

# Sorption-desorption behavior of pesticides and their degradation products in volcanic and nonvolcanic soils: interpretation of interactions through two-way principal component analysis

María E. Báez · Jeannette Espinoza · Ricardo Silva ·  
Edwar Fuentes

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**Abstract** Sorption-desorption behavior of six pesticides and some degradation products was assessed on seven agricultural volcanic and nonvolcanic soils belonging to Andisol, Ultisol, Mollisol, and Alfisol orders. The global interpretation of sorption data was performed by principal component analysis. Results showed exceptionally high sorption of glyphosate and aminomethylphosphonic acid (AMPA) (the breakdown product) on volcanic soils ( $K_f > 1500 \mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$ ) related mainly to contents of amorphous aluminum oxides (Andisols) and crystalline minerals (Ultisols). The lower sorption on nonvolcanic soils was associated to low organic matter contents and lack of significant minerals. Metsulfuron-methyl and 3,5,6-trichloro-2-pyridinol (metabolite of chlorpyrifos) were weakly to substantially sorbed on Andisols and Ultisols, but the first one was not sorbed at  $\text{pH} > 6.4$ , including nonvolcanic soils. The metabolite of diazinon, 2-isopropyl-4-methyl-6-hydroxypyrimidine, was weakly sorbed on all soils ( $K_f = 0.4$  to  $3.6 \mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$ ). Acidic compounds would be lixiviated in Mollisols and Alfisols, but they could leach also in Andisols and Ultisols if they reach greater depths. Atrazine and deethylatrazine sorption was related to organic carbon content; therefore, they were weakly retained on nonvolcanic soils ( $K_f = 0.7$  to  $2.2 \mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$ ). Chlorpyrifos was highly sorbed on all soils reaching  $K_{OC}$  values of  $> 8000$ . Finally, the significant retention of chlorothalonil and diazinon on Mollisols and Alfisols in spite of their low OC contents showed the contribution of clay minerals in the sorption process.

**Keywords** Sorption-desorption · Pesticide degradation products · Volcanic ash-derived soils · Alluvial soils · Principal component analysis

## Introduction

Pesticides are susceptible to be adsorbed and immobilized on soils and sediments and be unavailable for microbial degradation. The decreased bioavailability influences the environmental persistence and results in the transport of a fraction to surrounding nontarget areas. Nowadays, there is an increasing concern on the presence of degradation products in environmental matrices. Associations such as atrazine (AT) and deethylatrazine (DEA); chlorpyrifos (CPF)/triclopyr and 3,5,6-trichloro-2-pyridinol (TCP); diazinon (DZN) and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP); and chlorothalonil (CTL) and 4-hydroxy-2,5,6-trichloroisophthalonitrile are considered as possible contaminants of drinking water (Sinclair et al. 2006).

Agricultural activities developed in Chile have led to the very increased use of pesticides. Glyphosate, CPF, DZN, CTL, metsulfuron-methyl (MSM), and AT are between the most consumed compounds; however, antecedents related to their sorption behavior in Chilean soils are still scarce and there are few antecedents related to degradation products.

Glyphosate is a zwitterion because of its amino, carboxylic, and phosphonic functional groups; consequently, it can be highly sorbed on different classes of soils. The contribution of soil constituents to its sorption process has been intensively debated (Glass 1987; Piccolo et al. 1996; Yu and Zhou 2005; Pessagno et al. 2008; Albers et al. 2009; Waiman et al. 2012);

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M. E. Báez (✉) · J. Espinoza · R. Silva · E. Fuentes  
Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile,  
Sergio Livingstone Pohlhammer 1007, 8380000 Santiago, Chile  
e-mail: mbaez@ciq.uchile.cl

nevertheless, data regarding the main metabolite (aminomethylphosphonic acid, AMPA) are scarce or null. It was detected in soils at the same concentration levels than glyphosate (GPS), and both were frequent in suspended particulate matter and sediment (Aparicio et al. 2013). Chlorpyrifos is highly lipophilic ( $\log K_{OW}=4.7$ , Tomlin 2006) and sorbs strongly on soils (Gebremariam et al. 2011); however, its principal degradation product can present null sorption on soils with  $pH>6$ . Chlorpyrifos can be quickly degraded or be highly persistent (Chu et al. 2008; Liang et al. 2011; Zhang et al. 2012) with a slower degradation rate in subsoil (half-life of 173–257 days) (Chai et al. 2013). Chlorothalonil is lipophilic ( $\log K_{OW}=2.92$ , Tomlin 2006) with affinity for functional groups of organic matter (OM) of soils (Patakioutas and Albanis 2002; Piwowarczyk and Holden 2012). Both parental compounds are considered immobile, and metabolites are stable in soils (half-life of  $>6$  months for hydroxy-chlorothalonil and 65 to 360 days for TCP). They were detected in golf course leachates over a period of 1 year (Armbrust 2001). Diazinon is a potential leaching contaminant in soils with low OM content (Arienzo et al. 1994). It is persistent, and its transport through runoff events is high compared to alternative insecticides, with a higher toxicity for several aquatic organisms (Brady et al. 2006). The principal breakdown product is IMHP which is continuously increasing in soils incubated in environmental conditions (Bavcon et al. 2003). The contamination with IMHP was demonstrated in soils fertilized with sludge, showing its high persistence (Díaz-Cruz and Barceló 2006). Sorption behavior of this compound is practically unknown. The main degradates of AT, DEA, and deisopropylatrazine are detected frequently in surface and groundwater (Gilliom 2007). Sorption studies point out to their low reactivity (Mersie and Seybold 1996; Moreau-Kervéan and Mouvet 1998; Krutz et al. 2003; Abate and Masini 2005). The weak acid metsulfuron-methyl ( $pK_a=3.8$ , Tomlin 2006) can be partially or completely ionized in soils; therefore, it can leach when applied on soils with negative permanent charge (Sondhia 2009).

