	895
S1	4.0 (9.2)	8.1 (10.0)	26.5 (18.6)	43.2 (20.9)	65.4 (25.4)	121.1 (37.8)
S2	1.3 (21.7)	2.0 (15.7)	6.9 (32.1)	11.1 (40.3)	15.4 (42.6)	19.4 (39.4)

metalaxyl adsorption rate is inversely proportional to the adsorption capacity. The differences between the results obtained using the batch and stirred flow chamber methods may be attributable to the different limitations of each method (Amacher 1991). In the batch method, the concentration of metalaxyl in the solution diminishes with time until equilibrium, which is stated at a lower concentration than the initial concentration. This problem is avoided in the stirred flow chamber method in which the equilibrium is achieved at inflow concentration. The lower equilibrium concentration in the batch method could be a notably high limitation in metalaxyl adsorption, reducing the amount of metalaxyl adsorbed and its adsorption rate. In fact, the k_s parameter was similar in the two soils that were used, despite the high differences in metalaxyl adsorption capacity, suggesting that the metalaxyl adsorption rate in the batch experiment was limited by the method independently of the soil used. In the stirred flow chamber method, the metalaxyl adsorption rate was controlled mainly by intraparticle diffusion (Bermúdez-Couso et al. 2011a), providing different results with different soils.

Metalaxyl desorption using stirred flow chamber experiments

Figure 3 shows the amount of metalaxyl desorbed from the soil as a function of time in the stirred flow chamber experiments. The metalaxyl desorption was rapid; at 5 min, the amount of metalaxyl desorbed represented 50 % of the metalaxyl that was desorbed during the experiment, whereas in Soil 2, this percentage increased to 80 %.

The metalaxyl desorption kinetics were well fitted to the pseudo-first-order model (6) with R^2 values of 0.93 for Soil 1 and 0.90 for Soil 2. The amount of metalaxyl that could be desorbed under experimental conditions (q_0) was 43.3 ± 0.6 and 9.2 ± 0.4 μmol kg^{-1} for Soil 1 and Soil 2, respectively. These values represented 88 and 91 % of the metalaxyl previously adsorbed. Monkiedje and Spiteller (2002) suggest that the soil–metalaxyl interactions are notably weak, making the metalaxyl adsorption in the soil highly reversible. This weak bond could be attributed to the low hydrophobicity of metalaxyl (Marín-Benito et al. 2009b). These percentages of metalaxyl desorption were higher than those found in the batch equilibrium test. In a previous work, Bermúdez-Couso et al. (2011a) suggested that these differences could be attributed to the continuous removal of desorbed metalaxyl in the stirred flow chamber experiments, whereas in the batch experiments, the metalaxyl desorption could be limited by the amount present in solution. Higher percentages of desorption using stirred flow chamber experiments than using batch experiments were also found for other organic contaminants (Bermúdez-Couso et al. 2011b) and for heavy metals (Fernández-Calviño et al. 2010). The metalaxyl desorption rate constant (k_d) was 0.118 ± 0.005 min^{-1} for Soil 1 and 0.337 ± 0.035 min^{-1} for Soil 2. These values were higher than the k_s values, indicating that metalaxyl desorption is a faster process than metalaxyl adsorption. Moreover, the metalaxyl desorption from Soil 2 was faster than from Soil 1 ($t = -8.7; P < 0.05$).

Column test

Tracer and metalaxyl transport in soil columns

Figure 4 shows the breakthrough curves (BTCs) for bromide and metalaxyl in the two studied soils. In all cases, a strong symmetry between adsorption and desorption was found, suggesting similar limitations for adsorption and desorption processes. These results were different from those found by Marín-Benito et al. (2009a) in soil columns

