Urea Fertilizer and pH Influence on Sorption Process of Flumetsulam and MCPA Acidic Herbicides in a Volcanic Soil

Graciela Palma,* Milko Jorquera, Rolando Demanet, Sebastian Elgueta, Gabriela Briceño, and María de la Luz Mora

Abstract

The aim of this study was to evaluate the influence of urea fertilizer and pH on the sorption process of two acidic herbicides, flumetsulam (2¢,6¢-difluoro-5-methyl[1,2,4]triazolo[1,5-a]pyrimidine-2-sulfonanilide) and MCPA (4-chloro-o-tolylglyoxylic acid), on an Andisol. Urea reduced the adsorption of MCPA but not that of flumetsulam. The Freundlich parameter $K_f$ of MCPA decreased from 8.5 to 5.1 mg g$^{-1}$ L$^{n}$ kg$^{-1}$. This finding could be attributed to an increase in dissolved organic C due to an initial increase in soil pH for urea application. The higher acidic character of MCPA compared with that of flumetsulam produced a greater hydrolysis of urea, leading to a further pH increase. A marked effect of pH on the adsorption of both herbicides was observed. The organic C distribution coefficient ($K_d$) values for flumetsulam were in the range of 74 to 10 L kg$^{-1}$, while those of MCPA were in the range of 208 to 45 L kg$^{-1}$. In the kinetic studies, the pseudo-second-order model appeared to fit the data best ($R^2 > 0.994$). The initial adsorption rates ($h$) ranged from 20.00 to 4.59 mg kg$^{-1}$ h$^{-1}$ for flumetsulam and from 125.00 to 25.60 mg kg$^{-1}$ h$^{-1}$ for MCPA. Both herbicides were adsorbed rapidly during the first stage of the sorption process, and the rates of sorption were dependent on pH. The application of the Elovich and Weber–Morris models led us to conclude that mass transfer through the boundary layer and, to a lesser degree, intraparticle diffusion were influenced by the chemical character of the herbicide. These results suggest that urea application could increase leaching of acid herbicides in soils.

Core Ideas

- The effect of urea on adsorption depended on the acidic character of the herbicides.
- An increase in pH and dissolved organic C due to urea application was observed.
- The sorbed amount of MCPA was higher than that of flumetsulam.
- Urea application could increase the leaching of acid herbicides in Andisols.

The agronomic management of pastures requires the application of herbicides and nitrogenous fertilizers, such as urea, to achieve a productive and sustainable pasture. Permanent pastures are the main source of food for cattle in temperate regions of the world. In Chile, permanent pastures cover about 1 million ha, which are concentrated in the center and south of the country, where soils with a volcanic origin are located (Vera, 2006). Flumetsulam and MCPA are the most widely used herbicides to control broadleaf weeds in pastures. They are acidic herbicides with low acid dissociation constant ($pK_a$) values (Table 1) and exist mainly as anions in the soil environment. These herbicides are weakly sorbed to soil through hydrophobic interactions and H bonding with organic matter (OM). Additionally, hydrophilic mechanisms have been proposed to explain the sorption of several acidic pesticides in variable-charge soils, with anion exchange being the most important process that controls herbicide sorption on oxide surfaces. It has also been proposed that Ca$^{2+}$ bridging on mineral and organic matter surfaces can take place (Hyun, and Lee, 2004, 2005). Andisols are volcanic soils that are widely distributed throughout the world and consist of minerals with a low degree of crystallization and a variable pH-dependent charge. The mineral fraction has a high content of allophane, imogolite, and ferrihydrite, and in the most superficial horizons, Al–humus and Fe–humus complexes. These soils are rich in organic matter, with varying degrees of humification and an acid pH. Besides, Andisols are characterized by a high specific surface area, a low bulk density, and high water retention capacity (Escudey et al., 2004; Valle et al., 2015).