Volcanic ash soils contribute significantly to agriculture and forest production in countries of Europe, Africa, America, and Asia. These soils are abundant and widespread in the central and southern regions of Chile accounting for approximately 60 % of the arable land (Escudey et al. 2001). Two important orders are Andisols and Ultisols with common characteristics: acidic pH (4.5–5.5) and variable surface charge. Andisols are rich in OM and allophane, whereas Ultisols have lower OM and contain Kaolinite-type minerals and crystalline iron oxides. In previous works, surface horizons of Chilean Andisols showed a significant sorption capacity for several weak acidic and basic compounds (bensulfuron-methyl, metsulfuron-methyl, and atrazine) which are weakly sorbed on soils with permanent negative charge (Espinoza et al. 2009; Cáceres et al. 2010a,

b; Báez et al. 2013). Furthermore, in the central valley of Chile, important agricultural activities are also developed on alluvial soils belonging to Alfisol and Mollisol orders. They present a negative permanent surface net charge and neutral-to-basic pH. Mollisols have a higher OM content in the surface horizon, and Alfisols have an accumulation of clay in the B horizon.

In this work, we assess the adsorption-desorption parameters of ionizable and neutral compounds such as AT, glyphosate, CPF, DZN, MSM, and CTL and some degradation products such as DEA, AMPA, TCP, and IMHP in volcanic ash-derived soils and nonvolcanic soils. Seven agricultural soils belonging to Andisol, Ultisol, Mollisol, and Alfisol orders were selected. For three of them, surface and subsurface horizons were considered due to the significant change in several physical and chemical properties at greater depths. Given the broad range of physical and chemical properties of soils and the diverse chemical nature of compounds, a global interpretation of data based on principal component analysis (PCA) was performed to assess the main parameters related to soil properties affecting the sorption process of each compound.

## Material and methods

### Chemicals

Compounds were analytical standard grade (98.3 to 99.9 %). Atrazine, atrazine-desethyl, chlorpyrifos, chlorothalonil, diazinon, glyphosate, metsulfuron-methyl, aminomethyl phosphonic acid, 2-isopropyl-6-methyl-4-pyrimidinol, and 3,5,6-trichloro-2-pyridinol were from Sigma-Aldrich. The stock solutions were  $1 \text{ mg mL}^{-1}$  in acetonitrile, except for glyphosate and AMPA which were prepared in water as a composite solution. They were stored at  $4 \text{ }^\circ\text{C}$  in darkness. Reagents for analytical determinations and characterization of soil samples were HPLC or analytical grade.

### Soils

Samples from four soils representing Andisol and Ultisol orders were collected: Piedras Negras (0–20 and 40–60 cm, PN 1 and PN 2, medial, isomesic, type dystrandep), Romeral (0–20 cm, RML, thermic, humic haploxerands), Collipulli (0–15 and 15–30 cm, COLL 1 and COLL 2, fine, mesic, xeric, palehumult), and Metrenco (0–20 and 40–60 cm, MET 1 and MET 2, fine, mesic, palehumult). Samples from three soils representing Mollisol and Alfisol orders were obtained at 0–20 cm depth: San Vicente (SVT, silty fine, montmorillonitic, thermic, aquic argixerolls), Graneros (GRS, coarse loamy, thermic, aquic haploxerolls), and Comalle (CME, fine loamy, mixed, thermic, acultic haploxeralfs). Volcanic soils were sieved at their original moisture content, and

nonvolcanic soils were air-dried for 24 h, sieved, and stored at room temperature.

#### Characterization of soils

Soil organic carbon (OC) was determined according to the Walkley-Black method. The pH was measured in soil suspensions in deionized water and 1 M KCl at 1:2.5 w/v ratios. Cation exchange capacity (CEC) was calculated from the total exchangeable bases (Mg, Ca, K, and Na extracted by 1 M ammonium acetate at pH 7.0) plus extractable acidity ( $H^+_{ext}$ ) of soils. Extractable acidity was determined using a 2.5-g sample through extraction with 0.25 M  $BaCl_2$ +0.2 M triethanolamine at pH 8.2, during 16 h. Iron and Al were extracted with acid ammonium oxalate, representing active or poorly crystalline compounds (Blakemore et al. 1987), and were later determined by inductively coupled plasma-optical emission spectroscopy. Major mineralogy of soils was determined by X-ray diffraction. Properties of soils are shown in Table 1.

#### Batch sorption-desorption experiments

Duplicate samples equivalent to 2 g of dried soil were equilibrated at  $30 \pm 1$  °C with 10 mL of aqueous solutions at concentrations of 2, 4, 6, 8, and 10  $\mu\text{g mL}^{-1}$  of AT, DEA, DZN, TCP, IMHP, and MSM in polypropylene copolymer or glass centrifuge tubes. For glyphosate and AMPA, samples of 1 or 2 g and solutions at 10, 20, 30, 40, and 50  $\mu\text{g mL}^{-1}$  were used. The distribution constant  $K_d$  ( $\text{mL g}^{-1}$ ) was calculated from data obtained for the highest initial concentration. Solutions of CTL were prepared by adding 5 % v/v of acetone, and concentrations were 1, 2, 3, 4, and 5  $\mu\text{g mL}^{-1}$ . For CPF,  $K_d$

was obtained using a solution at 5  $\mu\text{g mL}^{-1}$  in 10 % v/v of acetonitrile and samples equivalent to 1 g of dried soils. KCl (0.01 M) was used as the background electrolyte. Tubes were shaken “end over end” at the pH of soils during 16 h to achieve equilibrium (no decomposition was observed, and 95 % of sorption took place within the first 6 h). The suspensions were centrifuged at 2750g for 15 min; a 2-mL supernatant was centrifuged again at 20,000g for 20 min and collected for HPLC analysis. Desorption was conducted for each soil and analyte (except for glyphosate and AMPA) at the highest concentration level used. After the adsorption equilibrium was reached, 5 mL of the supernatant solution (in this volume the aliquot removed for the analytical determination is included) was replaced with 5 mL of 0.01 M KCl solution; the samples were shaken for 2 h, followed by centrifugation. This step was repeated for three consecutive times; every time, an aliquot of supernatant was removed for analysis. The amount of sorbed pesticide ( $\mu\text{g g}^{-1}$ ) was determined as the difference between the initial and the equilibrium concentrations of compound in solution ( $\mu\text{g mL}^{-1}$ ).