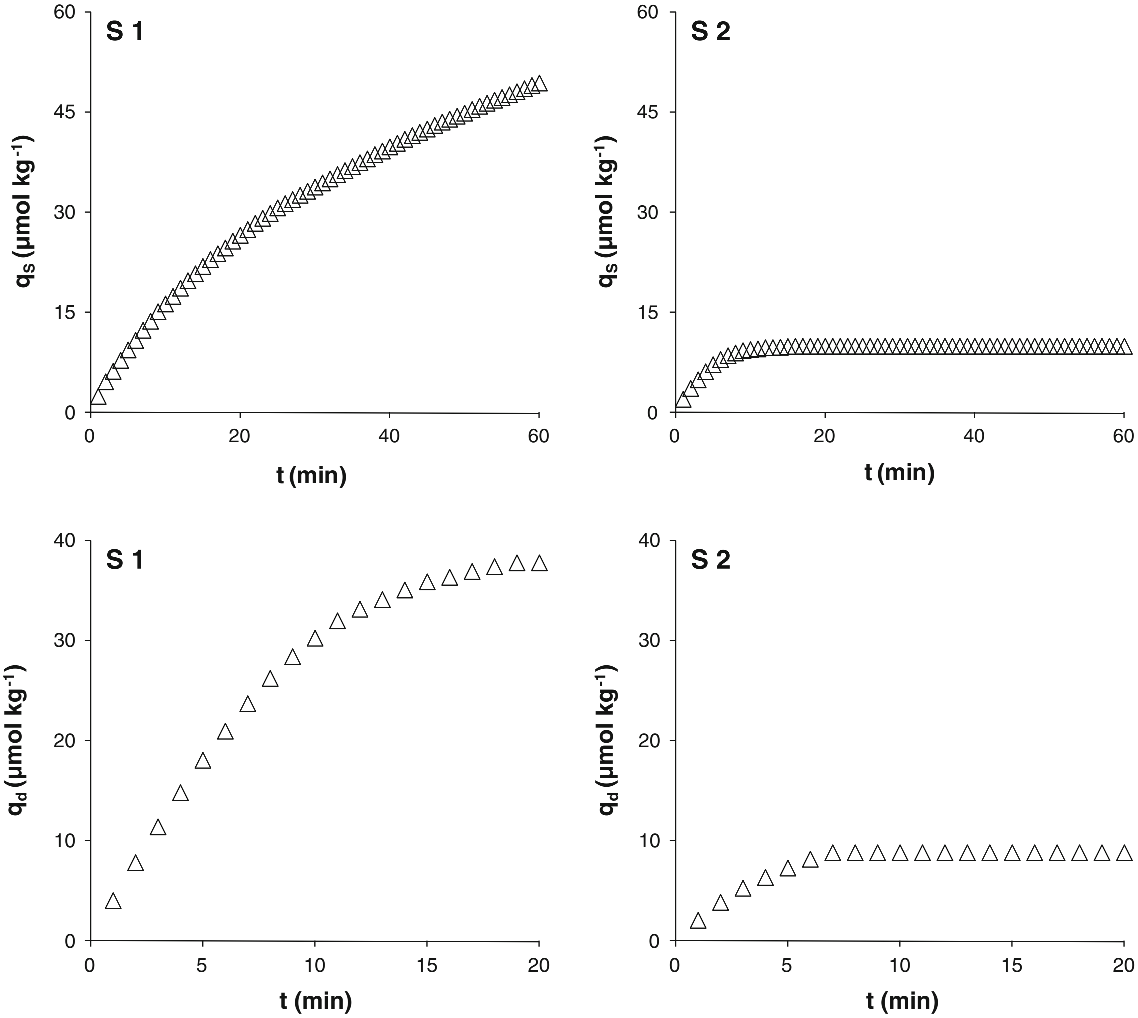

Fig. 3 Cumulative metalaxyl adsorption (q_s) and desorption (q_d) as a function of time (t) in the two studied soils, as determined in the stirred flow chamber experiments. The initial metalaxyl concentration was 7.2 µM. The cumulative standard error at the end of the experiment was lower than 5 %

under unsaturated conditions in which no symmetry was found between adsorption and desorption. This discrepancy suggests that the BTCs could be influenced by the saturation conditions.

In both soils, the BTCs for the tracer (Br^-) were similar, reaching the inflow concentration at approximately 2.5 pore volumes (PV). This finding suggests that the differences in the leaching of metalaxyl between soils were not related to water flow, and therefore, the differences in metalaxyl adsorption could be studied by this method. The BTCs for metalaxyl were different in Soil 1 and in Soil 2. In Soil 2, the inflow concentration was reached at seven PV, whereas in Soil 1, only 85 % of the inflow solution was reached at the end of the experiment (13.5 PV).

