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Article

HUMIC SUBSTANCES AND THEIR RELATION TO PESTICIDE SORPTION IN EIGHT VOLCANIC SOILS

Substâncias Húmicas e sua Relação com a Sorção de Pesticidas em Oito Solos Vulcânicos

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ABSTRACT - Pesticide soil sorption is a primary factor that influences the fate of pesticides in the environment, affecting regulation of microbiological and chemical degradation, volatilization and leaching. The main goal of this research was to study the effect of the organic phase of volcanic soils on sorption of agricultural pesticides. Sorption and desorption of eight agricultural pesticides were studied on eight volcanic soils that varied in the fulvic and humic constituents of their organic matter. For all pesticides, sorption was well described by a Freundlich isotherm where $1/n_{ads}$ values indicated that the sorption mechanism could be mainly explained by physical reactions in all soils. *Kf* values for carbaryl and flumioxazin were the highest with average values of 7.78 and 7.16 mL g^{-1}, respectively. By contrast, hexazinone and metsulfuron-methyl had the lowest average *Kf:* 0.86 and 0.81 mL g^{-1}, respectively, indicating that they were the least attracted to the soils. The organic fraction of the soil was the main soil factor related to the sorption of all study pesticides. Particularly, humic acid content regulated the sorption between pesticide and soil, especially through the carboxylic groups.

Keywords: adsorption, desorption, isotherms, Freundlich.

RESUMO - A sorção de pesticidas no solo é o principal fator responsável por regular o destino de pesticidas no ambiente, afetando a degradação microbiológica e química, volatilização e lixiviação. O principal objetivo deste trabalho foi estudar o efeito da fase orgânica de solos vulcânicos sobre a sorção de pesticidas agrícolas. A sorção e dessorção de oito solos vulcânicos cujos constituintes flúvico e húmico de sua matéria orgânica eram variáveis. Os resultados mostraram que, para todos os pesticidas, a sorção foi bem descrita por uma isoterma de Freundlich, e os valores $1/n_{ads}$ *indicam que o mecanismo de sorção poderia ser explicado principalmente por reações físicas em todos os solos. Carbaryl e flumioxazin foram mais adsorvidos, com Kf média de 7,78 e 7,16 mL* g^{-1}*, enquanto hexazinone e metsulfuron-methyl foram os pesticidas mais lábeis, com Kf de 0,86 e 0,81 mL* g^{-1}*, respectivamente. A fração orgânica do solo foi o principal fator relacionado à sorção de todos os pesticidas estudados. Especificamente, o teor de ácido húmico regulou a atração entre o pesticida e o solo, principalmente através dos grupos carboxílicos.*

Palavras-chave: adsorção, dessorção, isotermas, Freundlich.

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INTRODUCTION

Fate of pesticides in soil is affected by multiple variables that include physic-chemical soil properties, pesticide physicochemical properties, climatic conditions and agronomic soil management (Bollag et al., 1992; Sarmah et al., 2009; Fenoll et al., 2011). A primary factor governing environmental fate of chemicals is soil-pesticide interactions because they regulate the availability of a pesticide in soil solution, consequently affecting rates of microbiological and chemical degradation, volatilization, and leaching (Sánchez-Camazano et al., 1996; Habernahuer et al., 2001; Yu et al., 2006; Fenoll et al., 2011).

The ability of soil to retain pesticide residues is associated with several properties, such as texture, clay type, organic matter, and pH (Borisover and Graber, 1997; Gao 1998; Yang et al., 2005; Cao et al., 2008). Organic matter is known to be a major factor in the magnitude of sorption for many pesticides. Chemicals that are very lipophilic respond directly to increased organic matter content in soil (Fenoll et al., 2011). However, other chemicals, usually those with $LogK_{ow}$ values less than 3, which indicates similar leaching potential, exhibit important differences in sorption dynamics according to organic matter content (Sánchez-Camazano et al., 1996; Kogan et al., 2007; Fenoll et al., 2011). A cause for these differences could be the weathering of soil organic matter in soils, which results in variable concentration of humic and fulvic acids. The amount and ratios of humic and fluivic acids could subsequently affect the specific pesticide reactivity with the organic-clay fraction (Senesi, 1995; Borisover and Graber, 1997; Haberhauer et al., 2002; Iglesias et al., 2009; Alister et al., 2011)

Soils in the Chilean agricultural area were mainly originated from volcanic ash. Such ash was exposed to arid climatological conditions, generating different soil types. The variation in soils ranges from Andisol soils in the south, which have low pH values (below 5.5) and high organic matter (over 10%) and clay content (between 7 to 40%), to Entisol soils in the north, which have higher pH values (over 6.0) and lower organic matter (below 2.0%) and clay content (between 1 and 18%). Pesticide fate in these soils is difficult to predict. Therefore, the aim of this work was to study the relationship between the properties of these volcanic soils, focusing on differences in the humic and fulvic portion of the soil organic phase. The objective was to describe their effect on the sorption of eight agricultural pesticides that inherently have a wide range of soil sorption.

MATERIAL AND METHODS

Selection of soils

The eight volcanic soils represent five main soil families. They were collected at the 0-15 cm layer from agricultural and forestry areas in Chile. Andisol soil in Los Angeles and Temuco (AND-L and AND-T), Entisol in Los Angeles and Ovalle (ENT-L and ENT-O), Inceptisol in Teno and San Vicente (INC-T and INC-S), Ultisol in Temuco (UL-T) and Alfisol in Casablanca (ALF-C) were characterized for their soil properties (Table 1 and 2).