$K_f$  and  $1/n$  empirical constants from Freundlich equation, the organic carbon distribution coefficient ( $K_{OC}$ ), and the hysteresis coefficient,  $H$ , were calculated as described in a previous work (Cáceres et al. 2010b).

#### Chromatographic conditions

The HPLC system consisted of a quaternary gradient pump (model 600), an autosampler (model 717 Plus), a PDA detector (model 997), and a 2475 multi- $\lambda$  fluorescence detector, all from Waters. The column was a Zorbax Eclipse XDB C<sub>18</sub> (5- $\mu\text{m}$  particle size, 150 mm  $\times$  4.6 mm i.d.). Wavelengths for the quantification of AT, DEA, CTL, CPF, TCP, IMHP, DZN,

**Table 1** Physical and chemical properties of soils

Soil	OC (%)	pH H <sub>2</sub> O	pH KCl	CEC <sup>a</sup>	H <sup>+</sup> <sub>ext</sub> <sup>a</sup>	Al <sup>b</sup> (%)	Fe <sup>b</sup> (%)	Clay (%)	Major mineralogy
PN 1	11.2	4.7	4.4	86.3	83.3	4.4	2.3	8	–
PN 2	6.0	5.4	5.4	68.6	67.0	7.6	3.4	6	Pl <sup>3*</sup> Qz <sup>2*</sup> He <sup>2*</sup>
COLL 1	3.9	5.1	4.3	42.4	34.9	1.3	1.2	36	–
COLL 2	1.8	5.3	4.2	39.1	31.5	1.0	1.1	42	Qz <sup>3*</sup> K <sup>2*</sup> Pl <sup>1*</sup> He <sup>1*</sup>
MET 1	4.8	5.4	4.3	44.1	35.8	0.8	1.9	40	–
MET 2	1.5	5.6	4.2	35.5	28.4	0.7	2.5	52	Qz <sup>3*</sup> K <sup>3*</sup> P <sup>1*</sup>
RML	3.2	6.8	6.1	30.1	12.6	1.8	0.8	24	Qz <sup>3*</sup> Pl <sup>3*</sup> He <sup>1*</sup>
CME	1.4	6.4	5.1	36.3	8.6	0.2	0.5	45	Qz <sup>3*</sup> M <sup>1*</sup> He <sup>1*</sup>
SVT	1.4	7.5	6.5	34.0	5.5	0.2	0.2	33	Qz <sup>3*</sup> Pl <sup>3*</sup> He <sup>1*</sup> S <sup>1*</sup>
GRS	1.2	6.8	5.8	23.2	7.0	0.2	0.9	21	Qz <sup>3*</sup> M <sup>1*</sup>

Indicators 3\*, 2\*, and \* represent the relative amount of minerals

Pl plagioclase, Qz quartz, K kaolinite, H hematite, M montmorillonite, S smectite

<sup>a</sup> In mEq (+)/100 g

<sup>b</sup> Extracted with acid ammonium oxalate

and MSM were 221.0, 214.7, 233.4, 229.9, 232.2, 229.9, 247.5, and 224 nm, respectively. Under these conditions, limits of detection were 0.001, 0.003, 0.004, 0.030, 0.050, 0.010, 0.030, and 0.005  $\mu\text{g mL}^{-1}$ , respectively. Fluorescence detector was set at 263 nm (excitation) and 317 nm (emission) for the determination of glyphosate and AMPA which were previously derivatized with 9-fluorenylchloroformiato (FMOC-Cl $\geq$ 99 %). The analytical determination of these compounds was previously optimized, and the corresponding limits of detection were 0.6 and 0.4  $\text{ng mL}^{-1}$  (Báez et al. 2014). Chlorothalonil, CPF, and DZN were determined under isocratic conditions using different mixtures of acetonitrile and ultrapure water. For TCP, MSM, and IMHP, ultrapure water was acidified at pH 2.5 to be used also under isocratic conditions. For AT and DEA (under isocratic conditions) and for the glyphosate and AMPA derivatives (under gradient conditions), the mobile phase was controlled at pH 8 with a 6.25-mM borate buffer.

### Statistical analysis

The Freundlich parameters for adsorption and desorption processes ( $K_f$  and  $1/n$ ) were established through nonlinear analysis of data. The statistical significance of relationships between variables was established through ANOVA. The principal component analysis permitted to model the systematic variance associated to the physical and chemical properties of soils and the sorption behavior of pesticides and their degradation products. These analyses were performed using the statistical software Statgraphics Centurion XV.

## Results and discussion

### Soil properties

Andisols and Ultisols presented an acidic pH in water and 1 M KCl except for RML soil with a pH near neutral. This soil fulfills the parameter  $\text{Al}_{\text{Ox}} + 0.5\text{Fe}_{\text{Ox}} > 2\%$  (representing andic properties) and presents 5.5 % of allophane, and its OC content is higher than that found for nonvolcanic soils. The sign of  $\Delta\text{pH}$  ( $\text{pH KCl} - \text{pH H}_2\text{O}$ ) value represents the sign of the electric charge of a soil (Mekaru and Uehara 1972); therefore, all soils have a negative net charge. The highest differences are for the deeper COLL and MET samples and for CME soil. The lowest differences were for PN soil and for the deeper horizon agreeing with the highest content of variable-charge compounds such as amorphous aluminum and iron oxides and allophane (7.9 % for 0–20 cm and 19.6 % for 40–60 cm). The presence of phyllosilicates 2:1 in nonvolcanic soils and kaolinite in Ultisols can be a relevant feature for explaining the sorption process for several compounds.

