

Metsulfuron-methyl Sorption/Desorption Behavior on Volcanic Ash-Derived Soils. Effect of Phosphate and pH

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Metsulfuron-methyl sorption/desorption behavior was studied through batch sorption experiments in three typical volcanic ash-derived soils belonging to Andisol and Ultisol orders. Their distinctive physical and chemical properties are acidic pH and variable surface charge. Organic matter content and mineral composition affected in different ways sorption of metsulfuron-methyl (K_{OC} ranging from 113 to 646 mL g⁻¹): organic matter and iron and aluminum oxides mainly through hydrophilic rather than hydrophobic interactions in Andisols, and Kaolinite group minerals, as major constituents of Ultisols, and iron and aluminum oxides only through hydrophilic interactions. The Freundlich model described metsulfuron-methyl behavior in all cases ($R^2 > 0.992$). K_f values (3.1–14.4 $\mu\text{g}^{1-1/n}$ mL^{1/n} g⁻¹) were higher than those reported for different class of soils including some with variable charge. Hysteresis was more significant in Ultisols. A strong influence of pH and phosphate was established for both kinds of soil, intensive soil fertilization and liming being the most probable scenario for leaching of metsulfuron-methyl, particularly in Ultisols.

KEYWORDS: Sulfonyl urea herbicides; variable-charge soils; Andisols; Ultisols

INTRODUCTION

Sulfonylurea herbicides are characterized by broad-spectrum weed control at low application rates (3–40 g/ha), high selectivity, and very low acute and chronic animal toxicity. In the past decades these herbicides have been largely used to replace those with relatively high animal toxicity or which have contaminated groundwater of agro-ecosystems because of the high application rates. Metsulfuron-methyl (MSM) [methyl 2-(4-methoxy-6-methyl-1,3,5-triazine-2-ylcarbamoyl)sulfamoyl] benzoate] is an effective herbicide widely used pre- and postemergence in cereal, pasture, and plantation crops (1). Despite the low application rates the occurrence of sulfonylureas in surface or ground waters has been established (2); thus, there is some concern related to their effects on ecosystems and residual toxicity on susceptible crops, affecting yields. Accordingly, research ranging over different aspects related to the residual effect of MSM has been published (3–8).

Volcanic ash-derived soils have great importance in the agricultural economy of countries of Asia, Africa, Oceania, and America. They are widespread in central–southern Chile (latitude from 19° to 56° S) accounting for approximately 69% of the arable land. Andisols present high organic matter (OM) content and specific surface area, and the mineral composition is dominated by short-range ordered minerals such as allophane (Al₂O₃·SiO₂·*n*H₂O). Ultisols are more developed than Andisols, and amorphous

aluminosilicates progress to more crystalline compounds such as halloysite and kaolinite; the total content of iron oxides is higher (amorphous iron oxides become more crystalline) and organic matter content is reduced (9). Andisols and Ultisols typically range from pH 4.5 to 5.5, and surface charge may substantially change with pH. Variable charge is originated in inorganic constituents, such as goethite (FeOOH), ferrihydrite (Fe₁₀O₁₅·9H₂O), gibbsite (Al(OH)₃), imogolite, and allophane, where Fe–OH and/or Al–OH are the predominant groups, and in the amphoteric character of functional groups of OM and humus–Al and Fe complexes.

Surface reactivity of volcanic ash-derived soils confers to them a particular behavior in relation to the retention of organic contaminants, representing an environmental substrate that may become polluted over time due to intensive agronomic uses. However, there is not enough knowledge related to the behavior of many pesticides in these kinds of soils, including the target compound of this work. Sorption of sulfonylureas is highly sensitive to soil pH. Metsulfuron-methyl is a weak acid ($\text{p}K_a = 3.3$) and within the range of natural pH of soils can be partially or completely ionized. The anionic form is more soluble in water and less susceptible to hydrolysis (10). Under this condition the leaching potential increases as a consequence of a decreased soil sorption, especially when it is applied on soils with negative permanent charge.

