Acta Scientiarum

http://www.uem.br/acta
ISSN printed: 1679-9275
ISSN on-line: 1807-8621
Doi: 10.4025/actasciagron.v35i3.16374

The influence of organic matter from swine wastewater on the interaction and transport of alachlor in soil

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ABSTRACT. This study evaluated the effects of total and dissolved organic matter produced from two swine wastewater treatment systems, a biodigester and a manure lagoon, on the adsorption, desorption, and leaching of alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) in soil. It was used the batch equilibrium method to test adsorption and desorption, and the results are presented in Freundlich isotherms. It also used disturbed soil columns to evaluate the miscible displacement of alachlor in soil treated with total and dissolved organic matter. This assay was used to monitor the concentration of alachlor in the leached material, the amount of total organic carbon, and the pH. The addition of swine wastewater promoted greater adsorption and desorption of alachlor compared with the control. The dissolved organic matter promoted less soil adsorption of alachlor compared with the total organic matter and also interacted with the alachlor and/or competed with the exchangeable cation sites in the soil, resulting in greater leaching. The total organic matter contributed to the emergence of new sorption sites in the soil column, and the solids present in the composition may have blocked pesticide passage, resulting in lower loss of alachlor due to leaching.

Keywords: adsorption, hydro-dispersive parameters, infrared spectroscopy, leaching, pesticide.

Influência da matéria orgânica proveniente de água residuária de suinocultura na interação e transporte do alaclor no solo

RESUMO. Este trabalho avaliou o efeito da aplicação de matéria orgânica total e dissolvida proveniente de dois sistemas de tratamento de água residuária de suinocultura, biodigestor e esterqueira, na adsorção, dessorção e lixiviação de alaclor (2-cloro-2,6-dietil-N(metoximetil acetamida)) no solo. O método do equilíbrio foi utilizado para o teste de adsorção e dessorção e os resultados foram apresentados em isotermas de Freundlich. Utilizou-se também colunas de solo deformado para avaliar o deslocamento miscível do alaclor no solo tratado com matéria orgânica total e dissolvida. Este ensaio foi realizado para monitorar a concentração de alaclor no lixiviado, o teor de carbono orgânico total e o pH. A adição de água residuária de suinocultura promoveu maior adsorção e dessorção do alaclor comparado ao controle. A matéria orgânica dissolvida promoveu menor adsorção de alaclor ao solo comparada à total e também interagiu com o alaclor e/ou competiu com os sítios sortivos do solo, resultando em maior lixiviação. A matéria orgânica total contribuiu com o surgimento de novos sítios de sorção na coluna de solo e os sólidos presentes em sua composição podem ter bloqueado a passagem do pesticida, resultando em menores perdas de alaclor por lixiviação.

Palavras-chave: adsorção, parâmetros hidrodispersivos, espectroscopia infravermelha, lixiviação, pesticida.

Introduction

It is increasingly common to detect significant concentrations of pesticides and their metabolites in surface water (VECCHIA et al., 2009), underground water (POSTIGO et al., 2010), food, and soil (ABRANTES et al., 2010).

Swine-cultivating areas stand out in this regard due to their intense cultivation of corn, which is produced for (among other purposes) animal feed. Various herbicides are used in the cultivation of crops. One of these is alachlor, a pre-emergence herbicide used to control weeds that affect cotton, soybean, peanut, coffee, sugarcane, corn, and rice crops. However, as Choi et al. (2010) have shown, alachlor is a highly toxic pollutant for many organisms due to its strong aromaticity and high chemical stability.

According to Li et al. (2005), when applied to the soil, pesticides can be adsorbed by plants, volatilized into the atmosphere, photodegraded by the sun, adsorbed into soil particles, leached, lost by surface runoff, erosion, drainage or lateral subsurface flow.

Pesticides can also be further degraded by chemical, physical, or microbiological processes (CHENG et al., 2010).

The amount of organic matter and its two forms, dissolved and total, have become objects of concern because they influence the actions of pesticides in soil. In recent years, scientific interest in dissolved organic matter has increased (JIANG et al., 2008; SONG et al., 2008). In some cases, the addition of dissolved organic matter to soil leads to a reduction in pesticides leaching (DRORI, et al., 2005; ZHAOHAI et al., 2008). Other studies, however, have reported an increase in leaching (JIANG et al., 2008; LI et al., 2005; SONG et al., 2008).

There is thus no clear relationship between pesticides and the addition of dissolved organic matter in the form of waste to soil. Furthermore, most studies have added organic matter to soil in the form of solid waste such as sewage sludge (SONG et al., 2008), biocompost from sugar distillers (SINGH, 2008), rice straw (JIANG et al., 2008) and cow manure (DORADO et al., 2005) as well as with commercial organic fertilizer (LI et al., 2005). Few studies have examined the use of wastewater, which is characterized by the presence of large amounts of dissolved organic matter (MULLER et al., 2007).

For some pesticides, such as atrazine (DRORI et al., 2008) and diuron (PIÑEIRO et al., 2010), it is important to understand their mobility in soil. Even though alachlor represents a risk to both public health and the environment (CHOI et al., 2010), no studies have addressed its mobility in soil following the addition of organic matter from solid waste or wastewater.

Thus, the objective of this study was to evaluate the effects of applying dissolved organic matter and total organic matter from two swine wastewater treatment systems, a biodigester and a manure lagoon, on the adsorption, desorption, and leaching of alachlor in soil.

Material and methods

Treatments and materials

The treatments were assigned as follows: Control (no addition of swine wastewater (SWW)), TOM-B (total organic matter from swine wastewater treated in a biodigester), DOM-B (dissolved organic matter from swine wastewater treated in a biodigester), TOM-L (total organic matter from swine wastewater treated in a manure lagoon), and DOM-L (dissolved organic matter from swine wastewater treated in a manure lagoon).

The SWW treated with a biodigester was collected from the reactor. The wastewater treated in a manure lagoon was collected from the third lagoon, which is characterized as a facultative system. Both treatment systems were located on the property of a pig breeder.

Dissolved organic matter (DOM) was extracted from the SWW by adapting the methodology of Zhaohai et al. (2008). Samples were centrifuged at 2474 g-Force for 15 minutes, and the supernatant was filtered through a 0.45 μm cellulose acetate membrane. The SWW (Table 1) was characterized according to the APHA et al. (1998) methodologies.

Table 1. Basic physical-chemical characteristics of the swine wastewater.