When PCA was applied to the whole matrix describing soil properties, three components explained 96 % of data variance. The first component (PC1, 74 % of the variability of data) was described mainly for OC, CEC, and  $\text{H}^+_{\text{ext}}$ , whereas  $\text{Al}_{\text{Ox}}$  and  $\text{Fe}_{\text{Ox}}$  were related both to PC1 and PC2. The clay content and pH presented the highest contribution to PC2 (15 % of the variability of data). Organic carbon content, CEC, and  $\text{H}^+_{\text{ext}}$  presented a null or scarce relationship with PC2. In Fig. 1a, the combined plot of scores and loadings for the two most meaningful components is observed. The OC content,  $\text{H}^+_{\text{ext}}$  and CEC (PC1), and pH and clay content (PC2) are able to discriminate the different natures of soils. PC1 separates three groups of samples: PN soil (Andisol), COLL and MET soils (Ultisols), and SVT, GRS, and CME soils (Mollisols and Alfisol). GRS soil presents a low OC content, and the lowest CEC and PN 1 present the highest OC content and CEC. Moreover, they have low clay contents, so these samples are near to 0 in the PC2 plane. PC2 separates the samples of Ultisols from the samples of nonvolcanic soils mainly through pH values; however, in this group the Andisol RML, with a pH near to neutral, is also located. The relevant content of  $\text{Al}_{\text{Ox}}$  of PN 2 sample is also observed. The great variability in properties of different samples was well represented by this analysis; consequently, the set of data was considered appropriate for assessing the influence of each parameter on sorption of compounds.

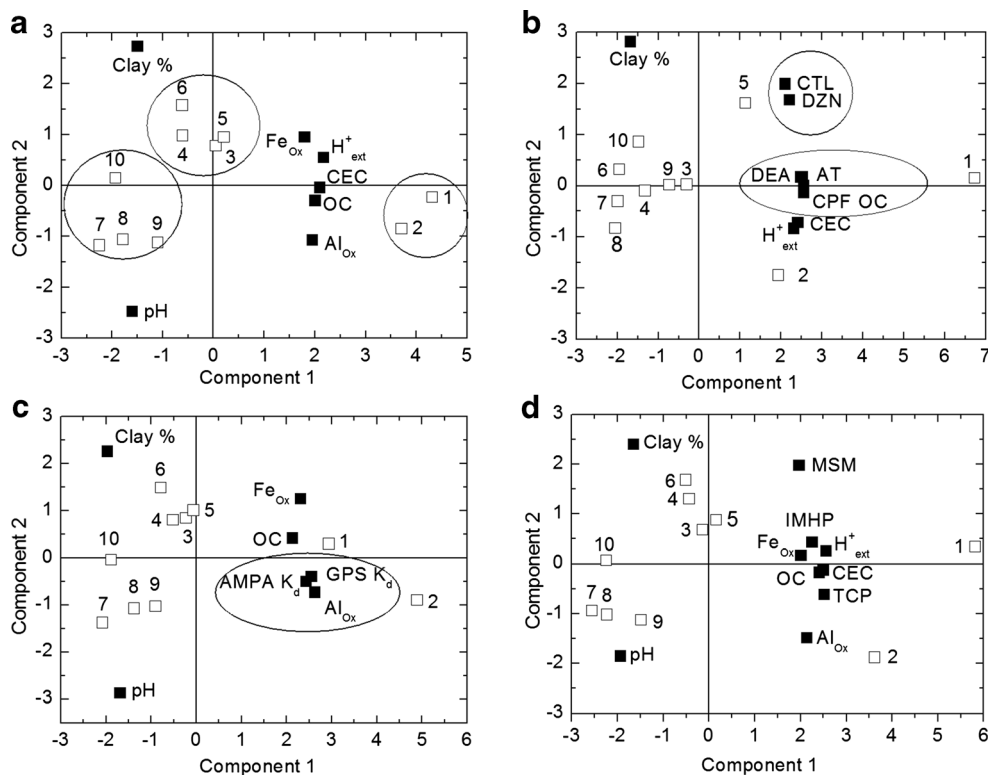
### Adsorption

Adsorption data are discussed according to results obtained by a first exploratory analysis based on PCA (not shown in Fig. 1), where  $K_f$  or  $K_d$  values (Tables 2, 3 and 4) were included. Thus, AT, DEA, and CPF were related only to PC1, and CTL and DZN were related to PC1 and PC2. These compounds were neutral species under conditions prevailing in soils, constituting the first group. Glyphosate and AMPA were mainly associated with PC1, and they constitute the second one. MSM, TCP, and IMHP constituted the third group due to their acidic character and because they were associated with PC1 and simultaneously with PC3 for MSM and IMHP and with PC2 for TCP. The three components accounted for 96.0 % of the variability.

### *Sorption of atrazine, deethylatrazine, chlorpyrifos, chlorothalonil, and diazinon*

Atrazine and DEA are weak bases with  $\text{pK}_a$  values of 1.71 and 1.65, respectively (Abate et al. 2004), so at the pH of soil solutions, ionic interactions are not favorable; therefore, sorption will occur mainly through hydrophobic interactions or van der Waals forces. The most relevant result was the low sorption capacity for both compounds in nonvolcanic soils with the lower OC contents (Table 2). The Freundlich model

**Fig. 1** Scores and loadings from PCA: **a** soil properties, **b** soil properties and sorption constants of neutral compounds, **c** soil properties and sorption constants of glyphosate (GPS) and AMPA, and **d** soil properties and sorption constants of acidic compounds 1 PN 0–20 cm, 2 PN 40–60 cm, 3 COLL 0–15 cm, 4 COLL 15–30 cm, 5 MET 0–20 cm, 6 MET 40–60 cm, 7 RML, 8 CME, 9 SVT, and 10 GRS



described suitably the sorption of both compounds ( $R^2 > 0.98$  for AT and  $> 0.94$  for DEA). Isotherms were L-type with  $1/n$  values of  $< 0.81$  for AT and  $< 0.77$  for DEA, accounting for heterogeneous sorption sites. A limited sorption capacity was observed for the deeper samples of volcanic soils. For AT,  $K_{OC}$  varied between 84 and 161 and both limits were for the surface and the deeper horizons of COLL soil, as opposed to that found in PN and MET. For DEA, the highest  $K_{OC}$  values were found for the deeper horizon of COLL (111) and the