Another difference between the BTCs of Soil 1 and Soil 2 was the slope of the curves (Fig. 4), which was higher in Soil 2 than in the Soil 1, suggesting faster adsorption and desorption processes in Soil 2 than in Soil 1. This result agrees with the results from the stirred flow chamber, suggesting that differences in the metalaxyl adsorption capacity were more important than differences in the column characteristics. Table S3 shows the column characteristics and the retardation factor (R), which was calculated according to the next Eq. (8) (Toride et al. 1999):

$$R = 1 + (\rho K_D/\theta) \tag{8}$$

where ρ is the bulk density, K_D is the coefficient of distribution ($cm^3\ g^{-1}$) and θ is the porosity ($cm^3\ cm^{-3}$). When there is no adsorption, $K_D = 0$ and $R = 1$.

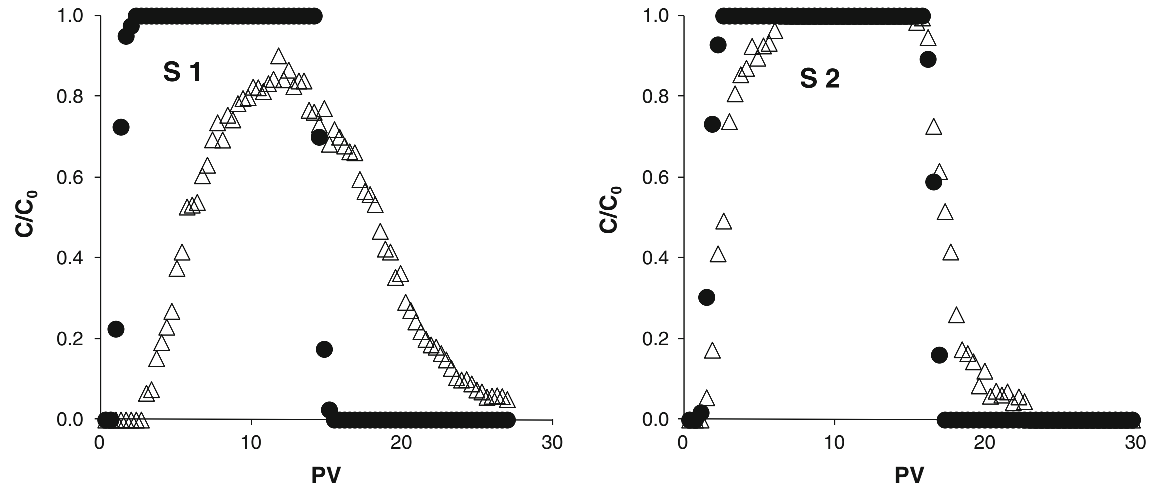

Fig. 4 Experimental BTCs for bromide (*circles*) and metalaxyl (*triangles*) in the column experiments. The initial metalaxyl concentration was 7.2 µM. The standard error was lower than 5 %, being smaller than the size of the symbols