Parameter	Unit	TOM-B	DOM-B	TOM-L	DOM-L
pH	-	7.15	8.27	7.20	8.07
COD[a]	$mg\ L^{-1}$	4830.00	1539.00	2154.00	1405.00
TOC[b]	$mg\ L^{-1}$	967.00	355.60	547.30	255.40
TS[c]	$mg\ L^{-1}$	3860.00	2510.00	3193.00	2104.00

[a]COD: chemical oxygen demand; [b]TOC: total organic carbon as assessed by a total organic carbon measurer (Shimadzu® - model TOC-V CPH); [c]TS: total solids.

Native forest soil collected at a depth of 30-60 cm was used to eliminate the effects of organic matter and the presence of pesticides in the litter layer. This soil was air dried and sieved (2 mm). The soil is extremely clayey, consisting of 10.87% sand, 12.32% silt, and 76.81% clay. Its Embrapa (2006) classification is Dystrophic red latosol or Orthic Ferralsol (FAO, 2006), and it displays the following characteristics: a pH (water) of 4.25, organic matter content of 20.33 g dm^{-3} and a cation exchange capacity of 15,1 $cmol_c\ dm^{-3}$.

Analytical standard (Pestanal®) alachlor herbicide (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) was applied to the soil. Quantification was performed by high efficiency liquid chromatography (Shimadzu Prominence®) with the following setup: a C-18 column (150 x 4.6 mm), mobile phase acetonitrile/water (60:40, $v\ v^{-1}$), a 220 nm UV detector, a continuous flow of 1 mL min^{-1}, an oven temperature of 35°C, and an injection volume of 20 μL (SOPEÑA et al., 2009). The samples were filtered (0,45 μm) before injection.

The SWW and alachlor were characterized by spectroscopy in the mid-infrared region with a Fourier transform infrared (FTIR) spectrometer using ATR (attenuated total reflection) equipment (Jasco® - model 4200). The spectra of the freeze-dried samples were obtained from 64 accumulations in the range of 4000-500 cm^{-1}, each with a resolution of 4 cm^{-1}. The organic attributes of the FTIR spectrum bands were determined by comparison with the data in Silverstein et al. (2007).

Adsorption and desorption assay

The adsorption and desorption of alachlor in the soil was assessed by the equilibrium method adapted from Dorado et al. (2005). Five grams of air-dried soil was weighed in triplicate in 50 mL centrifuge tubes containing 5 mL of alachlor solution (prepared in a solution of 0.01 M $CaCl_2$) at the following concentrations: 5, 10, 20, 30, 40, and 100 mg L^{-1}. Then, 5 mL of the DOM or TOM from the SWW was added to the tubes and separated according to the treatment in question. For the Control treatment, the same soil mass and alachlor concentrations were used, but without the addition of SWW.

The suspension was considered to be at equilibrium after 12 hours under mechanical agitation at 200 rpm in a dark environment at 20°C with more than 12 hours of contact. The material was then centrifuged at 2938 g-Force for 18 minutes, and the alachlor concentration in the supernatant was determined. The sorbed concentration was calculated using Equation 1,

$$Cs = \frac{[V.(Ci - Ce)]}{Ms} \tag{1}$$

where:

Cs is the sorbed concentration (mg kg^{-1}), V is the solution volume (L), Ms is the amount of soil (kg), Ci is the initial added concentration (mg L^{-1}), and Ce is the equilibrium concentration (mg L^{-1}).

After the adsorption test, the same samples were used to determine the desorption. A total of 5 mL of $CaCl_2$ (0.01 M) was added to the waste in the centrifuge tubes. The bottles were mechanically agitated at 200 rpm for 4 hours and then re-centrifuged. This process was repeated four more times. The herbicide concentration was measured in the supernatant after each desorption stage, and the amount of alachlor still adsorbed in the soil after each desorption process was calculated from the difference.

The results of the adsorption and desorption assay are presented in Freundlich isotherms (Equation 2) (ARCHANGELO et al., 2004) as:

$$Cs = k_{f_{(s)}} Ce^{1/n} \tag{2}$$

where:

k_f is the sorption coefficient representing the amount of alachlor sorbed by the soil at equilibrium and 1/n is the Freundlich exponent, indicating the degree of linearity of the isotherm.

To compare isotherms between the treatments, the Freundlich equation was linearized by taking the logarithm of both sides of the equation as recommended by Casagrande and Soares (2009) and Song et al. (2008).

The value of the coefficient of adsorption distribution ($k_{d(s)}$) was calculated in L kg^{-1} for each treatment by dividing Cs by Ce. When n = 1, the Freundlich isotherm is transformed into a linear isotherm, and the coefficient of adsorption ($k_{f(s)}$) is called k_d (CASAGRANDE; SOARES, 2009).

The concentration of alachlor present in the desorption solutions (Ce_d mg L^{-1}) and the amount of remaining herbicide adsorbed by the soil (Cs_d mg kg^{-1}) were calculated based on the difference between Cs and Ce_d.

The sum of the amount of pesticide determined for each of the five extractions is equal to the total desorbed amount (CASAGRANDE; SOARES, 2009).

The hysteresis index (H) was calculated by dividing n_s (the curvature of the adsorption isotherm) by n_d (curvature of the desorption isotherm (BARIZON et al., 2006).

Studies of adsorption and desorption normally include descriptive analyses of the data without using statistical tests to compare the k_f, k_d, and n values (ANDRADE et al., 2010; BARIZON et al., 2006; MAJUMDAR; SINGH, 2007; SINGH, 2008; SONG et al., 2008; ZHAOHAI et al., 2008). For the adsorption data in our study, ANOVA was used with a completely randomized design to compare the means of $k_{f(s)}$ and $k_{d(s)}$ for the two treatments using Tukey's Test (5% significance). For the desorption data, this same method was applied for the desorption coefficient ($k_{f(d)}$).

Leaching assay

The miscible displacement of alachlor in the soil treated with SWW was characterized with disturbed soil column assays. The columns were acrylic, 5.5 cm in diameter, and 30 cm in length. They were prepared by adding 50 g of uniformly compacted soil to avoid the formation of preferential paths and to make the column density approximate the density of the collected soil (Table 2).

Table 2. Physical characteristics of the soil column by treatment

Characteristic	Unit	Control	TOM-B	DOM-B	TOM-L	DOM-L
Soil density[(a)]	g cm^{-3}	0.84	0.82	0.86	0.86	0.87
Particle density	g cm^{-3}	2.66	2.66	2.66	2.66	2.66
Porosity	%	68.33	69.09	67.50	67.65	67.40
1 Pore volume	mL	487.00	492.46	481.08	482.18	480.37

[(a)]Value calculated with the soil mass corrected for moisture. Note: the density of the collected soil was 0.88 g cm^{-3}.