surface horizon of PN (91) soils; however, the other data that included those for nonvolcanic soils were lower and more homogeneous than those calculated for AT ( $\approx 60$ ). According to PCA of sorption constants combined with the variables OC, CEC, clay content, and  $H^+_{ext}$  (Fig. 1b), AT, DEA, and CPF are related to OC and describe the PC1 (82.5 % of the variability). Sorption was linearly correlated with soil OC with  $R^2$  values between 94.5 and 98.9 % [ $K_{f, AT} = 1.211(\pm 0.073) \times OC$ ;  $K_{f, DEA} = 0.767(\pm 0.06) \times OC$ ;  $K_{d, CPF} = 112.9(\pm 4.0) \times OC$ ] and did

**Table 2** Sorption parameters ( $K_f$ ,  $1/n$ ,  $K_d$ ,  $K_{OC}$ ) and hysteresis coefficient ( $H$ ) of atrazine, deethylatrazine, and chlorpyrifos

Soil	AT			DEA			CPF		
	$K_f^a$	$1/n$	H	$K_f$	$1/n$	H	$K_d^b$	% ads	$K_{OC}$
PN 1	15.4 (0.3) <sup>c</sup>	0.71 (0.02)	0.44	10.2 (0.2)	0.69 (0.02)	0.51	1344	99.2	11,589
PN 2	5.5 (0.2)	0.76 (0.02)	0.51	3.2 (0.1)	0.72 (0.02)	0.52	644	98.4	10,703
COLL 1	3.2 (0.2)	0.79 (0.03)	0.61	2.0 (0.1)	0.65 (0.03)	0.92	370	97.3	9566
COLL 2	2.9 (0.2)	0.71 (0.03)	0.58	2.0 (0.1)	0.62 (0.02)	1.02	150	93.8	8253
MET 1	5.2 (0.3)	0.74 (0.03)	0.57	3.0 (0.0)	0.72 (0.01)	0.74	517	98.1	10,708
MET 2	1.4 (0.1)	0.80 (0.05)	0.66	1.0 (0.1)	0.64 (0.04)	1.70	125	92.5	8142
RML	3.0 (0.2)	0.80 (0.04)	0.46	1.5 (0.1)	0.68 (0.03)	1.01	287	96.7	9005
CME	2.2 (0.2)	0.78 (0.05)	0.41	0.9 (0.1)	0.77 (0.03)	0.87	237	95.7	16,980
SVT	1.8 (0.2)	0.75 (0.04)	0.37	0.8 (0.1)	0.76 (0.00)	0.64	127	92.6	9105
GRS	1.5 (0.1)	0.81 (0.05)	0.28	0.7 (0.1)	0.70 (0.07)	0.63	136	93.1	11,100

<sup>a</sup> In  $\mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$

<sup>b</sup> At  $5 \mu\text{g mL}^{-1}$

<sup>c</sup> Standard error

**Table 3** Sorption parameters ( $K_f$ ,  $1/n$ ,  $K_d$ ,  $K_{OC}$ ) and Hysteresis coefficient (H). Chlorothalonil, Diazinon, and IMHP

Soil	CTL				DZN			IMHP		
	$K_f^a$	$1/n$	$K_d^b$	$K_{OC}$	$K_f^a$	$1/n$	H	$K_f^a$	$1/n$	H
PN 1	77.4 (4.2) <sup>c</sup>	0.80 (0.03)	128	1142	39.4 (0.4)	0.77 (0.02)	0.23	3.6 (0.3)	0.66 (0.04)	0.53
PN 2	28.9 (0.4)	0.84 (0.02)	37	611	20.3 (0.5)	0.84 (0.04)	0.14	1.2 (0.1)	0.71 (0.03)	0.52
COLL 1	21.4 (0.3)	0.76 (0.02)	28	734	22.6 (0.4)	0.78 (0.03)	0.17	0.6 (0.1)	1.03 (0.08)	0.39
COLL 2	15.3 (0.3)	0.94 (0.06)	16	872	15.3 (0.2)	0.77 (0.02)	0.12	0.8 (0.1)	0.97 (0.04)	0.52
MET 1	62.2 (6.6)	1.12 (0.08)	50	1035	31.6 (0.2)	0.87 (0.01)	0.16	1.0 (0.1)	0.74 (0.03)	0.51
MET 2	17.7 (0.9)	0.96 (0.12)	17	1104	12.7 (0.4)	0.81 (0.03)	0.08	1.0 (0.1)	0.68 (0.03)	0.69
RML	32.4 (1.7)	0.86 (0.05)	39	1213	22.2 (0.4)	0.81 (0.03)	0.19	0.8 (0.1)	0.66 (0.07)	0.25
CME	38.2 (0.7)	0.74 (0.02)	60	4321	17.2 (0.3)	0.86 (0.03)	0.14	0.5 (0.1)	0.81 (0.07)	0.55
SVT	29.0 (1.5)	0.82 (0.05)	34	2464	11.2 (0.3)	0.76 (0.02)	0.14	0.6 (0.1)	0.62 (0.08)	0.46
GRS	20.2 (0.2)	0.81 (0.02)	24	1926	11.0 (0.3)	0.77 (0.03)	0.19	0.4 (0.1)	0.59 (0.08)	0.22

<sup>a</sup> In  $\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$

<sup>b</sup> At  $2 \mu\text{g mL}^{-1}$

<sup>c</sup> Standard error

not correlate significantly with any other physical or chemical individual characteristics, agreeing with PCA.