Sorption of MSM has been studied mainly on soils with a relatively low OM content and pH > 6, all of them with negative

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permanent charge, presenting low sorption capacity (11–16). High mobility under these conditions has also been demonstrated (11, 13, 17, 18). Works related to MSM sorption on volcanic ash-derived soils are scarce. Distribution coefficients (K_d) obtained for seven allophanic soils were between 0.53 and 1.53 for the Ah horizons despite the considerable organic carbon (OC) content of soils (5.8–16.7%) and acidic pH. Sorption in general decreased with depth, and this fact was explained through the contribution of OM and iron and aluminum oxides of soils (19).

In general, Andisols have higher total phosphorus concentrations than Ultisols, although both have low available P and poor fertility. These soils require frequent adjustments of soil pH, replenishment of exchangeable Mg, and heavy P applications. These amendments may enhance the potential for leaching of recently applied acidic pesticides as a consequence of possible competition with phosphate for surface sites, an increase in surface negative charge resulting from phosphate sorption, or a decreased hydrophobic and hydrophilic sorption with increasing pH, as has been demonstrated for 2,4-D and prosulfuron on variable-charged soils (20, 21).

Taking into account the scarce or null antecedents in the literature about sorption behavior of MSM in soils of variable charge and the increasing use of this sulfonylurea in Chilean agriculture, the aim of this work was to study adsorption and desorption of this herbicide on three typical volcanic ash-derived soils belonging to Andisol and Ultisol orders, as a function of their physical and chemical properties. The influences of phosphate addition and pH amendment were also studied to evaluate possible consequences of intensive soil fertilization and liming.

MATERIALS AND METHODS

Chemicals. Certified analytical reference standard of MSM was obtained from Dr. Ehrenstofer, Germany. Water solubility is 270, 1750, and 2790 mg L⁻¹ at pH 4.6, 5.4, and 7, respectively. All reagents used for the analytical determination of MSM were of analytical or HPLC grade. The stock solution for all purposes was 1 mg mL⁻¹ MSM in acetonitrile (AcN). Reagents for sample treatments were of analytical grade.

Soil Samples. Fresh samples from the surface 0–20 cm of three volcanic ash-derived soils were collected: one Andisol, Nueva Braunau (Medial, Isomesic, typic Dystrandep; NB), and two Ultisols, Metrenco (Fine, mesic, Palehumult; MET) and Collipulli (Fine, mesic, Xeric, Palehumult; COLL) (22), the first from the Región de los Lagos and the two others from the Región de la Araucanía (36° 58′–41° 19′ S). They were air-dried, passed through a 2 mm diameter sieve, and stored at room temperature.

Soils Characterization. Soil organic carbon (OC) content was determined according to the Walkley–Black method (23). The pH was measured in soil suspensions with a soil to water ratio of 1:2.5 (w/v). Cation exchange capacity (CEC) was calculated from the total exchangeable bases (i.e., amounts of Mg, Ca, K, and Na extracted by 1 M ammonium oxalate at pH 7.0) plus extractable acidity of soils (determined through extraction with 0.25 M BaCl₂ + 0.2 M triethanolamine at pH 8.2). To establish the isoelectric point (IEP), samples were suspended in 0.01 M CaCl₂ and electrophoretic measurements were performed in a zeta-meter (ZM-77). The zeta potential (ZP) was calculated using the Helmholtz–Smoluchowski equation (24). The active and free iron oxides (Fe_{OX} and Fe_{DCB}, respectively) and iron oxides complexed by the organic matter (Fe_{PYRO}) have been reported in a previous work (25).

Batch Sorption Experiments. All isotherm experiments were carried out at 30 ± 1 °C. Duplicate samples of 2 g of air-dried soils were mixed with a 10 mL aliquot of aqueous solutions of MSM at 5, 10, 15, 20, 25, 50, and 100 μg mL⁻¹ (in 0.01 M CaCl₂) in 30 mL polypropylene copolymer centrifuge tubes. The tubes were shaken end-over-end at the natural pH of soils during 16 h to ensure equilibrium and then centrifuged at 2750g for 20 min; the supernatant was filtered through a 0.22 μm membrane. Desorption was performed using the samples treated at 100 μg mL⁻¹. After the adsorption equilibrium was reached, 5 mL of the supernatant