In the leaching assay, the columns were connected to hoses attached to a peristaltic pump that was connected to a reservoir. The leachate material was collected with a fraction collector (Gilson® - model FC 204).

Before beginning the tests, as per Corrêa et al. (1999), the columns were saturated by passing a 0.01 M $CaCl_2$ solution at a low flow rate from the base of the column.

After the columns were saturated, the SWW was passed through with a downward flow of 3.5 mL min^{-1}. The volume of SWW applied to the columns was equal to the pore volume (Table 2).

Alachlor diluted in acetone (1 mL) was then applied at an amount equivalent to 35 L ha^{-1}. The columns were left to settle overnight in the dark at room temperature (MAJUMDAR; SINGH, 2007).

The equivalent of 12 pore volumes of ultrapure water was passed through the columns to simulate rain and to avoid ionic influences on the dynamics of the solute in the soil. Samples were stored to determine the alachlor concentration, TOC, and pH.

Elution curves were constructed from the alachlor concentration values in the leachate based on each type of treatment.

A statistical curve comparison test was performed at the 5% significance level with the leaching assay values starting from the beginning of alachlor detection up to the peak in the alachlor concentration (i.e., the initial part of the curve) in order to determine the intensity of alachlor leaching at that time. To evaluate the leaching behavior resulting from the treatments, this test was also performed with the values from the peak in concentration up to the sixth pore volume, which is the time at which the concentration of the herbicide tended to become constant. This test involved regression analysis and a statistical test (Student's t-test) between the respective angular and linear coefficients (SAMPAIO et al., 2010).

A Pearson's correlation test was performed to test for relationships between the concentration of alachlor, TOC, and pH.

The retardation factor (R) and the coefficient of hydro-dynamic dispersion (D) were estimated with STANMOD software (SIMUNEK et al., 2008) and with the convection-dispersion equation (CDE) for two sorption sites. A pulse application was used, providing a pulse for consideration at a concentration of 58,800 mg L^{-1} with an application time of 0.0024 hours. Based on these results, the distribution coefficient (k_d) was determined for the soil columns along with the Péclet number (Pe) (CORREIA et al., 2006) and the dispersivity (λ) (MILFONT et al., 2006).

Results and discussion

Adsorption and desorption

Table 3 shows the adsorption and desorption parameters based on the isotherms. The $k_{f(s)}$ and $k_{d(s)}$ values obtained were higher in the presence of SWW than in the Control treatment except in the case of DOM-B, which was statistically equivalent to the Control. This result indicates that soil with organic matter from SWW has greater sorption capacity. Other authors have observed this behavior with chloroacetamide pesticides and with different methods of adding organic carbon to soil (ARCHANGELO et al., 2004). According to Torrents et al. (1997), chloroacetamide herbicides may be adsorbed by organic matter due to charge transfer, due to Van der Waals forces involving the aromatic moiety, and/or due to hydrogen bonds between carboxyl or hydroxyl groups on the surface of the organic matter and the carbonyl oxygen of the amide group of the herbicide.

Table 3. Adsorption and desorption parameters according to Freundlich and linear isotherms.

Treatment	Adsorption				Desorption			
	$k_{f(s)}$* (L kg^{-1})	$n_{(s)}$	r^2	$k_{d(s)}$ (L kg^{-1})*	$k_{f(d)}$* (L kg^{-1})	$n_{(d)}$	r^2	H (n_s n_d^{-1})
Control	2.47 (a)	0.93	0.98	2.12 (a)	3.85 (a)	0.88	0.95	1.06
TOM B	7.49 (b)	1.22	0.97	9.28 (b)	7.57 (b)	0.93	0.99	1.31
DOM-B	5.98 (ab)	1.11	0.99	6.98 (b)	7.87 (b)	0.95	0.99	1.17
TOM-L	8.57 (b)	1.01	0.93	8.70 (b)	8.23 (b)	0.88	0.98	1.15
DOM-L	7.04 (b)	1.04	0.96	7.48 (b)	7.08 (b)	1.00	1.00	1.04

*The same lowercase letter in a column designates a lack of a difference by Tukey's Test at the 5% significance level. The variables and coefficients indicated are adsorption coefficients ($k_{f(s)}$), desorption coefficients ($k_{f(d)}$), linearity factors of the equation (n), adsorption distribution coefficients ($k_{d(s)}$), correlation coefficients (r^2), and hysteresis indices (H).

The lower $k_{f(s)}$ value for DOM-B in comparison to TOM-B, TOM-L, and DOM-L may be linked to the greater TOC proportion of DOM in TOM (Table 1), which were 46.67 and 36.77% for the SWW from the manure lagoon and the biodigester, respectively, leading to greater leaching and less adsorption.