Table 1 - Physico-chemical soil properties

Soil	Region	pH	Electrical conductivity (EC)	Cation exchange capacity (CEC)	Texture		
					Sand	Clay	Silt
			(mS cm^{-1})	(meq 100 g^{-1})	(%)		
Entisol (ENT-L)	Bio-Bio	6.11	0.02	10.57	95.0	1.0	4.0
Andisol (AND-L)	Bio-Bio	5.77	0.10	55.36	43.0	43.0	14.0
Inceptisol (INC-S)	O’Higgins	7.27	0.14	24.58	45.0	23.0	32.0
Ultisol (UL-T)	Araucanía	5.50	0.03	24.15	24.1	40.9	35.0
Entisol (ENT-O)	Coquimbo	8.00	3.14	16.67	61.3	14.7	24.0
Inceptisol (INC-T)	Maule	6.10	0.21	22.01	33.0	17.0	50.0
Alfisol (ALF-C)	Valparaiso	5.88	0.21	5.98	63.4	10.0	26.6
Andisol (AND-T)	Araucania	5.80	0.12	29.99	64.0	7.0	29.0

Table 2 - Organic soil phase characterization

Soil	Region	Organic carbon	Humic acids[1]	Fulvic subtances[1]	Functional groups			
					Humic acids		Fulvic substances	
					Carboxylic	Phenolic	Carboxylic	Phenolic
		%			(meq g^{-1})			
Entisol (ENT-L)	Bio-Bio	1.64	0.01	0.38	<0.01	47.91	61.41	<0.01
Andisol (AND-L)	Bio-Bio	7.57	1.07	0.55	0.64	<0.01	23.28	26.96
Inceptisol (INC-S)	O'Higgins	1.26	0.05	0.24	<0.01	15.93	33.73	<0.01
Ultisol (UL-T)	Araucanía	2.05	0.52	0.57	0.03	44.41	30.86	<0.01
Entisol (ENT-O)	Coquimbo	0.65	0.01	0.24	0.42	4.75	28.22	<0.01
Inceptisol (INC-T)	Maule	2.23	0.66	0.30	0.28	5.05	9.67	<0.01
Alfisol (ALF-C)	Valparaiso	1.77	0.01	0.27	<0.01	14.04	12.74	<0.01
Andisol (AND-T)	Araucanía	8.30	1.39	0.62	1.01	6.08	33.73	<0.01

(1) Humic acids and fulvic substances expressed as percentage of organic carbon content.

Extraction of humic acids and fulvic fraction

Twenty grams of dried soil were transferred to a round-bottom flask and 200 mL of HCl 0.1 M was added. The suspension was stirred for 1 h and then the supernatant was separated from the residue by decantation. The surpernatant (Extrac 1) was kept in a glass flask.

The soil residue was resuspended with 200 mL of NaOH 0.1 M and neutralized (pH = 7.0) with NaOH 1 M under N_2 atmosphere. This suspension was shaken for 4 h, and the suspension was then allowed to settle overnight; after that, the supernatant was collected. This supernatant was acidified with 6 *M* HCl, under constant stirring until pH was equal to 1.0. After standing for 16 h, the supernatant was centrifuged to separate the humic acid (precipitate) and fulvic fractions (supernatant-Extract 2).

The humic acid fraction was redissolved by adding 20 mL of 0.1 M KOH and 0.3 g of KCl under N_2. It was then centrifuged at high speed to remove the suspended solids. At the end, the humic acid fraction was reprecipitated while adding HCl at 6 M, with constant stirring to pH = 1.0. The suspension was allowed to stand again for 16 h, and then centrifuged; the supernatant was discarded. The humic acid precipitate was suspended in 0.1 M HCl/0.3 M HF solution in a plastic flask and shaken overnight at room temperature, centrifuged, and the HCl/HF procedure was repeated until ash content was below 1%. The humic acid soil content and fulvic fraction (combination of extracts 1 and 2) were expressed by percentage of organic carbon.

Humic acids and fulvic fraction characterization

Both components of organic fraction were characterized according to their total phenolic and carboxylic groups. Four mg of each organic fraction was placed in a volumetric flask with 100 mL of 0.1 M NaCl and the solution was transferred to a glass flask. Initial pH was then measured (3.0-3.5). The solution was titrated with 0.1 M NaOH to 8.0 and 10.0 pH values. Charge density of the carboxylic groups was estimated as (meq g^{-1} C) at pH 8.0 and for phenolic groups at pH 8.0 and 10.0.

Isotherms studies

Six milliliters of aqueous 0.01 M $CaCl_2$ solution, in five concentrations between 0-25 μg mL^{-1} for metsulfuron-methyl, carbaryl, imidacloprid, hexazinone, atrazine and MCPA; 0-5 μg mL^{-1} for terbuthylazine and 0-1.7 μg mL^{-1} for flumioxazin were added to a 3 g air-dried sample of each study soil. Analyses for each pesticide-soil contamination were replicated three times in polypropylene centrifuge tubes. These soil suspensions were shaken end-over-end for 12 h at

180 rpm at 20±1 °C in darkness. Preliminary kinetic studies showed that potential adsorption was reached between 2 to 4 h and equilibrium after 8 to 12 h, depending on the specific soil and pesticide combination. At the end of equilibrium, each tube was centrifuged for 15 min at 5000 rpm, and 1 mL of each supernatant was passed through a 0.45 µm fiberglass filter and directly quantified with high performance liquid chromatography (HPLC) (Hitachi model Elite LaChrom L-2300) and gas chromatography (GC) (Shimadzu model GC-2010 QPlus). The amount of herbicide adsorbed was calculated as the difference between the amount in the initial solution and the amount remaining in the solution after centrifugation.