solution was replaced with 5 mL of herbicide-free 0.01 M CaCl₂ solution, and samples were shaken again for 2 h, followed by centrifugation. The same step was repeated for four consecutive times; every time, an aliquot of the centrifuged supernatant was removed for analysis. The final concentration of MSM in solution was determined by HPLC-DAD (Waters, Milford, MA), by using YMC-Pack Pro C₁₈ (250 × 4.6 mm i.d., 5 μm, 12 nm) column, connected to a μBondapak C₁₈ (10 μm) precolumn. Mobile phase was 65:35 (v/v) AcN/water (pH 2.6) at 1.1 mL min⁻¹ flow rate and 35 °C. Injection volume was 20 μL, and detector wavelength was 224 nm. Interferences from soils were discarded through the spectral purity test of the corresponding chromatographic peak and the spectral matching test by using the analytical standard. No decomposition or losses of MSM were detected in a soil solution extracted from NB sample, the more complex matrix. Detection and quantification limits were 0.0082 and 0.025 μg mL⁻¹, respectively. These parameters were calculated from a calibration curve carried out at 0.025, 0.05, 0.075, and 0.1 μg mL⁻¹. The chromatographic response was linear up to 25 μg mL⁻¹ ($R = 0.999$). The amount of adsorbed herbicide was calculated from the difference between the initial and final herbicide concentrations in solution.

Sorption was described by the Freundlich equation

$$C_s = K_f C_e^{1/n}$$

where C_s is the amount of herbicide adsorbed, C_e is the equilibrium concentration in solution, and K_f and $1/n$ are empirical constants. The organic carbon distribution coefficient (K_{OC}) was calculated as

$$K_{OC} = \frac{K_f}{\%OC} \times 100$$

The hysteresis coefficient, H , for the desorption isotherms was calculated as

$$H = \frac{1/n_{des}}{1/n_{ads}}$$

where $1/n_{des}$ and $1/n_{ads}$ are the corresponding Freundlich exponents for the desorption and adsorption process.

Effect of pH and Phosphate on MSM Sorption. Two experiments were carried out to establish the pH effect on sorption. For the first one, sorption isotherms were determined for COLL and NB soils by modifying the initial pH of each MSM solution in contact with the soil by adding 0.1 M NaOH with a continuous stirring. The final values were 6.1 and 6.0, respectively. Following this step, sorption was performed as described above. The second experiment was done for the same soils, but sorption was carried out at four different pH values at 20 μg mL⁻¹ MSM concentration. The initial pH of each MSM solution in contact with the soil was modified by adding 0.1 M HCl or 0.1 M NaOH. A previous experiment was done to obtain the amount of each solution to be added. Duplicate samples were always considered, and in all cases a 0.01 M CaCl₂ solution was used as background electrolyte. The pH conditions obtained for COLL soil were 3.0–4.6–5.5 and 7.1 and 3.6–5.0–5.7 and 6.8 for NB soil.

To establish the effect of phosphate, duplicate samples of 2 g of air-dried soils were pre-equilibrated at the natural pH of soils in a 30 mL centrifuge tube by shaking end-over-end with 5 mL of 50 mM KH₂PO₄ solution during 60 min. Following pre-equilibration a 5 mL aliquot of aqueous solutions of MSM at 10, 20, 30, 40, and 50 μg mL⁻¹ (in 0.01 M CaCl₂) was added to achieve a final volume of 10 mL. Tubes were shaken end-over-end during 16 h and then centrifuged and filtered. Solute concentrations in solutions were determined as described above. Sample blanks with phosphate and without the herbicide were included as control. The pH of soil slurries was measured after sorption of phosphate and after MSM sorption equilibrium.

Effect of MSM Sorption on Surface Charge of Soils. Surface charge effects of MSM sorption were measured by electrophoresis migration by means of zeta-meters (ZM-77). One hundred milligrams of soil was suspended in 200 mL of 15 and 50 μg mL⁻¹ MSM solutions in 0.01 M CaCl₂. Samples were sonicated during 30 min to allow complete dispersion of soil particles. Modification of pH was done by the addition of 0.1 M NaOH or HCl. To evaluate the surface charge changes, the corresponding measurements on soil blanks were performed simultaneously, under the same conditions.