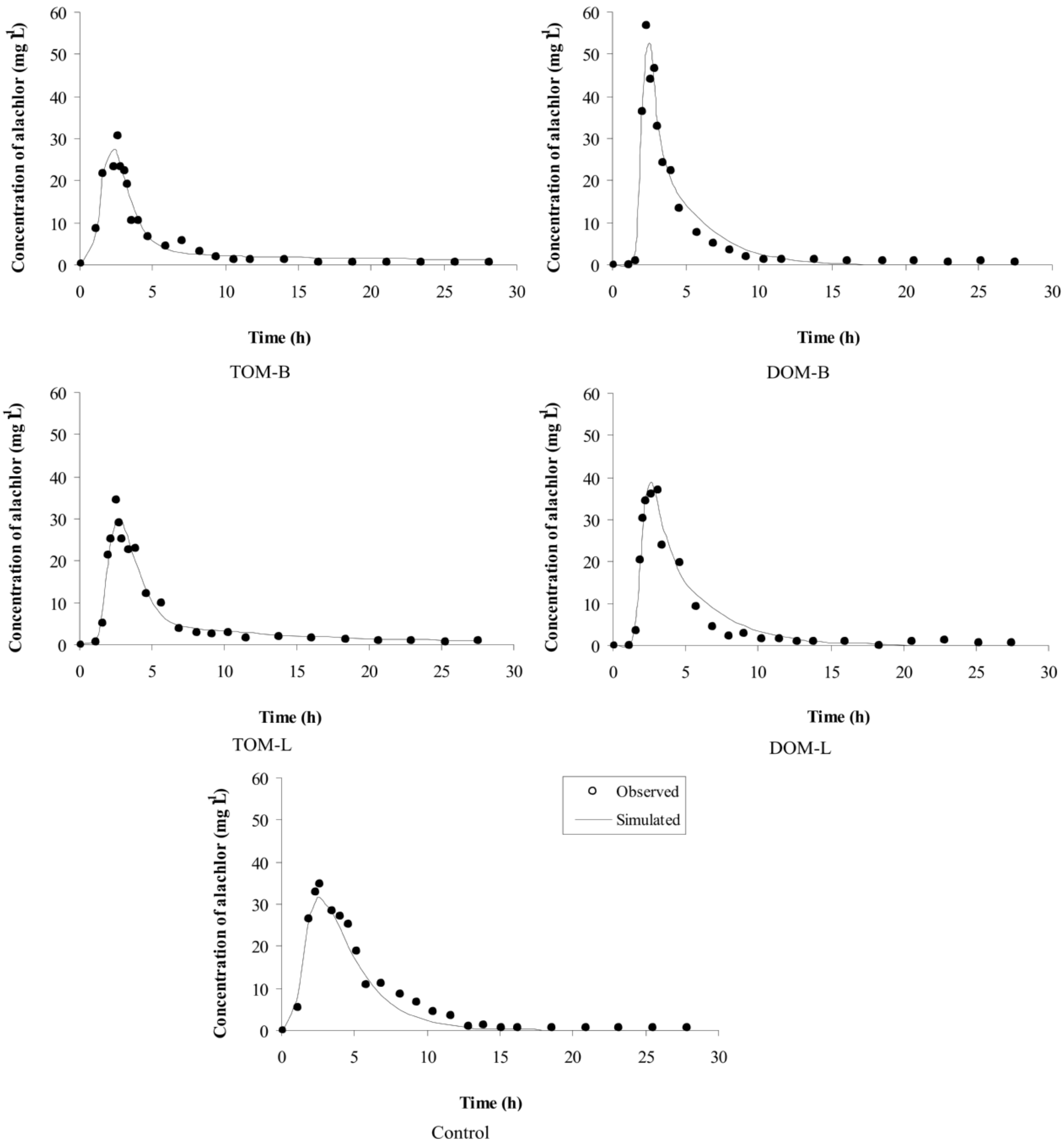
According to Anderson and Christensen (1988), low $k_{d(s)}$ values indicate that the majority of the pesticide present in a system remains in solution and is therefore available for transport, for other chemical processes, and for adsorption by plant roots. Table 3 shows that the Control treatment had the lowest $k_{d(s)}$ value and that there was a tendency for the DOM form of SWW to display lower $k_{d(s)}$ values than the TOM form. This pattern was also observed by Li et al. (2005), and it may be attributable to the formation of compounds between the DOM and the pesticide or to competition for binding sites (CESPEDES et al., 2002).

Independently of the type of treatment (biodigester or manure lagoon) and the type of organic matter (DOM or TOM), SWW led to higher $kf_{(d)}$ values (Table 3). A similar pattern was observed by Song et al. (2008), for whom the application of DOM from sewage sludge and wheat straw increased the desorption of the pesticide chlorotoluron. These authors explained this effect as being due to the formation of a compound consisting of the pesticide and DOM and to the exchange of pesticide sorbed in the soil by the DOM.

Given that the lowest desorption capacity (DOM-L) did not correspond to the lowest level of alachlor adsorption, the H values (Table 3) indicate that the mechanisms active in the sorption process are different for the different treatments. According to Andrade et al. (2010), higher H values indicate lower herbicide desorption capacity and less availability of the herbicide for plants. Comparing the H values for the SWW in the DOM form, it is evident that in these treatments alachlor is more available in the soil solution than in the treatment with SWW in the TOM form or in the Control (Table 3).

Miscible displacement of alachlor

Alachlor was detected in all the leachates based on the average pore volume and the breakpoint, which occurred at the same time for all of the treatments (between 1 and 2 pore volumes) (Figure 1).



TOM-B

DOM-B

TOM-L

DOM-L

Control

Figure 1. Observed and simulated elution curves for alachlor.

However, the spikes in the concentration of alachlor varied, with the largest peak occurring with DOM-B, followed by DOM-L, the Control, TOM-L, and TOM-B. This sequence confirms the results obtained in the adsorption test in which the treatments that received DOM had lower $k_{f(s)}$ values than those that received TOM (Table 3), resulting in greater leaching potential.

DOM displayed a higher breakpoint than the Control, indicating that the leaching of the pesticide is increased by the presence of this type of organic matter (DRORI et al., 2005; JIANG et al., 2008; LI et al., 2005; SONG et al., 2008). Fenoll et al. (2011) and Li et al. (2005) explained that competition for sorption sites in the soil between the pesticide and DOM, which presents dissolved salts that also can contribute to this competition, might increase leaching. Song et al. (2008) further added that there is in these cases an increase in $k_{f(d)}$, as observed in the desorption test (Table 3), in which the $k_{f(d)}$ values of the treatments that received DOM were higher than those of the Control, especially in the case of DOM-B. In addition to competition for sorption sites, Cornejo et al. (2005) considered the possibility of interaction between DOM-B and pesticide molecules in solution, an interaction that might facilitate pesticide transport. In this sense, Fawcett et al. (1994) noted that 60 to 90% of the loss of chloroacetamides such as metolachlor and alachlor occurs in the aqueous phase, which is a testament to the relative water solubility of these chemicals.

Modeling

These findings were confirmed by curve-fitting the hydro-dispersive parameters as determined by the convection-dispersion equation (CDE) for two sorption sites (Table 4).

Table 4. Observed hydro-dispersive parameters and their fit with the CDE model of two sorption sites based on miscible displacement assays with alachlor.

Treatments	D[a]	R[b]	r^2[c]	kd[d]	Pe[e]	λ[f]
	$cm^2 h^{-1}$		%	$L kg^{-1}$		cm
Control	68.46	1.89	96.30	1.01	5.67	5.29
TOM-B	37.74	7.21	95.96	7.32	10.17	2.95
DOM-B	6.82	1.95	97.36	1.03	57.62	0.52
TOM-L	27.78	4.21	96.73	3.54	14.11	2.13
DOM-L	14.01	2.17	96.98	1.28	28.09	1.07

[a] D: coefficient of dispersion; [b] R: retardation factor; [c] r^2: coefficient of determination; [d] k_d: coefficient of distribution; [e] Pe: Péclet number; [f] λ: dispersivity.

A good fit of the simulated elution curves was observed for all the treatments (Table 4). The R-values are all greater than unity, indicating that, as a function of the sorption process along the column, the alachlor moves at a slower velocity than the water (BENEDÍ et al., 2005). This result was expected given that the elution curves (Figure 1) show a rightward shift, indicating that part of the solution adsorbed in the soil column is desorbed by desorption kinetics (FERREIRA et al., 2006). Ferreira et al. (2006) stated that R-values increase with greater solute-soil interactions. The Control, DOM-B, and DOM-L treatments displayed R-values closer to unity, matching the adsorption results (Table 3). Greater leaching was therefore likely because these groups displayed lower $k_{f(s)}$ values.