Desorption from the soil was also determined. After measuring adsorption, 4.5 mL of the remaining supernatant solution in each of the centrifuge tubes at the maximum pesticide concentration was replaced with the same volume of fresh background solution containing no pesticide. The new soil suspensions were shaken for 6 h and centrifuged as described earlier. This desorption procedure was repeated three times, and the amount of pesticide desorbed was calculated by determining its concentration in each of the three new supernatant solutions. Control samples were included at the different pesticide concentrations in the adsorption and desorption batch experiments to determine pesticide stability and possible losses. No pesticide losses were measured during the sorption experiments.

Pesticide quantification

Quantification of atrazine, carbaryl, flumioxazin, hexazinone and terbuthylazine was performed using gas chromatography with a mass detector unit (Shimadzu GCMS-QP2010 plus) fitted with a RTX® 5-MS column (30 m x 0.25 mm x 0.25 µm). The gas carrier was He at a flow rate of 1 mL min^{-1} with the injector temperature set at 270 °C. The samples were injected at 1 µL with the autosampler in the splitless mode. Oven temperature was: 80 °C (2 min), increased to 200 °C (at 10 °C min^{-1}), followed by an increase to 220 °C (at 2 °C min^{-1}), and finally raised to 300 °C (at 4 °C min^{-1}). Quantification ion mass was: atrazine at 200 m/z, carbaryl at 115 m/z, flumioxazin at 354 m/z, hexazinone at 71 m/z and terbuthylazine at 214 m/z. Recovery from spiked samples was 98±11%; 82±9%; 87±11%; 91±2 and 91±4%, respectively, and retention times (RT) were 14.467; 11.383; 41.523; 26.873 and 14.8 min, respectively.

Analyses for imidacloprid, MCPA and metsulfuro-methyl were conducted by using High Pressure Liquid Chromatography with a diode-array detector (Hitachi LaChrom Elite Model L-2300) fitted with a Performance RP-18e 5 µm column (100 mm length). The liquid phase in use was acetonitrile; buffer phosphate was set at 13 mM and pH was 3.4. Acetonitrile gradient was: 0 at 6 min 15%; 6-15 min 30%; 15-16 min 60%, and 16-17 min 90%. Column temperature was 30 °C and flow rate was 1 mL min^{-1}. Injection volume was 40 µL. The *diode array* was set at 230 nm for imidacloprid (RT: 16.117 min), 205 nm for MCPA (RT: 3.112 min) and 244 nm for metsulfuron-methyl (RT: 4.998 min). Recoveries were 88±15% for imidacloprid; 92±8%, for MCPA, and 90±9% for metsulfuron-methyl.

Statistical data analysis

Adsorption and desorption isotherms were expressed by the Freundlich equation:

$$Cs = Kf * Ce^{1/n} \qquad \text{(eq. 1)}$$

where C_s (mg kg^{-1}) is the sorbed pesticide and Ce (mg L^{-1}) is the pesticide in solution after the equilibrium period. Kf_{ads} and Kf_{des} are the Freundlich adsorption and desorption constants (mg^{1-n} L^{n} kg^{-1}) that reflect sorption capacity while $1/n$ indicates adsorption intensity (Celano et al., 2008). Hysteresis (H) was calculated as the ratio between $1/n_{des}$ and $1/n_{ad}$, corresponding to desorption and adsorption Freundlich constants, respectively. An increase in this ratio is an indication that herbicide sorption had a high degree of reversibility (Barriuso et al., 1994).

The isotherms were fitted using nonlinear regression analysis. Pearson correlation was used to determine the relation between soil physicochemical properties and pesticide sorption coefficients, and multiple linear regression analysis was used to quantify the effects of physicochemical soil properties on Kf_{ads} and Kf_{des} of pesticides, using the stepwise procedure with a variable input and output significance of $p<0.1$.

RESULTS AND DISCUSSION

Soil organic phase characterization showed that soil varied mainly in their humic fractions, while fulvic fractions were more homogenous between them. The fulvic fractions showed more concentration of carboxylic groups that phenolic groups. On the other hand, humic acids showed more carboxylic groups, except in AND-L soil, which showed more phenolic groups (Table 2). These results are similar to those of Kipton et al. (1996).

All sorption processes were well-described by L-type Freundlich isotherm, except terbuthylazine and metsulfuron-methyl in some soils (Tables 3 and 4), which suggests that the main sorption mechanism would be physical reactions e.g., London-van der Waals forces, hydrophobic retention and H-bonds interactions (Calvet, 1989). Most soils present pH values that generate carboxylic and phenolic groups in a nonpolar form (Strobel, 2001), which would result in pesticide hydrophobic adsorption or hydrogen bonds that explained the low free energy determined in this study (Table 5) (Mamy and Barriuso, 2007).