Table 1. Some Physical and Chemical Properties of Soils

soil	OC ^a	pH ^b	CEC ^c	Fe _(PYRO) ^d	Fe _(OX) ^e	Fe _(DCB) ^f	sand (%)	silt (%)	clay (%)	IEP ^g
NB	9.5	4.1	10.3	1.8	3.3	5.1	6.2	66.2	27.6	6.2
MET	2.3	4.7	9.3	0.8	1.8	7.1	8.0	56.7	35.3	2.0
COLL	1.5	5.2	8.7	0.7	0.9	6.2	13.7	40.7	45.7	2.0

^aOrganic carbon (%). ^b1:2.5 = soil/water ratio. ^cCation exchange capacity (mequiv (+)/100 g). ^dIron oxide extracted with sodium pyrophosphate solution (expressed as % Fe₂O₃). ^eIron oxide extracted with dithionite–bicarbonate solution (expressed as % Fe₂O₃). ^fIron oxide extracted with ammonium oxalate at pH 3 (expressed as % Fe₂O₃). ^gIsoelectric point measured by electrophoretic mobility.

Table 2. Adsorption/Desorption of Metsulfuron-methyl on Volcanic Ash-Derived Soils and Phosphate and pH Effects: Freundlich Parameters (K_f , $1/n$, and Determination Coefficients) Values

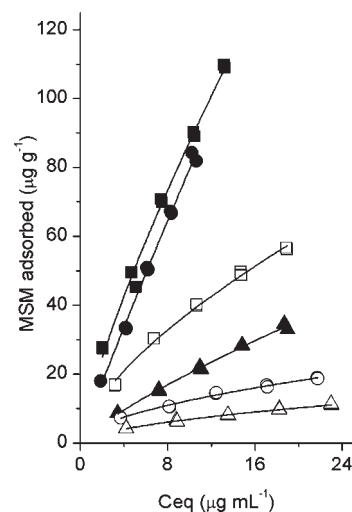
	soil		
	COLL	MET	NB
adsorption			
$K_{f,ads}$ ($\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$)	9.1 ± 0.6^a	3.1 ± 0.2	14.4 ± 1.0
n_{ads}	0.94 ± 0.03	0.81 ± 0.02	0.78 ± 0.03
R^2	0.994	0.996	0.992
K_{OC}	606	134	152
K_d^b (mL g^{-1})	9.7	2.6	13.4
K_{OC} from K_d	646	113	141
desorption			
$K_{f,des}$ ($\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$)	67.4 ± 4.9	20.3 ± 1.1	58.3 ± 2.7
n_{des}	0.40 ± 0.02	0.21 ± 0.02	0.44 ± 0.01
R^2	0.974	0.955	0.993
H	0.42	0.26	0.56
phosphate effect			
$K_{f,ads}$ ($\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$)	3.5 ± 0.2	1.8 ± 0.1	8.5 ± 0.4
n_{ads}	0.55 ± 0.02	0.57 ± 0.02	0.65 ± 0.02
R^2	0.989	0.993	0.995
K_{OC}	233	78	89
K_d (mL g^{-1})	1.98	1.0	5.2
K_{OC} from K_d	132	43	55
pH effect			
$K_{f,ads}$ ($\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$)	1.1 ± 0.2		8.6 ± 1.4
n_{ads}	0.70 ± 0.06		0.52 ± 0.06
R^2	0.984		0.962
K_{OC}	73		90.5
K_d (mL g^{-1})	0.6		3.7
K_{OC} from K_d	40		39

^aStandard error for each parameter. ^b K_d values obtained at equilibrium with a $5 \mu\text{g mL}^{-1}$ MSM solution (in 0.01 M CaCl_2).

Data Analysis. Fitting of data to the Freundlich model was performed by the least-squares regression analysis. Data for each parameter representing isotherms were calculated with the corresponding standard error, and the quality of fitting was evaluated through R^2 values. All statistical analysis was performed using Origin software (Origin Pro 8).