The influence of humic substances on the sorption of both compounds has been broadly reported. Sorption of AT on a clay-rich soil was increased twice when soil was modified by adding humic acid; however, DEA behavior was slightly modified (Abate et al. 2004). The low sorption of DEA related to AT with  $K_{OC}$  values that are twice lower is frequently reported (Mersie and Seybold 1996; Moreau-Kervévan and Mouvet 1998; Krutz et al. 2003), and these values are in the same order of magnitude than those found in the present work. A high sorption of AT was established for humic acid and humin fractions of Andisols and Ultisols and  $K_{OC}$  values varied between 300 and 700 (Báez et al. 2013). A key role is

attributed to hydrophobic interactions in binding of AT to humic substances (Kulikova and Perminova 2002; Celano et al. 2008). The influence of minerals such as smectite and kaolinite on AT and DEA sorption is also reported (Moreau-Kervévan and Mouvet 1998), explaining the coexistence of heterogeneous adsorption sites and the broader range of  $K_{OC}$  found especially for AT.

Chlorpyrifos presented a very high sorption; therefore, concentrations of aqueous solutions at equilibrium (initial concentrations up to  $2 \mu\text{g mL}^{-1}$ ) could not be measured.  $K_d$  values for eight soil and sediments with different organic matter contents obtained at lower concentrations levels varied from 35.2 to  $123.2 \text{ L kg}^{-1}$ , being sorbed at 92 to 97 % of the initial amount used (Gebremariam et al. 2011); therefore, a higher retention

**Table 4** Sorption parameters ( $K_f$ ,  $1/n$ ,  $K_d$ ) and hysteresis coefficient (H) of glyphosate, AMPA, metsulfuron-methyl, and TCP

Soil	Glyphosate			AMPA			MSM			TCP		
	$K_f^a$	$1/n$	$K_d^b$	$K_f^a$	$1/n$	$K_d^b$	$K_f^a$	$1/n$	H	$K_f^a$	$1/n$	H
PN 1	–	–	17,342	–	–	7421	7.2 (0.1)	0.66 (0.01)	0.44	56.1 (1.3)	0.80 (0.06)	0.54
PN 2	–	–	36,066	–	–	30,739	1.6 (0.1)	0.66 (0.03)	0.87	49.7 (1.1)	0.80 (0.06)	0.72
COLL 1	2045 (157) <sup>c</sup>	0.57 (0.03)	5574	1517 (56)	0.65 (0.02)	2675	2.1 (0.2)	0.99 (0.06)	0.09	11.1 (0.2)	0.75 (0.02)	0.85
COLL 2	2754 (392)	0.54 (0.04)	11,174	1422 (74)	0.58 (0.02)	2943	4.0 (0.2)	0.83 (0.03)	0.10	10.1 (0.2)	0.74 (0.02)	0.85
MET 1	902 (11)	0.51 (0.01)	1600	791 (9)	0.56 (0.01)	1144	2.5 (0.2)	0.85 (0.04)	0.09	11.0 (0.3)	0.88 (0.03)	0.62
MET 2	1404 (19)	0.38 (0.00)	7383	1026 (25)	0.54 (0.01)	1869	3.8 (0.1)	0.79 (0.02)	0.03	3.8 (0.3)	0.92 (0.05)	0.87
RML	562 (7)	0.58 (0.01)	621	567 (6)	0.62 (0.01)	614	0	–	–	2.2 (0.2)	0.84 (0.06)	1.34
CME	342 (11)	0.41 (0.02)	525	191 (3)	0.50 (0.03)	161	0	–	–	1.5 (0.1)	0.74 (0.04)	0.85
SVT	134 (2)	0.57 (0.02)	85	38 (1)	0.63 (0.01)	15	0	–	–	0	–	–
GRS	93 (3)	0.59 (0.03)	53	99 (4)	0.52 (0.03)	50	0	–	–	0.7 (0.1)	0.88 (0.05)	1.22

<sup>a</sup> In  $\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$

<sup>b</sup> At  $50 \mu\text{g mL}^{-1}$

<sup>c</sup> Standard error

capacity for all soils under study in the present work can be assumed. Thus, sorption on soils was compared through  $K_d$  values ( $\text{mL g}^{-1}$ ) obtained by using an aqueous solution at  $5 \mu\text{g mL}^{-1}$  in 10 %v/v AcN (Table 2). The influence of co-solvent on adsorption coefficients for some lipophilic organic compounds resulted in a log-linear decrease as a volumetric fraction of methanol ( $f^c$ ) was increased in mixtures with water ( $f^c$  from 0.005 to 0.20). This relationship has been used to predict the adsorption of other organic compounds in soil-water system (Kookana et al. 1990; Ni et al. 2004). Consequently, sorption coefficients obtained would represent the behavior of CPF in soils under study. The adsorbed percentage was higher than 92 %, and  $K_d$  values were between 125 and 1344  $\text{mL g}^{-1}$ . The  $K_{OC}$  values presented a similar order of magnitude, but they were twofold higher than those reported for soils mentioned above ( $\approx 3500$ – $6000$ ). The distinctive high  $K_{OC}$  found for CME soil could be attributed to its high clay content and to the presence of montmorillonite. This compound is sorbed on montmorillonite, kaolinite, and gibbsite (Seger and Maciel 2005; Van Emmerik et al. 2007).

In spite of the lipophilic character of CTL and DZN (log  $K_{OW}$ =3.30, Tomlin 2006), coefficients of determination for the simple linear regression with OC were lower than those obtained for the other neutral compounds ( $R^2$ =84.7 and 86.8 %, respectively). According to PCA, CTL was related to PC1, PC2, and PC3 (cumulative variability=96 %) and DZN to PC1 and PC2. Clay percentage was mainly associated with PC2 and  $H^+_{ext}$  with PC3. Consequently, the multiple linear regression analysis for CTL adsorption related to OC,  $H^+_{ext}$ , and clay percentage and for DZN adsorption related to OC and clay percentage gave higher  $R^2$  (95.5 and 96.8 %, respectively) with the following coefficients:  $K_f_{CTL} = 12.5(\pm 2.2) \times OC + 0.44(\pm 0.10) \times \text{clay} - 0.79(\pm 0.26) \times H^+_{ext}$  and  $K_f_{DZN} = 3.4(\pm 0.3) \times OC + 0.24(\pm 0.04) \times \text{clay}$ .