Table 3 - Freundlich adsorption and desorption isotherm parameters for metsulfuron-methyl, carbaryl, terbuthylazine and MCPA. Values are mean ± standard error(1)

Soil	Metsulfuron-methyl		Carbaryl		Terbuthylazine		MCPA	
	Kf_{ads} $(1/n_{ads})$	Kf_{des} $(1/n_{des})$	Kf_{ads} $(1/n_{ads})$	Kf_{des} $(1/n_{des})$	Kf_{ads} $(1/n_{ads})$	Kf_{des} $(1/n_{des})$	Kf_{ads} $(1/n_{ads})$	Kf_{des} $(1/n_{des})$
ENT-L	0.436 ± 0.053 (0.577 ± 0.130)	0.535 ± 0.044 (0.515 ± 0.027)	1.741 ± 0.169 (0.805 ± 0.058)	6.032 ± 0.316 (0.382 ± 0.022)	2.922 ± 0.151 (1.126 ± 0.049)	4.180 ± 0.128 (0.824 ± 0.033)	1.733 ± 0.180 (0.703 ± 0.040)	9.575 ± 0.249 (0.109 ± 0.014)
AND-L	1.341 ± 0.137 (0.740 ± 0.071)	0.929 ± 0.102 (0.865 ± 0.054)	11.532 ± 0.942 (0.885 ± 0.047)	30.293 ± 0.871 (0.249 ± 0.025)	10.131 ± 0.279 (0.777 ± 0.052)	13.487 ± 0.183 (0.110 ± 0.032)	9.910 ± 0.502 (0.564 ± 0.029)	23.366 ± 0.439 (0.053 ± 0.011)
INC-S	0.433 ± 0.060 (0.599 ± 0.038)	0.342 ± 0.045 (0.670 ± 0.099)	6.132 ± 0.271 (0.681 ± 0.048)	13.988 ± 0.767 (0.333 ± 0.026)	4.015 ± 0.246 (0.899 ± 0.067)	5.145 ± 0.310 (0.611 ± 0.074)	1.383 ± 0.263 (0.765 ± 0.072)	10.544 ± 0.527 (0.071 ± 0.021)
UL-T	0.701 ± 0.079 (0.734 ± 0.075)	0.917 ± 0.088 (0.646 ± 0.082)	2.307 ± 0.235 (0.596 ± 0.023)	4.834 ± 0.305 (0.343 ± 0.027)	1.947 ± 0.091 (1.237 ± 0.039)	2.088 ± 0.122 (1.164 ± 0.051)	2.743 ± 0.201 (0.774 ± 0.031)	13.465 ± 0.394 (0.168 ± 0.015)
ENT-O	0.110 ± 0.027 (1.031± 0.080)	0.291 ± 0.062 (0.724 ± 0.045)	2.755 ± 0.444 (0.681 ± 0.065)	10.724 ± 0.515 (0.214 ± 0.024)	1.903 ± 0.087 (1.094 ± 0.036)	2.047 ± 0.128 (1.019 ± 0.051)	0.945 ± 0.093 (0.616 ± 0.036)	1.743 ± 0.139 (0.415 ± 0.030)
INC-T	1.020 ± 0.083 (0.656 ± 0.069)	0.982 ± 0.099 (0.668 ± 0.080)	12.054 ± 0.505 (0.597 ± 0.026)	30.221 ± 0.744 (0.102 ± 0.018)	4.715 ± 0.297 (0.883 ± 0.071)	8.304 ± 0.237 (0.289 ± 0.040)	2.190 ± 0.191 (0.890 ± 0.036)	15.739 ± 0.354 (0.147 ± 0.012)
ALF-C	0.137 ± 0.026 (1.038 ± 0.059)	0.551 ± 0.057 (0.602 ± 0.096)	3.896 ± 0.419 (0.558 ± 0.044)	4.376 ± 0.363 (0.510 ± 0.035)	2.811 ± 0.287 (1.012 ± 0.091)	2.983 ± 0.280 (0.986 ± 0.091)	0.768 ± 0.177 (0.876 ± 0.084)	7.353 ± 0.436 (0.118 ± 0.028)
AND-T	2.366 ± 0.109 (0.691 ± 0.038)	7.544 ± 0.302 (0.286 ± 0.016)	21.905 ± 0.353 (0.726 ± 0.018)	36.523 ± 1.175 (0.229 ± 0.039)	16.242 ± 0.436 (0.865 ± 0.046)	14.079 ± 0.221 (0.123 ± 0.032)	10.956 ± 0.302 (0.686 ± 0.022)	32.229 ± 0.338 (0.084 ± 0.008)

(1) Kf_{ads} and Kf_{des} = mg^{1-n} L^{n} kg^{-1}.

The hysteresis coefficient was variable, and according to some authors, the small contact time between pesticide and soil during the batch experiments only allows the development of fast sorption reactions with low calculated Gibbs free energy (Pignatello and Xing, 1995; Weber and Huang, 1996; Lesan and Bhandari, 2003).

According to the literature, imidacloprid reacts with clay and organic carbon soil content, and soil cation exchange capacity (Cox et al., 1998; Papiernik et al., 2006). The correlation analysis found a relation only with organic carbon content, particularly with the carboxylic groups of humic acids (Tables 6 and 7). Liu et al. (2002) proposed hydrogen bonding between hydroxyl groups on the surfaces of humic acids and nitrogen present at imidazolidine ring of imidacloprid molecule, in accordance with the L-type isotherm and free energy determined in all soils (Tables 4 and 5). Similarly, carbaryl soil adsorption showed a strong relation with humic acids, particularly with carboxylic groups (Table 6), which could indicate the existence of hydrogen bindings in concordance with Zhang et al. (2008). The affinity of carbaryl with humic acids has been found under slurry environments, resulting in a modification of its degradation (Yu et al., 2009). However, our results showed that Kf_{des} were related to phenolic groups of humic acids in addition to carboxylic groups (Table 7).