Once urea fertilizer comes in contact with soil, significant pH changes occur. First, urea is hydrolyzed to NH$_4^+$–N, releasing OH$^-$ ions and increasing the soil pH by up to 0.5 units. This process is rapid and occurs within the first 24 h. Subsequent oxidation of NH$_4^+$–N to NO$_3^-$–N releases H$^+$, decreasing the pH by between 0.5 and 0.7 pH units below the natural soil pH, depending on the urea dose and the OM content of the soil (Campillo and Rodriguez, 1984; Mora et al., 2004; Cartes et al., 2009). Thus, the final pH effect of adding urea is soil acidification. The changes in soil pH under these conditions can strongly modify
Sorption processes and, consequently, the mobility and degradation of acidic herbicides. Besides soil properties and herbicides characteristics, it is well known that the urea and herbicide process in soil will be also affected by temperature and soil humidity.

Various sorption studies have been published on acidic herbicides in soils with different pH values and OM contents, which were discussed in detail in a review by Kah and Brown (2006). Flumetsulam sorption in soils has been rarely studied (Fontaine et al., 1991; Lehmann et al., 1992; Shaw and Murphy, 1997; Strebe and Talbert, 2001). In general, it has been established that the OM content and pH, which are not independent, are important factors regulating flumetsulam sorption in soils and that sorption of the neutral flumetsulam molecule is largely influenced by OM. For MCPA, numerous studies have evaluated sorption and other processes such as leaching and degradation in soils with different pH values and OM contents. The main conclusion of these studies is that MCPA is weakly adsorbed by the soil, and sorption increases with increasing OM content and decreases with increasing soil pH (Thorstensen et al., 2001; Sørensen et al., 2006; Fredslund et al., 2008; Hiller et al., 2008, 2012; Piwowarczyk and Holden, 2013; Paszko, 2007).

No studies on the sorption of flumetsulam and MCPA in Andisols have been reported. However, some studies of acidic herbicides in Andisols have been reported for metsulfuron-methyl [methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)sulfamoyl]benzoate; \( pK_a = 5.2 \) (Espinoza et al., 2009) and bensulfuron methyl (methyl \( \alpha^-\{(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl\}-o-toluene; \( pK_a = 5.2 \) (Espinoza et al., 2009). Moreover, some studies on the effects of nitrogenous fertilizers on the availability of herbicides established that increases in pH due to urea application resulted in increased dissolved organic C (DOC) contents in soil solutions. This could modify the herbicide adsorption depending on its chemical nature. Decreases in adsorption have been reported for atrazine (6-chloro-N\(^2\)-ethyl-N\(^\prime\)-isopropyl-1,3,5-triazine-2,4-diamine; García-Varcárcel and Tadeo, 2003) and pendiethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine; Liu et al., 1995], whereas increases in adsorption have been reported for metolachlor (2-chloro-6'-ethyl-N\(^\prime\)-(1RS)-2-methoxy-1-methylcarbamoyl)acet-o-toluidide; Singh, 2003) and metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one; Singh, 2006).

Sorption studies are usually conducted under apparent equilibrium conditions because although rapid sorption may occur, a long time may be required to reach equilibrium. The interaction of the herbicide with soil is a time-dependent process that defines its bioavailability in the soil. The sorption kinetic is characterized by an initial rapid sorption stage followed by a second slower stage. Fernández-Bayo et al. (2008) proposed that this process can be understood to occur in three stages: the first stage is the diffusion of the pesticide to the surface of the sorbent, which is called film mass transfer or boundary diffusion; the second stage, which is slower and involves the diffusion of the solute within internal mesopores and micropores, is referred to as the particle diffusion stage; the final stage is the sorption of the solute in the interior surface of the sorbent through mass-action-controlled mechanisms, in which rapid uptake occurs. Few kinetic studies have been reported on pesticides in soil; reports on the sorption of flumetsulam and MCPA in Andisols and its dependence on soil pH are particularly lacking, although studies have been reported on other acidic herbicides in these soils (Nkedi-Kizza et al., 2006; Espinoza et al., 2009; Cáceres et al., 2010b). Taking these previous reports into account, in this study, we used various mathematical models widely used to define equilibrium time, rate of reaction, and soil sorption capacity and to investigate the mechanisms involved in the adsorption process of pesticides in soils (Fernández-Bayo et al., 2008; Cáceres et al., 2010a, 2010b).