RESULTS AND DISCUSSION

Adsorption and Desorption of MSM and Soil properties. All soils exhibited the characteristic properties of their order. The three selected soils present acid pH (4.1–5.2, **Table 1**), and the highest OC and Fe present as amorphous oxide phase (Fe_{OX}) contents were found in NB soil. The most relevant difference between the two Ultisols is related to the texture, with a high percentage of clay in COLL soil. Conversely, NB soil presents a high IEP despite its high OC content, which can be attributed to the dominance of allophane within the mineral composition (> 50% of the total minerals) (26). At the natural pH this soil presents a positively charged surface. For Ultisols, IEP is lower than the corresponding pH, so these soils present a negative net charge.

**Figure 1.** Adsorption isotherms of metsulfuron-methyl on Andisol and Ultisol soils: (■) NB; (●) COLL; (▲) MET (open symbols correspond to isotherms with presorbed phosphate).

Data for adsorption of MSM on all unmodified soils were well described by the Freundlich model with $R^2 \geq 0.995$ (isotherms range between 5 and $25 \mu\text{g mL}^{-1}$, **Table 2**). A significant adsorption was produced on NB and COLL soil samples, being moderate on MET soil; $1/n$ values were lower than 1, which corresponds to L-type isotherms, indicating heterogeneous sorption sites (**Figure 1**). Adsorption was studied over a wide range of concentrations (up to $100 \mu\text{g mL}^{-1}$), a significant amount being adsorbed without a clear trend to the saturation of sites in COLL and NB soils; in MET soil data over $25 \mu\text{g mL}^{-1}$ showed a deviation from the Freundlich model, and the trend was to the saturation of sites.

Desorption data fitted well the Freundlich model with $R^2 \geq 0.955$. The hysteresis coefficient for all soils was always < 1 , this effect being more pronounced in Ultisols, and the ratio between $K_{f,des}$ and $K_{f,ads}$ was ≈ 7 for Ultisols and 4 for the Andisol, both facts showing that an important fraction of sorbed MSM remains bound to high-energy reactive sites (**Table 2**).

The contribution of different sorption mechanisms to model organic acids by variable-charge soils has been reported, and this process will depend on both hydrophobic and hydrophilic sorption domains (21, 27). The influence of these domains will be a function of the quantity and quality of soil minerals and OC. Under several conditions ionic interactions could contribute to some degree to anionic pesticide sorption. In soils with low OC content and high clay content, the mineral blockage by OM would be less, allowing a higher mineral contribution; thus, several authors have proposed a ratio of mineral to organic carbon fraction of > 30 to expect that ionic interaction be at a maximum (14, 28). In COLL and MET soils a high ratio of clay mineral to OC fractions was observed (30.5 and 15.3, respectively), so a different but significant contribution of clay minerals on sorption might be expected for Ultisols.

The pH of NB soil would be the sole favorable situation for hydrophobic interactions of MSM with soil OM because a fraction of neutral acid species ($\approx 15\%$) will be present. However, the dissociation of the acidic functional groups on soil OM at the pH of soil can change the overall hydrophobicity; therefore, binding of neutral species would be possible only through the high amount of this soil component. In the equilibrium solution with Ultisols, MSM was almost completely in the anionic form (96–99%); consequently, a very low or null sorption could occur. However, adsorption capacity was higher compared to those previously mentioned values for different soils, including allophanic soils with

high OC contents (11–16). According to these antecedents, hydrophobic interactions and the negative electrostatic interactions with the dissociated fraction of MSM are not enough to explain the different sorption behaviors on the three soils. The organic carbon distribution value is used to evaluate the contribution of OM in the sorption process on soils. In this case a wide range of K_{OC} values (134–606) was observed; consequently, MSM was adsorbed not only on the OM surface but also on the inorganic soil constituents, especially for COLL soil, which presented the highest value.

Kaolinite and halloysite are the primary clay minerals found in Collipulli and Metrenco soils (> 50% of the total mineral content) (26), but goethite/hematite in MET soil and allophane and goethite/hematite and gibbsite in COLL soil are also present as extractable or free species of iron and aluminum oxides (22). Goethite, hematite, and gibbsite present IEP values of > 7 (29); therefore, at the natural pH of soil the functional groups will be as cationic species favoring the electrostatic interaction with MSM.