Table 4 - Freundlich adsorption and desorption isotherm parameters for flumioxazin, imidacloprid, atrazine and hexazinone. Values are mean ± standard error[(1)]

Soil	Flumioxazin		Imidacloprid		Atrazine		Hexazinone	
	Kf_{ads} ($1/n_{ads}$)	Kf_{des} ($1/n_{des}$)	Kf_{ads} ($1/n_{ads}$)	Kf_{des} ($1/n_{des}$)	Kf_{ads} ($1/n_{ads}$)	Kf_{des} ($1/n_{des}$)	Kf_{ads} ($1/n_{ads}$)	Kf_{des} ($1/n_{des}$)
ENT-L	0.768 ± 0.027 (0.764 ± 0.075)	0.788 ± 0.031 (0.516 ± 0.049)	0.614 ± 0.098 (0.723 ± 0.057)	2.290 ± 0.146 (0.290 ± 0.026)	0.939 ± 0.122 (0.743 ± 0.048)	1.926 ± 0.176 (0.793 ± 0.054)	0.327 ± 0.095 (0.667 ± 0.102)	0.617 ± 0.084 (0.458 ± 0.048)
AND-L	15.348 ± 1.466 (0.844 ± 0.042)	6.585 ± 1.279 (0.421 ± 0.087)	5.527 ± 0.180 (0.829 ± 0.017)	15.602 ± 1.219 (0.314 ± 0.044)	6.393 ± 0.372 (0.810 ± 0.032)	17.711 ± 1.452 (0.320 ± 0.048)	1.441 ± 0.091 (0.827 ± 0.024)	0.813 ± 0.088 (1.026 ± 0.041)
INC-S	9.616 ± 0.848 (0.803 ± 0.047)	7.958 ± 1.729 (0.716 ± 0.133)	2.396 ± 0.236 (0.835 ± 0.041)	11.775 ± 0.391 (0.219 ± 0.017)	2.285 ± 0.208 (0.738 ± 0.036)	5.288 ± 0.325 (0.435 ± 0.026)	0.501 ± 0.093 (0.963 ± 0.067)	0.359 ± 0.086 (1.066 ± 0.083)
UL-T	0.895 ± 0.037 (0.700 ± 0.081)	0.891 ± 0.026 (0.923 ± 0.045)	0.981 ± 0.123 (0.894 ± 0.047)	4.892 ± 0.309 (0.325 ±0.227)	0.736 ± 0.116 (0.843 ± 0.057)	0.779 ± 0.210 (0.822 ± 0.095)	0.432 ± 0.074 (0.809 ± 0.061)	0.657 ± 0.058 (0.673 ± 0.060)
ENT-O	1.774 ± 0.160 (0.767 ± 0.138)	1.640 ± 0.086 (0.357 ± 0.047)	1.034 ± 0.119 (0.828 ± 0.078)	4.125 ± 0.325 (0.448 ± 0.019)	0.606 ± 0.074 (0.902 ± 0.044)	0.709 ± 0.076 (0.845 ± 0.037)	0.503 ± 0.048 (0.774 ± 0.071)	1.015 ± 0.101 (0.548 ± 0.035)
INC-T	8.836 ± 0.689 (0.933 ± 0.051)	4.335 ± 0.169 (0.383 ± 0.024)	4.979 ± 0.343 (0.709 ± 0.032)	15.845 ± 0.518 (0.208 ± 0.018)	3.052 ± 0.324 (0.848 ± 0.047)	6.294 ± 0.624 (0.570 ± 0.046)	1.056 ± 0.082 (0.767 ± 0.053)	1.098 ± 0.079 (0.743 ± 0.054)
ALF-C	2.987 ± 0.202 (0.977 ± 0.091)	3.134 ± 0.294 (1.042 ± 0.121)	1.354 ± 0.131 (0.732 ± 0.036)	4.711 ± 0.231 (0.307 ± 0.021)	1.431 ± 0.157 (0.773 ± 0.041)	2.704 ± 0.271 (0.551 ± 0.038)	0.546 ± 0.056 (0.720 ± 0.059)	0.891 ± 0.056 (0.563 ± 0.022)
AND-T	17.090 ± 1.068 (0.869 ± 0.047)	4.438 ± 0.347 (0.205 ± 0.036)	13.625 ± 0.563 (0.727 ± 0.032)	34.946 ± 0.577 (0.078 ± 0.014)	8.612 ± 0.398 (0.777 ± 0.028)	26.499 ± 0.588 (0.186 ± 0.015)	2.088 ± 0.121 (0.797 ± 0.025)	4.720 ± 0.273 (0.492 ± 0.025)

[(1)] Kf_{ads} and Kf_{des}= mg $^{1-n}$ L^n kg^{-1}.

Table 5 - Hysteresis coefficient (*H*) and sorption energies (*ΔG*) for eight pesticides in the different soils

Soil	Metsufuron-methyl		Carbaryl		Terbuthylazine		MCPA	
	H	*ΔG*[(1)] (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})
ENT-L	0.893	-6.25	0.475	-9.63	0.732	-10.95	0.155	-9.62
AND-L	1.168	-5.26	0.282	-10.51	0.142	-10.20	0.094	-9.96
INC-S	1.119	-7.32	0.489	-13.80	0.680	-12.76	0.093	-10.16
UL-T	0.880	-6.86	0.575	-9.77	0.941	-9.36	0.217	-10.20
ENT-O	0.702	-5.60	0.314	-13.46	0.931	-12.56	0.673	-10.85
INC-T	1.019	-7.57	0.171	-13.61	0.327	-11.32	0.165	-9.44
ALF-C	0.580	-3.23	0.914	-11.41	0.974	-10.62	0.135	-7.44
AND-T	0.414	-6.42	0.316	-11.86	0.142	-11.13	0.122	-10.16