The aim of this study was to evaluate the influence of urea fertilizer and pH on the sorption processes of two acidic herbicides, MCPA and flumetsulam, in an Andisol characterized by high OM content and acidic pH. The kinetic parameters of sorption were determined using the hyperbolic, pseudo-first-order, and pseudo-second-order models, and the mechanistic aspects were analyzed using the Elovich and Weber–Morris models.

### Materials and Methods

#### Herbicides

The analytical standards for flumetsulam (98.8% purity) and MCPA (99.0% purity) were provided by Chem Service (West Chester, PA). All reagents used were analytical or high-performance liquid chromatography (HPLC) grade.
Soil

An Andisol from southern Chile belonging to the Freire family (38°30’ S, 72°35’ W; medial, mesic, Typic Placudands) was used (CIREN, 2002). Soil samples were collected from the surface layer (0–20 cm), air dried, sieved through a 2-mm mesh, and characterized according to the methods described by Sadzawka et al. (2006). Briefly, the OM content was measured using the Walkley–Black method. The pH was measured in soil suspensions with deionized water (1:2.5 w/v ratio) and with 0.01 mol L−1 CaCl2 solution. Small volumes of HCl and NaOH (1 mol L−1) were added to adjust the pH to 4.0, 5.0, 5.68 in H2O and 4.76 in 0.01 mol L−1 CaCl2. The pH was measured in soil suspensions with deionized water (1:2.5 w/v ratio) and with 0.01 mol L−1 CaCl2 solution. Small volumes of HCl and NaOH (1 mol L−1) were added to adjust the pH to 4.0, 5.0, 5.68 in H2O and 4.76 in 0.01 mol L−1 CaCl2 (equivalent to 200 kg N ha−1). The flumes (Durapore PVDF, Millipore) were placed in flasks, and 50 mL of aqueous solution of urea at 56.7 mg L−1 prepared in 0.01 mol L−1 CaCl2 was added to give final concentrations of 0.030, 0.050, and 0.100 mg L−1. Precision (relative standard deviation) was <5%, and the chromatographic response was linear up to 25 mg L−1 (R2 = 0.999) for both herbicides.

Dissolved Organic Carbon and pH Changes in Soil with Urea Application

To evaluate changes in soil pH and DOC content, 50 g of soil was placed in flasks, and 50 mL of aqueous solution of urea at 56.7 mg L−1 prepared in 0.01 mol L−1 CaCl2 (equivalent to 200 kg N ha−1) was added to each of them. The flasks were shaken for 1 to 60 d and were removed at different times, recording the solution pH. The supernatant solution was taken filtered and lyophilized for total OC analysis (EURO EA 300 elemental analyzer).

Adsorption Kinetics

Duplicate 2.0-g soil samples were placed in 50-mL centrifuge tubes (polypropylene copolymer) and mixed with approximately 18 mL of a 0.01 mol L−1 CaCl2 aqueous solution. Small volumes of HCl and NaOH (1 mol L−1) were added to adjust the pH to 4.0, 5.0, and 6.0. Preliminary tests were conducted in the presence of herbicides to determine the minimum volume of acid or alkali solution required for pH adjustment. Finally, the herbicide prepared in 0.01 mol L−1 CaCl2 was added to give a concentration of 1.0 mg L−1 in a final volume of 20 mL. The tubes were shaken at 20 ± 1°C in a rotary shaker for 15, 30, 45, 60, and 90 min and 2, 3, 8, 12, and 24 h. Samples were removed at these times, centrifuged at 2065 × g for 15 min, filtered using 0.22-μm membranes (Durapore PVDF, Millipore), and transferred to HPLC vials for analysis.