Ca-bridging on mineral surfaces has been established as a retention mechanism for 2,4-D, another weak acid herbicide, in variable-charge soils where kaolinite was the main mineral (27, 30). It is well-known that the organic amine and compounds containing a $-NH-$ group are efficient ligands for divalent metal ions such as Ca^{2+} or Mg^{2+} , so MSM through secondary amino group could be linked to this kind of mineral in both Ultisols.

Soil OM content plays a fundamental role in regulating the selectivity of K–Ca exchange equilibrium in volcanic soils. The highest K selectivity has been reported for Ultisols with a low OM content, whereas a reduction of this selectivity has been described as OM increases in Andisols (9). Given the increased selectivity for Ca in Andisols, a high OC content bridging with this metal could be an important additional mechanism for MSM sorption on OM of NB soil. Recently, the effect of Cu^{2+} on the sorption behavior of anionic MSM on peat and soil was reported. Sorption of this metal increased the sorption of MSM by making the zeta potential of these sorbents less negative, decreasing the repulsion between the herbicide and surfaces (31). However, another mechanism related to ionic interactions is probable through the amorphous iron oxide fraction, the content of which is higher than that presented by Ultisols (Table 1).

The marked irreversible sorption in both Ultisols indicates that this process can be attributed to the stronger interactions through metal binding rather than to weaker hydrophobic or electrostatic interactions. Likewise, although NB soil presented a less significant hysteresis coefficient, the fraction corresponding to hydrophilic sorption through Ca-bridging will be less susceptible to be desorbed.

Effect of pH and Phosphate on MSM Sorption. Sorption of MSM was significantly decreased when the equilibrium pH was increased to pH 6.0–6.1, and this effect was more pronounced for COLL soil as can be observed from K_f values (Table 2). The n_{ads} coefficient was also lower, and in this case the greatest difference was obtained for NB soil; therefore, a lower availability of sites can be deduced. When isotherms are not linear, a good approach to compare relative sorptivities of sorbents is to calculate K_{OC} from the distribution coefficient (K_d) obtained at the same concentration from the isotherm range; thus, K_{OC} values were also calculated from K_d determined for the first solution ($5 \mu\text{g mL}^{-1}$), taking into account the $1/n$ value for each soil (Table 2). As can be seen, a great change of K_{OC} was produced in both soils under study, but the highest ratio between K_{OC} of natural and modified samples was obtained for COLL soil (COLL = 16, NB = 3.6). As previously discussed, MSM is present exclusively as an anionic species at pH > 5.5; consequently, under this condition

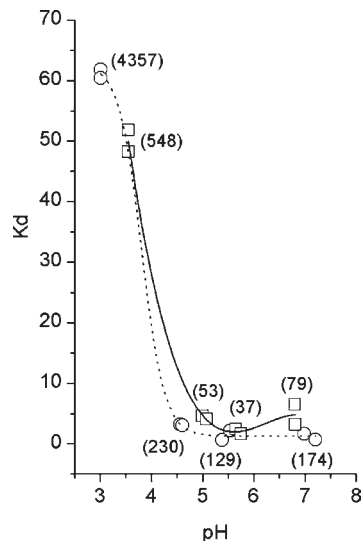


Figure 2. Effect of pH on K_d and K_{OC} values in NB (□) and COLL (○) soils (K_{OC} values at each pH are overlaid).

the mechanisms associated with the sorption process for both soils under study can be related to the anionic form. At pH values > IEP in both soils anion exchange capacity by deprotonation of pH-dependent surface species will be reduced and electrostatic repulsion from adjacent surface sites will increase; therefore, the anionic sorption to exchange sites becomes less favored, despite the increased fraction of organic anions in solution.

From experiments performed at a single concentration of MSM ($20 \mu\text{g mL}^{-1}$) at pH values ranging from acidic to neutral in both soils, a strong change of K_d values was also observed (from 60 to 0.6 for COLL and from 48 to 1.6 for NB, Figure 2). For COLL soil at pH 3.0 the K_{OC} value was $\cong 8$ times compared to that obtained at the natural pH of soil (at $20 \mu\text{g mL}^{-1}$) and 8 times the K_{OC} obtained for NB soil at pH 3.6 (K_{OC} values at each pH are overlaid in Figure 2).