The highest D-value was observed in the Control group, indicating more diffusion-dispersion of the contaminant by the soil in this treatment (COSTA et al., 2006). Based on the Péclet number, the predominant process in all of the assays that received SWW was convection ($Pe > 10$), a process in which the solute particles are transported by runoff water. In the Control treatment, this transport is diffusive ($Pe < 10$), or rather, the displacement of the solute is due to thermal movement caused by collisions of the molecules in the fluid and to the concentration gradient (COSTA et al., 2006).

According to Milfont et al. (2006), dispersivity is the relationship between the contributions of convection and dispersion in the transport of a solute. Table 4 shows that the dispersivity values were higher for the Control and TOM treatments. This result explains the greater leaching in the DOM treatments because the velocity differential of the solution among and within the pores was lower in the DOM treatments than in the TOM treatments.

The k_d values obtained by the equilibrium method (Table 3) were higher than those obtained by the column method (Table 4). Other studies have also reported this pattern (BARIZON et al., 2006; PIÑEIRO et al., 2010), and this discrepancy has been associated with various factors: (a) in the column assay, there is less contact between the pesticide and the soil relative to the equilibrium method, and the time to chemical equilibrium is also less; (b) the column is an open system, in which the pesticide is desorbed and removed from the system, in contrast to the equilibrium method, in which the desorbed pesticide may be re-adsorbed by the matrix; (c) in the equilibrium method, the specific soil surface area may be increased by abrasion resulting from constant agitation; and (d) the soil/solution ratio of the pesticide varies from 1/5 to 1/20 in the equilibrium method because the column conditions are different and are therefore not representative of the real transportation conditions of solutes in soil (KOOKANA et al., 1992).

FTIR Results and Correlations

Figure 2 shows the FTIR spectra of the SWW and the alachlor. There are spectral ranges that might indicate functional groups of the same chemical composition in the two materials (Figure 2). This observation helps to explain the affinity between SWW and alachlor in terms of the principle of solubility.

A curve comparison test for the initial part of the elution curves (Table 5) revealed a statistical difference in the angular coefficients between treatments. In other words, the lines display different slopes, indicating that leaching was more accentuated with the DOM-B treatment than with TOM-B. Leaching superior to that of the Control was obtained with both the DOM-B and TOM-L treatments, and it was greater for TOM-L than for TOM-B. The curve comparison test for the last part (from the peak concentration of alachlor up to the sixth pore volume) displayed a statistically significant difference between the following treatments: DOM-B and TOM-B, DOM-B and TOM-L, DOM-L and TOM-B, and DOM-L and TOM-L. It is evident that the treatments with DOM displayed a leaching behavior different from that of the treatments with TOM, with the DOM treatments providing greater potential for leaching of the herbicide.

Oliveira et al. (2000) observed that the increase in the concentration of total solids from SWW leads to a reduction of the soil's infiltration capacity that intensifies with successive applications. Table 1 shows that the DOM treatments had a lower (35% less) total solids content than the TOM treatments, which explains the difference in terms of movement of the pesticide in the soil’s macropores.

Fenoll et al. (2011) explained that the undissolved fraction of organic matter forms aggregates with soil particles, which block the larger soil pores (> 1 μm) and thus decrease leaching. McGechan (2002) stressed that approximately 50% of the organic matter in soil is highly mobile and that 25% of the fraction larger than 2000 μm tends to slow leaching, given that with these larger particles, preferential flow paths are not available.

A positive and significant correlation was obtained between alachlor and TOC for all of the treatments (Table 6). In the Control and DOM-B treatments only, there were significant negative correlations between alachlor and pH and between TOC and pH.

The peaks in the concentration of alachlor coincided with the peaks in the leaching of TOC (Figure 3) for all treatments. The greatest concentration of TOC as measured in the peak of the curve was for TOM-L, followed by DOM-L, TOM-B, DOM-B, and the Control. Majumdar and Singh (2007) explained that the added TOC might undergo sorption reactions in the soil and provide for the transport of contaminants.

The behavior of pH in the Control treatment (Table 6) may be explained by Pañuela and Barceló (1996) because the herbicides that belong to this class of chloroacetanilides are mostly acids, giving the molecules an anionic character and consequently promoting repulsion towards soil sorption sites with a negative charge. This is one of the characteristics of tropical soils with minerals at a 1:1 ratio, such as kaolinite (MEURER, 2000), that are rich in organic matter (RIBEIRO et al., 2011).

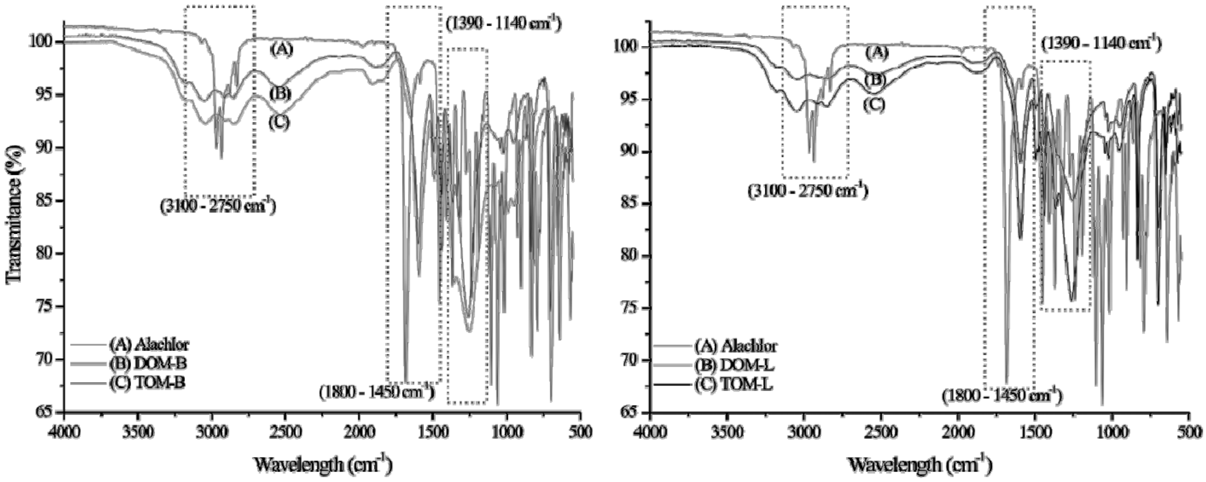


Figure 2. FTIR spectra for alachlor and lyophilized swine wastewater.