Adsorption Experiments

Duplicate 2.0 g soil samples were mixed with approximately 18 mL of a 0.01 mol L−1 CaCl2 aqueous solution in 50-mL centrifuge tubes (polypropylene copolymer). Small volumes of HCl and NaOH (1 mol L−1) were added to adjust the pH to 4.0, 5.0, and 6.0. A volume of a stock solution of each herbicide prepared in 0.01 mol L−1 CaCl2 was added to give final concentrations of 0.05, 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mg L−1 in final volumes of 20 mL. The tubes were shaken at 20 ± 1°C in a rotary shaker for 24 h. The tubes were then centrifuged at 2065 × g for 15 min, and the pH values of the supernatant solutions were recorded. The supernatants were filtered using 0.22-μm membranes (Durapore PVDF, Millipore), and 5-mL aliquots were transferred to HPLC vials for analysis.

The urea–herbicide isotherms were developed using the same herbicide concentrations as mentioned above, without pH adjustment. A 1000 mg L−1 stock urea solution was used to obtain a urea concentration of 56.7 mg L−1 in each tube, which is equivalent to 200 kg N ha−1 (0.572 g urea kg−1 soil). The flumetsulam–urea solutions had initial pH values of 4.9. The MCPA–urea solutions had initial pH values of 4.7. The isotherms were developed in parallel without urea by adjusting the flumetsulam and MCPA solutions to pH values of 4.9 and 4.7, respectively. Sorption experiments were repeated twice. For all experiments, the pH was adjusted to within ±0.1 pH unit.

The urea solution was spectrophotometrically measured using 1-phenyl-1,2-propanedione-2-oxime as a color reagent in accordance with the method described by Labanca and Glória (2008). In addition, the presence of NH4+ in solution at the end of the experiment was measured using the selective electrode method (García et al., 2003).

Sorption was described by the Freundlich model, and the constants were determined by linear fitting as

\[ C_s = K_f C_e^{1/n} \]  

\[ \log C_s = \log K_f + \frac{1}{n} \log C_e \]  

where \( C_s \) (mg kg−1) is the herbicide adsorbed by the soil, \( C_e \) (mg L−1) is the equilibrium concentration in the solution, and \( K_f \) and 1/n are empirical constants.

The organic C distribution coefficient (\( K_{oc} \)) was calculated as

\[ K_{oc} = \frac{K_f}{OC(\%)} \]  

where \( K_f \) is the distribution coefficient for a specific concentration within the concentration range of the adsorption isotherm, and OC is the soil organic C content.

Herbicide Analysis

The herbicides were analyzed using a Shimadzu Prominance HPLC chromatograph LC-20AT with a diode array detector (SPD-M20A) and a prontoSil column RP-C18 (250 × 4, 6 mm). The mobile phase was a 50:50 (v/v) mixture of acetonitrile and water adjusted to pH 2 with H3PO4. The detection wavelengths were 215 and 225 nm for flumetsulam and MCPA, respectively. The injection volume was 20 μL, the flow rate was 1.0 mL min−1, and the oven temperature was 30°C. Calibration curves were prepared for each herbicide.

Detection limit and quantification limits for both herbicides were 0.010 and 0.030 mg L−1, respectively. These parameters were calculated from a calibration curve developed at 0.030, 0.050, 0.075, and 0.100 mg L−1. Precision (relative standard deviation) was <5%, and the chromatographic response was linear up to 25 mg L−1 (R2 = 0.999) for both herbicides.

Data Analysis

Fitting of data to the model was performed by least-squares regression analysis. Data for each parameter were calculated with the corresponding standard error, and the quality of fitting was evaluated through R2 values.
Hyperbolic Model

Some sorption parameters can be obtained by fitting experimental data with the linear form of this model:

$$\frac{1}{q_t} = \frac{1}{B} \frac{1}{q_{\text{max}}} t + \frac{1}{q_{\text{max}}}$$

where $q_t$ is the sorbed quantity (mg kg$^{-1}$) at time $t$, $q_{\text{max}}$ (mg kg$^{-1}$) is the maximum sorbed amount, $t$ (h) is the solid–solution contact time, and $B$ is an empirical constant.

Pseudo-First-Order Kinetic Reaction Model

Some sorption parameters can be obtained by fitting experimental data with this model:

$$\log(q_{\text{max}} - q_t) = \log q_{\text{max}} - \frac{k_1}{2.303} t$$

where $q_t$ and $q_{\text{max}}$ are defined as in the hyperbolic model and $k_1$ (h$^{-1}$) is the first-order rate constant.