At pH 3.6 approximately 40% of MSM is in the nonionized form, so increased hydrophobic interactions are supported by this fact and by the high OC content of NB soil, increasing substantially its sorption capacity. This single criterion could not be applied for COLL soil, where a very high K_{OC} value was obtained. At pH near 3 only 33% of MSM is anionic; therefore, despite the higher anion exchange capacity of soil and the development of positive surface charge at acid pH, anionic exchange and electrostatic interactions are less probable contributions. Nevertheless, MSM sorption via Ca-bridging could take place on silanol edges (Si–OH) of kaolinite where neutral active sites will be present. As the pH increases, MSM interactions with the mineral surfaces are substantially reduced due to the increased electrostatic repulsion; the remaining adsorption could be ascribed to hydrophilic interaction between the mineral components of soils and the anionic species of MSM. At pH near neutral, K_{OC} values presented approximately the same order of magnitude, being always higher those obtained for COLL soil (Figure 2).

In the present work the effect of presorbed phosphate on MSM sorption was studied. Isotherm experiments were performed at a relatively low concentration of phosphate to avoid deeper changes in the pH of systems which could produce dissolution of OM.

Isotherm data were well described by the Freundlich model with R^2 values of ≥ 0.989 , and the most pronounced sorption suppression was observed for COLL soil with a K_f value 2.6 times lower than that corresponding to the original soil. The same was obtained for the n_{ads} coefficient, with the highest trend to the saturation of sites (Table 2; Figure 1).

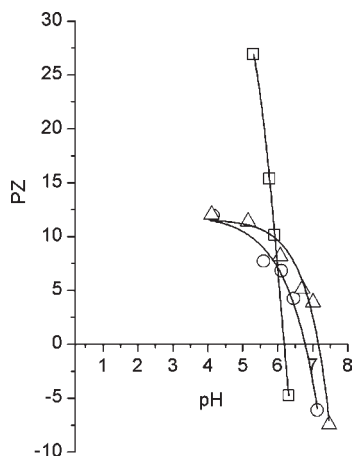


Figure 3. Electrophoretic migration curves on NB soil: (□) without metsulfuron-methyl; (○) with sorbed metsulfuron-methyl at $15 \mu\text{g mL}^{-1}$; (Δ) with sorbed metsulfuron-methyl at $50 \mu\text{g mL}^{-1}$.

In a previous study, a strong capacity to retain phosphate was established for NB and COLL soils (32). For Chilean volcanic ash-derived soils the total P contents of Andisols are greater than those of Ultisols, and organic P is prominent in all soils (> 45% of the total P). The inorganic P fraction has been associated with iron and aluminum in the soil, and the organic P fraction has been linearly correlated to the OC content (9).

Phosphate effect on sulfonylurea herbicide sorption has been scarcely studied. A diminished sorption for Prosulfuron by variable-charge soils was observed when equilibrium was obtained by using a pH-adjusted 5 mM $\text{Ca}(\text{H}_2\text{PO}_4)_2$ electrolyte (21). The difference relative to sorption in 5 mM CaCl_2 was assumed to represent hydrophilic sorption. The hydrophilic fraction was $\approx 23\%$ for two Ultisols (OC 2.0–2.3%) and < 19% or null for three Andisols (OC 4.5–15.3%), kaolinite being in all soils the major mineral component. In our experience two facts have to be considered, the intensive phosphate sorption as well as the pH change induced prior to the addition of MSM. Furthermore, in soils where the main mineral is allophane a shift of ZPC (zero point charge) toward higher pH value must be expected. This effect was established for 0.1 and 1.0 mM phosphate sorption on a synthetic allophane, where ZPC shifted from 4.8 to 6.0 at the highest concentration, a characteristic behavior of sorption through inner-sphere complexes (33). The most significant shift of pH was for NB soil: from the natural pH up to 5.4 after phosphate sorption, with an additional change to 6.0 after equilibrium with MSM. For MET soil a total shift of 0.4 unit of pH was observed, whereas for COLL soil change was negligible. At $\text{pH} > 5$ the fraction of anionic MSM is > 98%, so a very low contribution of hydrophobic interactions with OM is probable for all soils. A displacement of IEP for NB soil (where allophane is the major mineral component) toward a higher pH would be a most favorable condition for electrostatic interaction between anionic MSM and free or active iron and aluminum oxides; therefore, the lower sorption of MSM can be attributed mainly to the decrease of available sites, despite its high maximum sorption capacity of phosphate (32). This fact agrees with the less pronounced decrease of $n_{f,ads}$ in the presence of phosphate, compared to the effect on COLL and MET soils. Maximum phosphate sorption capacity for COLL soil (mainly attributed to kaolinite content) was 1.7 times lower than that established for NB soil, so a lower amount of common sites will be also available for MSM sorption. Taking into account the same criterion above-mentioned for Prosulfuron to assess hydrophilic and hydrophobic contributions to sorption on variable-charge soils, the hydrophilic