Soil	Flumioxazin		Imidacloprid		Atrazine		Hexazinone	
	H	*ΔG*[(1)] (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})	*H*	*ΔG* (kJ mol^{-1})
ENT-L	0.675	-7.63	0.401	-7.08	0.664	-8.12	0.686	-5.54
AND-L	0.499	-11.21	0.379	-8.72	0.396	-9.07	1.242	-5.43
INC-S	0.892	-14.90	0.263	-11.50	0.589	-11.39	1.107	-7.67
UL-T	1.319	-7.46	0.364	-7.68	0.974	-6.98	0.832	-5.68
ENT-O	0.465	-12.39	0.541	-11.06	0.937	-9.76	0.708	-9.30
INC-T	0.410	-12.85	0.293	-11.45	0.672	-10.25	0.969	-7.66
ALF-C	1.067	-10.76	0.420	-8.83	0.713	-9.00	0.782	-6.61
AND-T	0.236	-11.25	0.107	-10.70	0.240	-9.58	0.618	-6.11

[(1)] $\Delta G=-R*T*Ln\ (Kf_{ads})$. *R*= Gas Constant (8.314 J K^{-1} mol^{-1}); *T*=absolute temperature (°K) [36].

Table 6 - Pearson correlation coefficients for Freundlich adsorption (Kf_{ads}) and physicochemical soil properties

Soil physicochemical properties	Metsulfuron -methyl	Carbaryl	Terbuthylazine	MCPA	Flumioxazin	Imidacloprid	Atrazine	Hexazinone
pH	-0.4841 p=0.2242	-0.3044 p=0.4636	-0.3512 p=0.3928	-0.4462 p=0.2677	-0.2121 p=0.6141	-0.3099 p=0.4551	-0.3644 p=0.3748	-0.3558 p=0.3870
E. conductivity (*EC*)	-0.3801 p=0.3530	-0.2710 p=0.5162	-0.2909 p=0.4846	-0.2909 p=0.4840	-0.3137 p=0.4493	-0.2434 p=0.5613	-0.3193 p=0.4408	-0.2190 p=0.6024
Cat. exch. capacity (*CEC*)	0.6002 p=0.1157	0.5171 p=0.1894	0.5991 p=0.1165	0.7545 p=0.0305	0.7449 p=0.0340	0.4695 p=0.2406	0.6835 p=0.0616	0.6167 p=0.1034
Sand (*%*)	-0.1256 p=0.7670	-0.1215 p=0.7744	0.0490 p=0.9083	-0.0562 p=0.8949	-0.1974 p=0.6395	-0.0327 p=0.9387	-0.0537 p=0.8994	-0.0995 p=0.8146
Clay (*%*)	0.0981 p=0.8728	-0.0658 p=0.8769	-0.0288 p=0.9461	0.2128 p=0.6129	0.1742 p=0.6800	-0.1170 p=0.7826	0.0722 p=0.8650	0.0295 p=0.9447
Silt (*%*)	0.1269 p=0.7645	0.2692 p=0.5192	-0.0471 p=0.9119	-0.1458 p=0.7305	0.1249 p=0.7683	0.1828 p=0.6649	0.0064 p=0.9879	0.1278 p=0.7630
Organic carbon (*OC*)	0.9055 p=0.0020	0.8349 p=0.0099	0.9463 p=0.0004	0.9900 p<0.0001	0.8550 p=0.0068	0.8531 p=0.0071	0.9571 p=0.0002	0.9249 p=0.0010
Humic acids (*HA*)	0.9598 p=0.0002	0.8815 p=0.0038	0.8874 p=0.0033	0.9337 p=0.0009	0.8184 p=0.0013	0.8783 p=0.0041	0.9069 p=0.0019	0.9323 p=0.0007
Fulvic substances (*FS*)	0.7712 p=0.0025	0.5137 p=0.1929	0.6643 p=0.0724	0.8173 p=0.0132	0.4532 p=0.2594	0.5866 p=0.1264	0.6350 p=0.0907	0.6208 p=0.1005
HA carboxylic groups (*HACa*)	0.8385 p=0.0093	0.8523 p=0.0072	0.8896 p=0.0031	0.8763 p=0.0043	0.7744 p=0.0241	0.8790 p=0.0040	0.8754 p=0.0044	0.9225 p=0.0011
HA phenolic groups (*HAPhe*)	-0.3278 p=0.4280	-0.5846 p=0.1280	-0.4689 p=0.2412	-0.3792 p=0.3543	-0.6580 p=0.0761	-0.4977 p=0.2095	-0.5486 p=0.1592	-0.5955 p=0.1194
FS carboxylic groups (*FSCa*)	-0.0281 p=0.9473	-0.2366 p=0.5726	-0.0161 p=0.9698	0.0121 p=0.9773	-0.2294 p=0.5847	-0.1218 p=0.7739	-0.1254 p=0.7673	-0.2272 p=0.5885
FS phenolic groups (FS*Phe*)	0.2805 p=0.5010	0.2165 p=0.6066	0.3628 p=0.3771	0.5225 p=0.1558	0.5043 p=0.2025	0.1579 p=0.7088	0.4631 p=0.2748	0.3765 p=0.3580

Table 7 - Pearson correlation coefficients for Freundlich desorption (Kf_{des}) and physicochemical soils properties