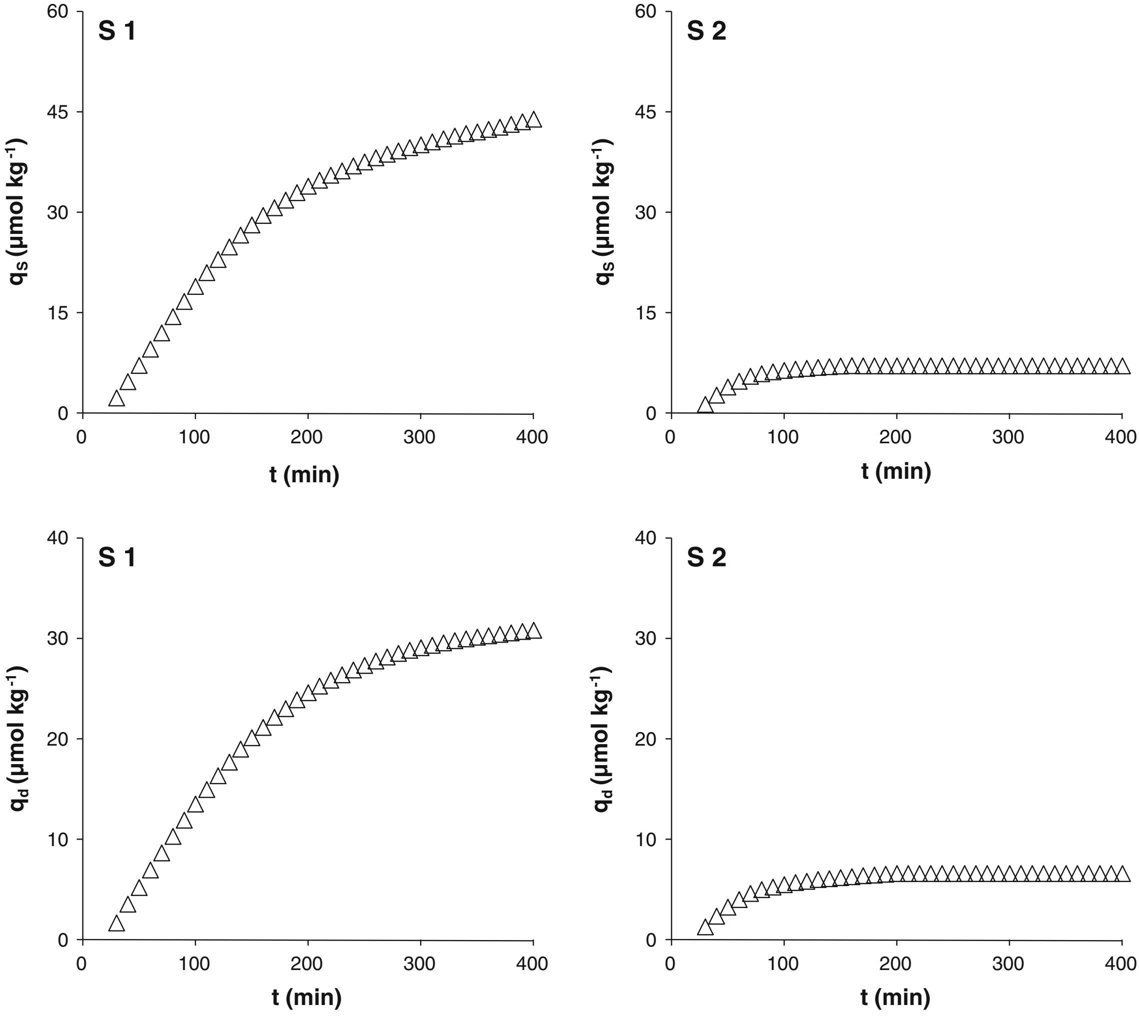

Fig. 5 Cumulative metalaxyl adsorption (q_s) and desorption (q_d) as a function of time (t) in the two studied soils, as determined in the column experiments. The initial metalaxyl concentration was 7.2 µM. The cumulative standard error at the end of the experiment was lower than 5 %

The values of ρ and θ (Table S3) suggest that R should be higher in Soil 2 than in Soil 1. However, R was 7.8 for Soil 1 and 2.1 for Soil 2, indicating that the K_D parameter was more important than ρ and θ, i.e., the differences in the metalaxyl adsorption capacity were more important than the differences in the column characteristics. The R values of both soils are in the same order of magnitude as those found by Marín-Benito et al. (2009a) under unsaturated conditions.

Metalaxyl adsorption using column experiments

Figure 5 shows the amount of metalaxyl adsorbed as a function of time. The amount of metalaxyl adsorbed at the end of the experiment was 43.9 ± 0.6 µmol kg^{-1} in Soil 1 and significantly lower, 7.3 ± 0.3 µmol kg^{-1}, in Soil 2 ($t = 73.2$; $P < 0.05$) These results agreed with the batch and stirred flow chamber experiments. Therefore, the three methods tested in this study provided the same qualitative result, i.e., the soil with higher organic matter and clay content has a higher capacity to adsorb metalaxyl. This result agrees with previous work (Andrades et al. 2001; Bermúdez-Couso et al. 2011a; Marín-Benito et al. 2009b), and therefore, the three methods are adequate to compare the metalaxyl adsorption capacity from different soils.