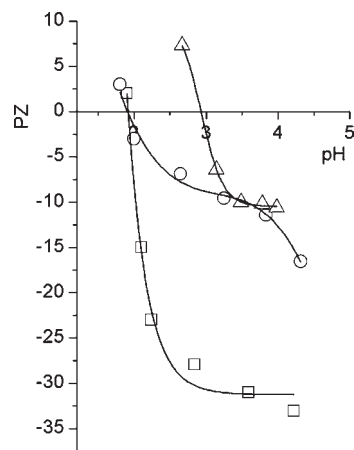


Figure 4. Electrophoretic migration curves on COLL soil: (□) without metsulfuron-methyl; (○) with sorbed metsulfuron-methyl at $15 \mu\text{g mL}^{-1}$; (Δ) with sorbed metsulfuron-methyl at $50 \mu\text{g mL}^{-1}$.

fractions for COLL, MET, and NB soil would be 79, 62, and 61%, respectively (calculated from the comparison of K_d values at $5 \mu\text{g mL}^{-1}$ MSM for soils with and without presorbed phosphate). Under this criterion, organic acid sorption to positively charged soil surface sites would be blocked in the presence of specifically sorbed phosphate. However, a limited phosphate sorption capacity should be also considered; this condition is not valid for soils used in the present work; therefore, this approach has to be considered critically to explain the phosphate influence on MSM sorption on soils under study.

Effect of MSM Sorption on Surface Charge of Soils. The curves of PZ versus pH for NB and COLL soils are shown in **Figures 3** and **4**, respectively. As can be observed, a change in the behavior of both soil surfaces was produced with sorbed MSM, being more important at the highest concentration level. From the graphics, if the same pH value is considered for soil blank samples and soils treated with MSM, a lower development of positive or negative charge is observed at the two MSM concentrations. A displacement of IEP to a higher pH value was established, from 6.2 to 7.2 and from 2.0 to 2.7 for NB and COLL soils, respectively, at the highest MSM concentration.

The change in the behavior of both soil surfaces with sorbed MSM confirms the contribution of charged surface sites to sorption of anionic MSM through electrostatic interaction. The decreasing reactive sites on both sorbents was clearly demonstrated through comparison with sample blanks, where the development of positive or negative charge as a function of pH is higher when all reactive sites are available. The displacement of IEP toward a higher pH value is similar to that described for the phosphate effect on allophane (33); however, additional experiences might be developed to establish the real sorption mechanism that produces these changes on soils.

This research constitutes a first approach to assess MSM behavior in Chilean agricultural variable-charge soils. A higher sorption capacity than that reported in the literature for variable-charge and negative permanent charge soils was established. However, a lower sorption capacity attributed to the low OM content was obtained for Ultisols. Organic matter and active and free iron and aluminum oxides will control the sorption process in Andisols mainly through hydrophilic rather than hydrophobic interactions. The kaolinite mineral group as major constituents of the inorganic fraction of Ultisols and minerals such as allophane, gibbsite, hematite, and goethite will contribute mainly through hydrophilic interactions. A strong influence of pH and phosphate addition was established for both kinds of soil, being most

important for Ultisols, so intensive soil fertilization and liming are the most probable scenarios for leaching of MSM in these soils.

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