Soil physicochemical properties	Metsulfuron -methyl	Carbaryl	Terbuthylazine	MCPA	Flumioxazin	Imidacloprid	Atrazine	Hexazinone
pH	-0.3912 0.4410	-0.1999 0.6351	-0.3788 0.3548	-0.5884 0.1250	0.1030 0.8083	-0.2492 0.5517	-0.3500 0.3954	-0.2324 0.5798
E. conductivity (*EC*)	-0.2003 0.6345	-0.1768 0.6754	-0.3620 0.3782	-0.5113 0.1653	-0.2898 0.4862	-0.2538 0.5441	-0.2965 0.4758	-0.0672 0.8744
Cat. exch. capacity (*CEC*)	0.2229 0.5957	0.6690 0.0696	0.7389 0.0363	0.7522 0.0313	0.5792 0.1324	0.4930 0.2145	0.6541 0.0785	0.1581 0.7085
Sand (*%*)	0.1263 0.7657	-0.2209 0.5992	-0.0688 0.8714	-0.1823 0.6657	-0.3221 0.4365	-0.1180 0.7809	0.0010 0.9981	0.1705 0.6864
Clay (*%*)	-0.2723 0.5141	0.0833 0.8445	0.1072 0.8005	0.2551 0.5420	0.2873 0.4903	-0.0701 0.8690	0.0348 0.9347	-0.3491 0.3967
Silt (*%*)	0.0988 0.8160	0.2637 0.5280	-0.0081 0.9848	0.0106 0.9802	0.2005 0.6341	0.2682 0.5207	-0.0403 0.9245	0.1127 0.7905
Organic carbon (*OC*)	0.7372 0.0369	0.7878 0.0202	0.9287 0.0009	0.9615 0.0001	0.3893 0.3404	0.8130 0.0141	0.9588 0.0002	0.6938 0.0563
Humic acids (*HA*)	0.7539 0.0307	0.8596 0.0062	0.8930 0.0028	0.9579 0.0002	0.3160 0.4458	0.8580 0.0064	0.8953 0.0027	0.7107 0.0481
Fulvic substances (*FS*)	0.6274 0.0959	0.4258 0.2928	0.5863 0.1267	0.8062 0.0157	-0.0563 0.8947	0.5291 0.1775	0.6557 0.0775	0.5399 0.1672
HA carboxylic groups (*HACa*)	0.7862 0.0207	0.8330 0.0667	0.8238 0.0199	0.7638 0.0274	0.2578 0.5376	0.8428 0.0086	0.8869 0.0033	0.8159 0.0135
HA phenolic groups (*HAPhe*)	-0.2416 0.5643	-0.6742 0.0667	-0.5460 0.1615	-0.3271 0.4290	-0.6126 0.1064	-0.5309 0.1758	-0.5111 0.1955	-0.3243 0.4332
FS carboxylic groups (*FSCa*)	0.0747 0.8604	-0.2883 0.4886	-0.1229 0.7718	-0.0638 0.8807	-0.3213 0.4337	-0.1599 0.7053	-0.0631 0.8819	0.0128 0.9761
FS phenolic groups (FS*Phe*)	-0.0960 0.8211	0.4050 0.3196	0.5557 0.1527	0.5225 0.1841	0.4404 0.2748	0.1416 0.7381	0.4294 0.2885	-0.1311 0.7569

On the other hand, MCPA sorption is mainly associated with the fulvic fraction (Iglesias et al., 2009; Alister et al., 2011). However, sorption coefficients (Kf_{ads} and Kf_{des}) showed a strong relation with humic acids, fulvic substances and cation exchange capacity (Tables 6 and 7), particularly with carboxylic groups of humic acid and phenolic groups of fulvic substances. However, MCPA hysteresis (Table 5) was related to electrical conductivity ($r = 0.971$; $p<0.0001$), pH ($r = 0.704$; $p = 0.0508$) and soil sum of bases ($r = 0.633$; $p = 0.0887$). Iglesias et al. (2009), indicated that MCPA-Humic acids binding is affected by solution pH, because it changes the ionic form of pesticides and the binding capacity of humic acids and fulvic substances (De Paolis and Kukkonen, 1997).

Flumioxazin sorption coefficients were similar to the values reported in the literature (Table 4) (Oliveira et al., 1999; Ferrell et al., 2005; Alister et al., 2008). However, in this study, correlation analysis showed a relation with soil organic phase, especially humic acids and cation exchange capacity (Table 6), but not with clay content. This contradictory result could be explained because flumioxazin clay adsorption is related to clay content (%) as well as specific clay type and structure (Alister et al., 2008). On the other hand, Kf_{ads} were only related to carboxylic groups and cation exchange capacity (CEC) of humic acids, but not Kf_{des}, which indicates that the adsorption/desorption mechanism could be different (Table 7).

Metsulfuron-methyl showed low adsorption coefficients (Table 3), and they were lower than the adsorption values determined by Caceres et al. (2010) in Chilean volcanic ash. Humic acids, mainly carboxylic groups and fulvic substances of humic acids, were the most relevant factor for soil sorption (Kf_{ads} and Kf_{des}), possibly reacting through hydrogen bonds or London-van der Waals forces, thus resulting in low sorption energy (Table 5) (Baskaran et al., 1996; Walker and Jurado-Exposito, 1998). Similarly to metsufuron-methyl, hexazinone showed low adsorption coefficients and linkage energy (Tables 4 and 5), and this phenomenon was related to soil OC (Bouchard and Lavy, 1985; Oliveira et al., 1999; Close et al., 2008; Sarmah et al., 2009), specially to carboxylic groups of humic acids (Tables 6 and 7). However, other authors have not found a relation between OC and soil adsorption of hexazinone (Koskinen et al., 1996).