These results explain the variability found for  $K_{OC}$  both for CTL (Table 3, calculated from  $K_d$ ) between 611 (PN 1) and 4321 (CME) and DZN (calculated from  $K_f$ ) between 337 (PN 2) and 1230 (CME).

Chlorothalonil data fitted the Freundlich model with an  $R^2$  value of  $>0.96$ . Sorption is associated mainly with soil OM (Patakioutas and Albanis 2002). Similar  $K_d$  values to those found in this work were described for soils with OC between 2.7 to 4.7 % (Piwowarczyk and Holden 2012). As values of  $1/n$  from the Freundlich model were  $<1.0$  (except for COLL 2 and MET both depth), the distribution coefficients for soils were obtained from the  $2 \mu\text{g mL}^{-1}$  initial concentration to make this comparison possible. Variability of  $K_{OC}$  from the cited work was also similar (978–2148). S-shape isotherms for soils with low OM content (0.48 and 0.90 %) and trends toward C-shape isotherms as OM increases were described, suggesting a variation of adsorption mechanism (Patakioutas and Albanis 2002). Agreeing with data for nonvolcanic soils (CME, SVT, and GRS), the low  $1/n$  and the high  $K_{OC}$  values,

a real contribution of clay minerals could be hypothesized. In contrast, the lower variability of  $K_{OC}$  data found for volcanic soils and the closeness to linear behavior for COLL 2 and MET samples indicate the relevance of OM in the whole adsorption process.

The intensive adsorption of DZN on soils is attributed to its hydrophobicity and lower solubility in water. Nevertheless, adsorption was described as a multistep process, suggesting the presence of different mechanisms according to different limits of concentration (Konda et al. 2002). Furthermore, S-type isotherms for soils with OM  $<0.77$  % and L-type for those with a higher content were described (Arienzo et al. 1994) with a significant correlation between OM and adsorption constants when contents were  $>2$  %. In contrast, the significant correlation with the silt plus clay content for soils with OM below 2 % revealed the importance of other soil properties on adsorption. Isotherms in this work (Table 3) were well described by a single step, and the data fitted to the Freundlich model with  $R^2 > 0.99$ . Isotherms were L-type with  $1/n < 1$  (0.77–0.86). Thus, results from the multiple linear regression analysis for DZN agree well with those found in the cited works, assessing the relevant contribution of OM on the whole process but associated with processes occurring on mineral surfaces.

#### Sorption of glyphosate and AMPA

The major differences between volcanic and nonvolcanic soils were obtained for these two compounds.  $K_f$  values for volcanic soils were between 30 and 40 times higher than the lowest values found in a nonvolcanic soil (Table 4). Data fitted to the Freundlich model with  $R^2 > 0.97$ . The exponent  $1/n$  was significantly lower than 1 with a trend to the saturation of sorption sites at higher concentrations. PCA was applied to  $K_d$  data combined with OC, clay percentage,  $Al_{Ox}$ ,  $Fe_{Ox}$ , and pH (Fig. 1c). Both compounds were associated with PC1, presenting a relationship only with the  $Al_{Ox}$  content with a minor weight on PC2 (cumulative variability=85 %). Clay percentage, pH, and  $Fe_{Ox}$  were mainly related to PC2. Only  $Al_{Ox}$  content showed a high adjustment in the linear regression analysis with  $K_d$  data, agreeing with PCA. Data for PN soil had a significant weight on this regression. The linear regression model for this relationship without PN data gave lower adjusted  $R^2$  (62 and 74 % for glyphosate and AMPA, respectively). This lack of agreement could be attributed to the high OC and  $Al_{Ox}$  contents for PN soil, making it difficult to detect the influence of other variables such as clay percentage or  $Fe_{Ox}$  contents. The correlation between glyphosate and AMPA adsorption was highly significant ( $R^2=96$  %,  $K_f_{GPS} = 1.50 \times K_f_{AMPA}$ ); therefore, glyphosate and AMPA are sorbed in the same extent because of their molecular weight ratio (1.5:1), without any evident competition for adsorption sites.

Glyphosate  $K_f$  values between 20 and 80 were reported for soils with different OM content (0.2–5.2 %) and pH (6.3–7.5) with a sorption capacity diminished when humic substances and amorphous Fe/Al hydroxides and OM were removed (Albers et al. 2009). Similar values are described for minerals such as montmorillonite and illite (Glass 1987), and the increasing sorption capacity with depth is described (Mamy and Barriuso 2005). A high sorption was assessed previously for three surface horizons of volcanic ash-derived soils, but the solutions used for equilibrium were much higher than those in the present work (between 100 and 3200  $\mu\text{g mL}^{-1}$ ) (Cáceres-Jensen et al. 2009). However, data fitted the Freundlich model with  $1/n$  values between 0.3 and 0.4.

A high adsorption of glyphosate is reported for goethite (Pessagno et al. 2008; Waiman et al. 2012), without effect of pH. In contrast, kaolinite adsorption capacity is greater at lower pH (Pessagno et al. 2008).  $\text{Al}_{\text{Ox}}$  and  $\text{Fe}_{\text{Ox}}$  are considered of great significance for GPS adsorption in variable-charge soils (Gimsing et al. 2007). The influence of OM is debated (Piccolo et al. 1996; Albers et al. 2009), and it has been positively correlated with adsorption capacity of soils (Yu and Zhou 2005; Pessagno et al. 2008).

The high adsorption found for Ultisols (with lower OM,  $\text{Al}_{\text{Ox}}$ , and  $\text{Fe}_{\text{Ox}}$  contents than Andisols) and its greater significance in deeper horizons can be attributed to kaolinite and acidic pH; for CME soil, it can be related to the high clay content and to montmorillonite and hematite. The lower  $K_f$  for GRS would be attributable to the low OC content and the lack of the most significant minerals and, for SVT soil, to the higher pH, which has been negatively correlated with sorption of GPS (Mamy and Barriuso 2005).