Table 5. Comparison of the angular coefficients for the initial and final sections of the alachlor elution curves.

	Initial section of the alachlor elution curve [(1)]			Final section of the alachlor elution curve [(2)]		
Treatment	Angular coefficient (b)	Linear coefficient (a)	T Test (b)	Angular coefficient (b)	Linear coefficient (a)	T Test (b)
DOM-B	10.90	1.78	$\lvert 2.74_{Tc} \rvert < 2.78_{Tt}$	-2.41	1.83	$\lvert 0.72_{Tc} \rvert < 2.09_{Tt}$
DOM-L	3.16	1.34	$b_{DOM-B} = b_{DOM-L}$	-2.52	1.90	$b_{DOM-B} = b_{DOM-L}$
DOM-B	10.90	1.78	$\lvert 4.67_{Tc} \rvert > 2.78_{Tt}$	-2.41	1.83	$\lvert 3.24_{Tc} \rvert > 2.06_{Tt}$
TOM-B	1.54	1.43	$b_{DOM-B} \neq b_{TOM-B}$	-1.97	1.51	$b_{DOM-B} \neq b_{TOM-B}$
DOM-B	10.90	1.78	$\lvert 2.67_{Tc} \rvert < 2.78_{Tt}$	-2.41	1.83	$\lvert 3.16_{Tc} \rvert > 2.07_{Tt}$
TOM-L	5.40	1.54	$b_{DOM-B} = b_{TOM-L}$	-1.95	1.65	$b_{DOM-B} \neq b_{TOM-L}$
DOM-B	10.90	1.78	$\lvert 4.39_{Tc} \rvert > 2.78_{Tt}$	-2.41	1.83	$\lvert 0.85_{Tc} \rvert < 2.09_{Tt}$
Control	2.33	1.50	$b_{DOM-B} \neq b_{Control}$	-2.22	1.95	$b_{DOM-B} = b_{Control}$
DOM-L	3.16	1.34	$\lvert 1.07_{Tc} \rvert < 2.78_{Tt}$	-2.52	1.90	$\lvert 3.30_{Tc} \rvert > 2.08_{Tt}$
TOM-B	1.54	1.43	$b_{DOM-L} = b_{TOM-B}$	-1.97	1.51	$b_{DOM-L} \neq b_{TOM-B}$
DOM-L	3.16	1.34	$\lvert 1.45_{Tc} \rvert < 2.78_{Tt}$	-2.52	1.90	$\lvert 3.19_{Tc} \rvert > 2.09_{Tt}$
TOM-L	5.40	1.54	$b_{DOM-L} = b_{TOM-L}$	-1.95	1.65	$b_{DOM-L} \neq b_{TOM-L}$
DOM-L	3.16	1.34	$\lvert 0.58_{Tc} \rvert < 2.78_{Tt}$	-2.52	1.90	$\lvert 1.09_{Tc} \rvert < 2.08_{Tt}$
Control	2.33	1.50	$b_{DOM-L} = b_{Control}$	-2.22	1.95	$b_{DOM-L} = b_{Control}$
TOM-B	1.54	1.43	$\lvert 4.77_{Fc} \rvert > 2.78_{Ft}$	-1.97	1.51	$\lvert 0.13_{Fc} \rvert < 2.07_{Ft}$
TOM-L	5.40	1.54	$b_{TOM-B} \neq b_{TOM-L}$	-1.95	1.65	$b_{TOM-B} = b_{TOM-L}$
TOM-B	1.54	1.43	$\lvert 1.13_{Tc} \rvert < 2.78_{Tt}$	-1.97	1.51	$\lvert 1.07_{Tc} \rvert < 2.06_{Tt}$
Control	2.33	1.50	$b_{TOM-B} = b_{Control}$	-2.22	1.95	$b_{TOM-B} = b_{Control}$
TOM-L	5.40	1.54	$\lvert 4.06_{Tc} \rvert > 2.78_{Tt}$	-1.95	1.65	$\lvert 1.10_{Tc} \rvert < 2.07_{Tt}$
Control	2.33	1.50	$b_{TOM-L} \neq b_{Control}$	-2.22	1.95	$b_{TOM-L} = b_{Control}$

(1) From the beginning of leaching until the peak in concentration. (2) From the peak in concentration until six pore volumes. Note: for the linear coefficients, there was no statistical difference at the 5% significance level.

Table 6. Pearson's correlation for alachlor, TOC, and pH in the leachate.

	Control		DOM-L		TOM-L		DOM-B		TOM-B	
	Alachlor	TOC	Alachlor	TOC	Alachlor	TOC	Alachlor	TOC	Alachlor	TOC
TOC	0.866*		0.985*		0.981*		0.969*		0.981*	
pH	-0.958*	-0.847*	-0.052^{ns}	0.049^{ns}	0.714^{ns}	0.752^{ns}	-0.872*	-0.958*	0.639^{ns}	0.527^{ns}

"*" = significant at the 5% significance level; "^{ns}" = not significant at the 5% significance level. Note: to perform the Pearson's correlation test, data from the elution curves between the peak and six pore volumes were used.

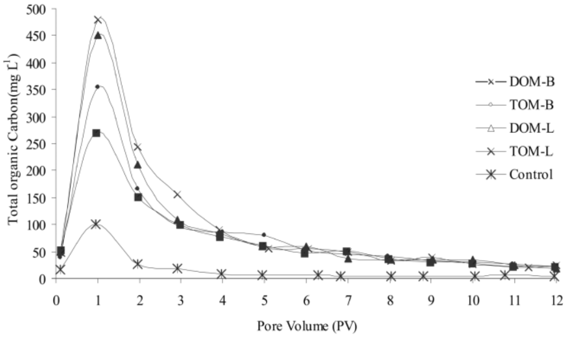


Figure 3. Elution curves for total organic carbon (TOC).

Muller et al. (2007) claimed that the addition of organic matter through wastewater increases the amount of DOM and the pH of the soil solution. With this increase in pH, acidic pesticides undergo ionization and become anions due to deprotonation, which also results in the repulsion of exchangeable cation sites, facilitating the process of leaching. Thus, a decrease in pH results from leaching.This decrease should have occurred in all of the treatments. However, DOM-B resulted in a higher pH value (8.27) (Table 1), a fact that explains why the Pearson's correlation was only significant for this treatment. Martin Neto et al. (2007) claim that humic substances have a variable charge and that carboxyl and phenolic groups gradually dissociate when there is an increase in pH, inducing the formation of negative charges in the soil. An increase in pH also leads to the release of native soil organic matter into solution, resulting in a decrease in adsorption (ZHAOHAI et al., 2008). This correlation has been observed by Zhaohai et al. (2008).