The results from Fig. 5 were well fitted to the pseudo-first-order Eq. (4) with R^2 values of 0.94 and 0.96 for Soil 1 and Soil 2, respectively. The $q_{\max}$ values were 49.0 ± 0.2 µmol kg^{-1} for Soil 1 and 7.3 ± 0.0 µmol kg^{-1} for Soil 2. These values were higher than those found with the batch method (32.8 ± 0.2 and 6.4 ± 0.0 µmol kg^{-1}) but lower than those found with the stirred flow chamber (54.7 ± 0.9 and 10.1 ± 0.2 µmol kg^{-1}), i.e., the metalaxyl adsorption capacity in one soil is different depending on the method employed in the following sequence: stirred flow chamber > column > batch for the same initial metalaxyl concentration. The metalaxyl adsorption rate constants (k_s) obtained using the column experiments were 0.006 ± 0.001 min^{-1} for Soil 1 and 0.031 ± 0.003 min^{-1} for Soil 2. As with the $q_{\max}$, the k_s values were higher in the stirred flow chamber experiments (0.032 ± 0.004 and 0.275 ± 0.0013 min^{-1} in Soil 1 and Soil 2, respectively) than in the column experiments, and the results for both experiments were higher than in the batch experiments (0.0037 ± 0.0004 min^{-1} in Soil 1 and 0.0045 ± 0.002 min^{-1} in Soil 2). The differences in both $q_{\max}$ and k_s among the three methods tested could be attributed to the different limitations of each method (Amacher 1991). In the batch methods, the soil suspension with metalaxyl was continuously stirred; however, the metalaxyl concentration in the solution diminished with time, and equilibrium was reached at a metalaxyl concentration lower than the initial concentration. In the column experiments, the soil remains without stirring, and therefore, film diffusion could be an important limitation, and the metalaxyl could not reach certain adsorption sites. These shortcomings are eliminated in the stirred flow chamber methods in which the soil suspension is continuously stirred, and equilibrium is reached at the inflow metalaxyl concentration. In the stirred flow chamber, the metalaxyl is adsorbed mainly via fast reactions (Bermúdez-Couso et al. 2011a), and it is well known that fast reactions are limited by intraparticle diffusion (Aharoni and Sparks 1991). These results show that the equilibrium concentration had more importance than film diffusion on the metalaxyl adsorption capacities and kinetics. Moreover, intraparticle diffusion is a limitation with less importance than the limitations in the other two processes.

Metalaxyl desorption using column experiments

The results for the metalaxyl desorption kinetics using the column technique are shown in Fig. 5. These results were well fitted to the pseudo-first-order model (6) with R^2 values of 0.94 in Soil 1 and 0.98 in Soil 2. The values of q_0 were 34.4 ± 0.2 and 6.7 ± 0.1 µmol kg^{-1} for Soil 1 and Soil 2, respectively, representing 78 and 92 % of the metalaxyl previously adsorbed in the soil. These results are notably similar to those found with the stirred flow chamber and higher than those found with the batch experiments. This means that the continuous removal of desorbed metalaxyl is important to an adequate determination of metalaxyl adsorption reversibility. With respect to the metalaxyl desorption rate constant (k_d), using column experiments, the rate was 0.007 ± 0.001 min^{-1} in Soil 1 and 0.026 ± 0.007 min^{-1} in Soil 2. These values were close to the k_s values found in metalaxyl adsorption using the column test; i.e. the adsorption and desorption rates are similar. This discrepancy with respect to the stirred flow chamber experiments was probably due to the high limitation of film diffusion with respect to the other kinetic limitations in the column experiments.

Conclusion

The three methods tested in this study show that the soil with higher organic matter and clay content has a higher capacity to adsorb metalaxyl, whereas the adsorption rates were faster in the soil with less organic matter and clay content. Batch experiments also showed low heterogeneity in the metalaxyl adsorption sites.

The percentage of metalaxyl desorbed was higher in Soil 2 than in Soil 1 in the three methods tested, and hence, the irreversibility of metalaxyl adsorption was increased as the soil organic matter content increased. These desorption processes were also faster in the soil with the lower organic matter and clay content. Moreover, the desorption processes were faster than adsorption processes in the stirred flow chamber experiments, whereas in the column experiments, the adsorption and desorption rates were similar. This means that the desorption was faster than the adsorption when the rate was limited by intraparticle diffusions, but in the real soil, the film diffusion masks the differences between adsorption and desorption rates.

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