#### Sorption of metsulfuron-methyl, TCP, and IMHP

Sorption data are presented in Tables 3 and 4. Data fitted well to the Freundlich model ( $R^2 > 0.97$ ), except for IMHP on soils with the lowest sorption capacity ( $R^2 = 0.89\text{--}0.95$ ).

PCA was applied to  $K_f$  values combined with clay percentage; OC,  $\text{Al}_{\text{Ox}}$ , and  $\text{Fe}_{\text{Ox}}$  contents;  $\text{H}^+_{\text{ext}}$ ; pH; and CEC (Fig. 1d). The metabolite TCP was related mainly to PC1 (cumulative variability = 74 %) with a close positive relationship with OC and  $\text{Al}_{\text{Ox}}$  and a negative relationship with pH. The high significant multiple regression with these soil properties agrees with PCA results [ $R^2 = 96.4\%$ ;  $K_{f \text{ TCP}} = 4.55(\pm 0.96) \times \text{Al}_{\text{Ox}} - 1.03(\pm 0.4) \times \text{pH} + 3.38(\pm 0.69) \times \text{OC}$ ]. It was not adsorbed on SVT soil (pH = 7.5) because of the negative interaction between the anionic specie and the negative permanent surface soil charge. The lower pH and the possible interaction of TCP with  $\text{Al}_{\text{Ox}}$  in soils CME and GRS allowed its sorption in a low degree. A distinctive behavior is observed for PN soil with  $K_f$  values higher than  $49 \mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$ . The contrasting behavior of TCP and CPF and the inverse relationship with pH were reported for two soil profiles ( $K_d$

$\text{TCP} = 0.45\text{--}2.86 \text{ L/kg}$  and  $K_{d \text{ CPF}} = 30.8\text{--}209.6 \text{ L/kg}$  (Baskaran et al. 2003). For a paddy soil (pH = 6.7 and OM = 2.68 %),  $K_f$  values were 4.34 and 20.3 for TCP and CPF, respectively (Liang et al. 2011). Thus, values observed for the metabolite in volcanic soils especially in both depths of PN soil are considerably higher than those mentioned in the literature.

Metsulfuron-methyl was related to PC1 and PC2 being positively associated with OC and negatively with pH. MSM constants and clay percentage described the PC2. Consistently, the higher  $R^2$  value was obtained for a multiple linear regression model including the three properties [ $R^2 = 82\%$ ,  $K_{f \text{ MSM}} = -0.52(\pm 0.21) \times \text{pH} + 0.72(\pm 0.14) \times \text{OC} + 0.08(\pm 0.03) \times \text{clay}$ ]. This compound was not sorbed on soils with a pH higher than 6.4, independent of their OM content, as was the case of the Andisol RML and the tree nonvolcanic soils. Sorption of MSM was previously studied for surface horizons of one Andisol and two Ultisols (Cáceres et al. 2010b). Hydrophilic interaction with OM and iron oxide was suggested as a mechanism to explain the sorption observed for the Andisol; however, in this work, the contribution of iron or aluminum oxides was not observed for volcanic soils with OC and pH as the most important variables. This compound has been considered as highly mobile in soils with low OC content and  $\text{pH} > 6$  (Sondhia 2009); however, in soils with higher OC content and acidic pH, MSM also leaches to deeper segments, but with a lower potential for groundwater contamination ( $K_f = 0.37\text{--}2.84$ , Ismail and Ooi 2012).

The metabolite of diazinon, IMHP, was the less adsorbed compound, regardless the higher or medium OM content of samples or the volcanic or nonvolcanic origin of soils. A significant linear relationship was found only for OC ( $R^2 = 93\%$ ) with a very low coefficient [ $K_f = 0.28(\pm 0.02) \times \text{OC}$ ]. The pKa value of this compound is not described in the literature; however, the acidic character was observed through its chromatographic behavior. Antecedents regarding its adsorption on different soils were not found; however, according to the acidic character and the constants established in this work, it is a compound which can be lixiviated along the profile of any type of soil.

#### Desorption

No desorption of CPF and CTL was observed; nevertheless, these results could represent a short-term behavior. A biphasic desorption was described for CPF through a labile fraction and a further slow partition to the aqueous phase implying long-term desorption from soils or sediments (Gebremariam et al. 2011). The hysteresis coefficients for AT, DEA, DZN, IMHP, MSM, and TCP are shown in Tables 2, 3 and 4. Atrazine presented hysteresis for all soils, and the low sorbed amounts of DEA were easily desorbed in the deeper horizons of Ultisols, RML, and CME soils. In all cases,  $K_{f \text{ des}}/K_{f \text{ ads}}$  ratio was  $< 1$ . Diazinon was highly retained with low  $H$  values and



$K_{f\ des}$  similar to  $K_{f\ ads}$ . IMHP was completely desorbed through the re-equilibration steps in the deeper horizon of MET soil. Results obtained for MSM and TCP were very different. The first one was desorbed from the deeper horizon of PN soil being strongly retained on the surface horizon and on Ultisols at both depths. Nevertheless, TCP was desorbed from all soils with  $pH > 6$  and from the deeper horizons of MET and PN soils and both depths of COLL soil.

## Conclusions

Acidic compounds are susceptible to be lixiviated through Mollisol and Alfisol profiles where neutral-to-basic pH and permanent negative charge are the prevalent conditions. However, they could also leach in Andisols and Ultisols at greater depths due to the low sorption (IMHP) or the feasibility of desorption processes (TCP). In spite of the significant relationship found between OC content and the retention of compounds such as AT and DEA, the amount sorbed was low in volcanic and nonvolcanic soils, proving once again their potential as highly mobile compounds. The exceptionally high sorption of CPF, glyphosate, and AMPA on volcanic soils, related to the high OC,  $Al_{Ox}$ , and/or Kaolinite contents, poses the need to establish the possible contamination of them. The significant retention of CTL and DZN on Mollisols and Alfisols in spite of their low OC contents showed the contribution of clay minerals in the sorption process. The principal component analysis allowed describing the general sorption pattern of compounds according to properties of soils.

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