Conclusion

The SWW, independent of treatment or form, promoted greater adsorption and desorption of alachlor in the soil than did the Control treatment.

The TOM contributed to the appearance of new sorption sites in the soil column, probably due to the presence of solids blocking the pesticide's passage, resulting in a reduced loss of alachlor by leaching.

The DOM interacted with the alachlor and/or competed with the cation exchange sites of the soil, promoting greater loss of the herbicide due to leaching.

SWW-B provided more leaching in the dissolved form and less leaching in the total form.

References

ABRANTES, N.; PEREIRA, R.; GONÇALVES, F. Occurrence of pesticides in water, sediments, and fish tissues in a lake surrounded by agricultural lands: Concerning risks to humans and ecological receptors. **Water Air Soil Pollution**, v. 212, n. 1/4, p. 77-88, 2010.

APHA-American Public Health Association. AWWA, WEF. **Standard methods for the examination of water and wastewater**. 20th ed. Washington, D.C.: American Public Health Association, 1998.

ANDERSON, P. R.; CHRISTENSEN, T. H.; Distribution coefficients of Cd, Co, Ni and Zn in soils. **Journal of Soil Science**, v. 39, n. 1, p. 15-22, 1988.

ANDRADE, S. R. B.; SILVA, A. A.; QUEIROZ, M. E. L. R.; LIMA, C. F.; D'ANTONINO, L. Sorção e dessorção do ametryn em argissolo Vermelho-amarelo e Latossolo Vermelho-amarelo com diferentes valores de pH. **Planta Daninha**, v. 28, n. 1, p. 177-184, 2010.

ARCHANGELO, E. R.; KARAN, D.; FERREIRA, F. A.; PRATES, H. T.; FERREIRA, L. R.; CARDOSO, A. A. Sorção, dessorção e potencial de lixiviação de dimethenamid em solos brasileiros. **Planta Daninha**, v. 22, n. 3, p. 467-477, 2004.

BARIZON, R. R. M.; LAVORENTI, A.; REGITANO, J. B.; PRATA, F.; TORNISIELO, V. L. Simulação do transporte e da sorção de imazaquin em colunas de solo. **Revista Brasileira de Ciência do Solo**, v. 30, n. 4, p. 615-623, 2006.

BENEDÍ, J. A.; REGALADO, C. M.; RITTER, A.; BOLADO, S. Characterization of solute transport through miscible displacement experiments. In: BENEDÍ, J. A.; CARPENA, R. M. (Ed.). **Soil-water-solute process characterization**: an integrated approach. Boca Raton: CRC Press, 2005. p. 391-433.

CASAGRANDE, J. C.; SOARES, M. R. Modelos químicos de adsorção. In: MELO, V. F.; ALLEONI, L. R. F. (Ed.). **Química e mineralogia do solo**. Viçosa: SBCS, 2009. v. 2, p. 131-160.

CESPEDES, F. F.; PRADAS, E. G.; PEREZ, M. F.; SANCHEZ, M. V.; VICIANA, M. S.; AMATE, M. D. U. Effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. **Journal of Environmental Quality**, v. 31, n. 3, p. 880-888, 2002.

CHENG, X.; SHI, H.; ADAMS, C. D.; TIMMONS, T.; MA, Y. Simultaneous screening of herbicide degradation byproducts in water treatment plants using high performance liquid chromatography-tandem mass spectrometry. **Journal of Agricultural and Food Chemistry**, v. 58, n. 8, p. 4588-4593, 2010.

CHOI, D.; LEE, O.; YU, S.; JEONG, S. W. Gamma radiolysis of alachlor aqueous solutions in the presence of hydrogen peroxide. **Journal of Hazardous Materials**, v. 184, n. 1/3, p. 308-312, 2010.

CORNEJO, J.; HERMISÍN, M. C.; CELIS, R.; COX, L. Methods to determine sorption of pesticides and other organic compounds. In: BENED, J. A.; CARPENA, R. M. (Ed.). **Soil – water – solute process characterization**. Boca Raton: CRC Press, 2005. p. 435-463.

CORRÊA, M. M.; LIMA, L. A.; MARTINEZ, M. A.; RIGINATO, R. L. O.; SAMPAIO, S. C. Deslocamento miscível de sulfona de aldicarbe em colunas de solo. **Engenharia Agrícola e Ambiental**, v. 3, n. 2, p. 217-221, 1999.

CORREIA, F. V.; LANGENBACH, T. Dinâmica da distribuição e degradação de atrazina em Argissolo Vermelho-amarelo sob condições de clima tropical úmido. **Revista Brasileira de Ciência do Solo**, v. 30, n. 1, p. 183-192, 2006.

COSTA, C. T.; ANTONINO, A. C. D.; NETTO, A. M. Ensaios de Deslocamento de líquido miscível na determinação dos parâmetros hidrodispersivos de um solo Aluvial. **Revista Brasileira de Recursos Hídricos**, v. 11, n. 2, p. 111-122, 2006.

DORADO, J.; LÓPES-FANDO, C.; ZANCADA, M. C.; ALMENDROS, G. Sorption-desorption of alachlor and linuron in a semiarid soil as influenced by organic matter properties after 16 years of periodic inputs. **Journal of Agricultural and Food Chemistry**, v. 53, n. 13, p. 5359-5365, 2005.

DRORI, Y.; AIZENSHTAT, Z.; CHEFETZ, B. Sorption-desorption behavior of atrazine in soils irrigated with reclaimed wastewater. **Soil Science Society of America Journal**, v. 69, n. 6, p. 1703-1710, 2008.

EMBRAPA-Empresa Brasileira de Pesquisa Agropecuária. **Sistema Brasileiro de Classificação de Solo**. 2. ed. Rio de Janeiro: Embrapa, 2006.

FAWCETT, R. S.; CHRISTENSEN, B. R.; TIERNEY, D. P. The impact of conservation tillage on pesticide runoff into surface water: a review and analysis. **Journal of Soil and Water Conservation**, v. 49, n. 2, p. 126-135, 1994.

FENOLL, J.; RUIZ, E.; FLORES, P.; VELA, N.; HELLÍN, P.; NAVARRO, S. Use of farming and agro-industrial wastes as versatile barriers in reducing pesticide leaching through soil columns. **Journal of Hazardous Materials**, v. 187, n. 1/3, p. 206-212, 2011.