Acidic pesticides, e.g., metsulfuron-methyl or hexazinone, present a high potential to develop ionic interaction with clay surface; however, it did not happen in this case, possibly because soils with a high content of organic substances prevent ionic herbicides from interacting with the acidic interlayer of clay particles (Celis et al., 2002). Some authors suggest that the pesticide-soil clay interaction will occur with a ratio of 30 Clay mineral/OC. In this study, soils ratios were 0.61 to 19.9 (Villaverde et al., 2008; Caceres et al., 2010).

Sorption coefficients and energy linkage of triazine herbicides were higher than several values reported in the literature (Tables 3, 4 and 5) (Singh et al., 2001; Lesan and Bhandari, 2003; Celano et al., 2008; Delgado-Moreno et al., 2010). These, herbicides showed a direct relation of sorption with soil OC, mainly with carboxylic groups, fulvic subtances and CEC of humic acids (Tables 6 and 7), similarly to other studies (Senessi et al., 1995; Singh et al., 2001; Celano et al., 2008; Delgado-Moreno et al., 2010).

However, triazines presented different sorption coefficients in soils with similar organic carbon content (Tables 3 and 4). Some works showed that type and age of organic matter present in the soil could affect the triazine sorption process (Lesan and Bhandari, 2003; Delgado-Moreno, 2010). Moreover, the structure of humic substances varied as a result of attractive and repulsive forces in the organo-clay particle (Erny et al., 2011).

Multiple regression analysis determined that pesticides Kf_{ads} and Kf_{des} can be highly and significantly predicted for all compounds, except for imidacloprid (Table 8). Most selected models included humic acid fraction as a significant predictive factor.

These results, and the existent literature, show that the organic phase could be the main soil factor related to adsorption/desorption of most agricultural pesticides currently in use. However, the relation between soil organic content and pesticide adsorption is not lineal, because of soil organic matter evolution. Thus, the content of humic and fulvic acids and their functional groups could generate particular behaviors of pesticides in the soil that are very difficult to predict.

Table 8 - Multiple linear regression models for Freundlich adsorption (Kf_{ads}) and desorption (Kf_{des})

Pesticide	Multiple Regression Model[(1)]	Adjusted-R^2	Root MSE
Metsulfuron-methyl	Kf_{ads}= 0.3748 – 0.0113*Clay + 1.4283*HA	0.95 (P<0.0001)	0.1564
	Kf_{des}= -0.9128 + 0.8551*OC + 1.2893*HACa – 0.2024*FSPhe	0.99 (P<0.0001)	0.2182
Carbaryl	Kf_{ads}= 4.3889 + 4.6394*K – 2.9194*Na – 1.4756*OC + 25.936*HA	0.82 (P=0.0004)	0.5991
	Kf_{des}= 24.3592 + 0.0819*CEC + 40.9571*HA - 86.218*FS + 0.2035 * FSCa	0.99 (P=0.0002)	0.8909
Terbuthylazine	Kf_{ads}= 2.2982 + 2.3214*OC – 8.7844*FS – 0.1821*FSPhe	0.97 (P<0.0001)	0.7811
	Kf_{des}= 0.3339 + 3.6261*K + 1.3734*OC	0.91 (P<0.0001)	1.4215
MCPA	Kf_{ads}= -1.388 + 0.9602*OC + 3.7555*FS + 1.9515*HACa	0.98 (P<0.0001)	0.4535
	Kf_{des}= 4.6052 + 2.3629*OC + 11.2261*HA – 8.2927*HACa	0.91 (P<0.0001)	1.9126
Flumioxazin	Kf_{ads}= -2.0107 + 9.5994*K + 1.2269*OC + 0.1569*FSPhe	0.97 (P<0.0001)	1.0633
	Kf_{des}= 0.5077 + 5.5289*K + 0.1433*FSPhe	0.77 (P=0.0102)	1.2429
Imidacloprid	Kf_{ads}= 0.7382 + 10.3247*HACa	0.73 (P=0.004)	2.2585
	Kf_{des}= 3.9445 + 16.9851*HA	0.69 (P=0.0064)	5.9514
Atrazine	Kf_{ads}= -0.5167 + 1.8113*K – 8.1027*Al + 0.911*OC	0.99 (P<0.0001)	0.2721
	Kf_{des}= -4.0668 + 5.8295*K + 2.8039*OC	0.95 (P<0.0001)	1.8799
Hexazinone	Kf_{ads}= 0.4904 – 6.1177*Al + 1.2353*HA	0.97 (P<0.0001)	0.1077
	Kf_{des}= -0.0054 + 0.3582*OC + 1.711*HACa – 0.1108-FSPhe	0.98 (P<0.0001)	0.1789

(1) Clay = Soil clay content (%); HA = Humic acids (% of OC); OC = Soil organic carbon content (%); FS = fulvic substances (% of OC); HACa = Carboxylic groups in Humic acid (meq g^{-1}); HAPhe = Phenolic groups in Humic acid (meq g^{-1}); FSCa = Carboxylic groups in Fulvic substances (meq g^{-1}); FSPhe = Phenolic groups in Fulvic substances (meq g^{-1}); Na = Sodium soil content (meq 100 g^{-1}); K = Potassium soil content (meq 100 g^{-1}); CEC = Cation Echange Capacity (meq 100 g^{-1}).

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