FERREIRA, P. F.; GARCIA, G. O.; MATOS, A. T.; RUIZ, H. A.; BORGES JURNIOR, C. F. Transporte no solo de solutos presentes na água residuária de café Conilon. **Acta Scientiarum. Agronomy**, v. 28, n. 1, p. 29-35, 2006.

FAO-Food and Agriculture Organization. **Guidelines for soil description**. Rome: FAO, 2006.

JIANG, L.; HUANG, J.; LIANG, L.; ZHENG, P. Y.; YANG, H. Mobility of prometryne in soil as affected by dissolved organic matter. **Journal of Agricultural and Food Chemistry**, v. 56, n. 24, p. 11933-11940, 2008.

KOOKANA, R. S.; AYLMORE, L. A. G.; GERRITSE, R. G. Time-dependent sorption of pesticides during transport in soils. **Soil Science**, v. 154, n. 3, p. 214-225, 1992.

LI, K.; XING, B.; TORELLO, W. A. Effect of organic fertilizers derived dissolved organic matter on pesticide sorption and leaching. **Environmental Pollution**, v. 134, n. 2, p. 187-194, 2005.

MAJUMDAR, K.; SING, N. Effect of soil amendments on sorption and mobility of metribuzin in soils. **Chemosphere**, v. 66, n. 4, p. 630-637, 2007.

MARTIN NETO, L.; VAZ, C. M. P.; MATTOSO, L. H. C.; SILVA, W. T. L. Pesticidas: Mecanismos de reação no solo e técnicas não convencionais de análise. In: MARTIN

NETO, L.; VAZ, C. M. P.; CRESTANA, S. (Ed.). **Instrumentação avançada em ciência do solo**. São Carlos: Embrapa Instrumentação Agropecuária, 2007. p. 261-290.

McGECHAN, M. B. Transport of particulate and colloid-sorbed contaminants through soil, Part 2: Trapping processes and soil pore geometry. **Biosystem Engineering**, v. 83, n. 4, p. 387-395, 2002.

MEURER, E. J. **Fundamentals of soil chemistry**. Porto Alegre: Gênesis, 2000.

MILFONT, M. L.; ANTONINO, A. C. D.; MARTINS, J. M. F.; NETTO, A. M.; CORRÊA, M. M. Caracterização hidrodispersiva de dois solos do Vale do Rio São Francisco. **Revista Brasileira de Ciências Agrárias**, v. 1, p. 81-87, 2006.

MULLER, K.; MEGASAN, G. N.; BOLAN, N. S. A critical review of the influence of effluent irrigation on the fate of pesticides in soil. **Agriculture, Ecosystems and Environment**, v. 120, n. 2/4, p. 93-116, 2007.

OLIVEIRA, R. A.; CAMPELO, P. L. G.; MATOS, A. T.; MATINEZ, M. A.; CECON, P. R. Influência da aplicação de águas residuárias de suinocultura na capacidade de infiltração de um solo podzólico vermelho-amarelo. **Revista Brasileira de Engenharia Agrícola e Ambiental**, v. 4, n. 2, p. 263-267, 2000.

PAÑUELA, G. A.; BARCELÓ, D. Comparative degradation kinetics of alachlor in water by photocatalysis with $FeCl_3$, TiO_2 and photolysis, studied by solid phase disk extraction followed by gas chromatographic techniques. **Journal of Chromatography A**, v. 754, n. 1/2, p. 187-195, 1996.

PIÑEIRO, A. L.; CABRERA, D.; ALBARRÁN, A.; PENA, D. Cumulative and residual effects of de-oiled two-phase olive mill waste application to soil on diuron sorption, leaching, degradation, and persistence. **Chemosphere**, v. 78, n. 2, p. 139-146, 2010.

POSTIGO, C.; ALDA, M. D.; BARCELÓ, D.; GINEBREDA, A.; GARRIDO, T.; FRAILE, J. Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): An approach based on on-line solid phase extraction–liquid chromatography–electrospray-tandem mass spectrometry detection. **Journal of Hydrology**, v. 383, n. 1/2, p. 83-92, 2010.

RIBEIRO, B. T.; LIMA, J. M.; CURI, N.; OLIVEIRA, G. C.; LIMA, P. L. T. Cargas superficiais da fração argila de solos influenciadas pela vinhaça e Fósforo. **Química Nova**, v. 34, n. 1, p. 5-10, 2011.

SAMPAIO, S. C.; CAOVILLA, F. A.; OPAZO, M. A. U.; NÓBREGA, L. H. P.; SUSZEK, M.; SMANHOTTO, A. Lixiviação de íons em colunas de solo deformado e indeformado. **Engenharia Agrícola**, v. 30, n. 1, p. 150-159, 2010.

SILVERSTEIN, R. M.; WEBSTER, F. X.; KIEMLE, D. J. **Spectrometric identification of organic compounds**. 7. ed. Rio de Janeiro: LTC, 2007.

SIMUNEK, J.; GENUCHTEN, M.; SEJNA, M. Development and applications of the HYDRUS and STANMOD software packages and related codes. **Vadose Zone Journal**, v. 7, n. 2, p. 587-600, 2008.

SINGH, N. Biocompost from sugar distillery effluent: effect on metribuzin degradation, sorption and mobility. **Pest Management Science**, v. 64, n. 10, p. 1057-1062, 2008.

SONG, N. H.; CHEN, L.; YANG, H. Effect of dissolved organic matter on mobility and activation of chlorotoluron in soil and wheat. **Geoderma**, v. 146, n. 1/2, p. 344-352, 2008.

SOPEÑA, F.; MAQUEDA, C.; MORILLO, E. Formulation affecting alachlor efficacy and persistence in sandy soils. **Pest Management Science**, v. 65, n. 7, p. 761-768, 2009.

TORRENTS, A.; JAYASUNDERA, S.; SCHMIDT, W. J. Influence of the polarity of organic matter on the sorption of acetamide pesticides. **Journal of Agricultural and Food Chemistry**, v. 45, n. 8, p. 3320-3325, 1997.

VECCHIA, A. V.; GILLIOM, R. J.; SULLIVAN, D. J.; LORENZ, D. L.; MARTIN, J. D. Trends in concentrations and use of agricultural herbicides for corn belt rivers, 1996-2006. **Environmental Science Technology**, v. 43, n. 24, p. 9096-9102, 2009.

ZHAOHAI, S.; LI, M.; QIMING, X.; YIJUN, Y.; HUI, L.; HONGXIA, Y. Effects of dissolved organic matter from sewage sludge on sorption of tetrabromobisphenol A by soils. **Journal of Environmental Sciences**, v. 20, n. 9, p. 1075-1081, 2008.

Received on March 16, 2012.
Accepted on May 26, 2012.