Pseudo-Second-Order Kinetic Reaction Model

This model assumes that the sorption capacity is proportional to the number of active soil sites:

$$\frac{t}{q_t} = \frac{1}{q_{\text{max}}^2 k_2} + \frac{t}{q_{\text{max}}}$$

where $q_t$ and $q_{\text{max}}$ have the same meaning as before and $k_2$ (mg kg$^{-1}$ h$^{-1}$) is the second-order rate constant.

Elovich Equation

The Elovich equation describes the sorption kinetics in two phases: a rapid initial stage associated with the movement of the pesticide to the most accessible parts of the soil, followed by a slower second stage where pesticide molecules diffuse in the soil micropores. Its linear form is expressed as

$$q_t = \frac{1}{Y} \ln(XY) + \frac{1}{Y} \ln t$$

where $q_t$ is the sorbed quantity (mg kg$^{-1}$) at time $t$, and $X$ and $Y$ are empirical constants. The intercept $[(1/Y)\ln(XY)]$ corresponds to the sorbed quantity in the fast phase, while the slope $1/Y$ represents the duration of the second phase.

Weber–Morris Model

The Weber–Morris equation describes sorption processes that vary proportionally with $t^{1/2}$:

$$q_t = k_{\text{int}} t^{1/2} + C$$

where $q_t$ is the amount of pesticide adsorbed (mg kg$^{-1}$) at time $t$, $C$ (mg kg$^{-1}$) is a constant related to the thickness of the boundary layer, and $k_{\text{int}}$ (mg kg$^{-1}$ h$^{-1/2}$) is the intraparticle diffusion rate constant.

Results and Discussion

Herbicide–Urea Adsorption

Adsorption studies of flumetsulam and MCPA included studies of the herbicide–urea isotherms and artificially modified pH effect on adsorption. As mentioned above, the initial reaction of urea increases the alkalinity of the soil solution, but the subsequent NH$_4^+$ transformation results in soil acidification (Campillo and Rodríguez, 1984; Mora et al., 2004; Cartes et al., 2009).

Herbicide adsorption on soil was well described by the Freundlich model for all isotherms, with $R^2 \geq 0.990$ (Table 2). The $1/n$ values were <1, suggesting L-type isotherms, which indicate heterogeneous adsorption sites (Fig. 1 and 2) (Giles et al., 1960). The $K_v$ values for flumetsulam with and without urea addition were similar. However, the $K_v$ value for MCPA with urea (5.1 mg$^{1-1/n}$ L$^{1/n}$ kg$^{-1}$) was substantially lower than that of MCPA without urea addition (8.5 mg$^{1-1/n}$ L$^{1/n}$ kg$^{-1}$; Table 2; Fig. 1). At the end of the experiment, pH increases of 0.4 and 0.2 units were observed for MCPA and flumetsulam, respectively. The urea concentration showed a decrease of approximately 10 to 15% for flumetsulam and 20 to 30% for MCPA, and the NH$_4^+$–N in solution was 17.7 and 7.4 mg L$^{-1}$ for MCPA and flumetsulam, respectively. The higher MCPA acidity compared

Table 2. Adsorption of flumetsulam and MCPA on an Andisol soil at different pH values and the effect of urea according to the Freundlich parameters ($K_v$ and 1/n), distribution coefficient $K_d$, and organic C distribution coefficient $K_{oc}$.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$K_v$ (mg$^{1-1/n}$ L$^{1/n}$ kg$^{-1}$)</th>
<th>1/n</th>
<th>$R^2$</th>
<th>$K_d$ (L kg$^{-1}$)</th>
<th>$K_{oc}$ (L kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flumetsulam</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 4</td>
<td>5.9 ± 0.2†</td>
<td>0.84 ± 0.02</td>
<td>0.998</td>
<td>6.4</td>
<td>74</td>
</tr>
<tr>
<td>pH 5</td>
<td>3.1 ± 0.2</td>
<td>0.87 ± 0.01</td>
<td>0.999</td>
<td>3.3</td>
<td>38</td>
</tr>
<tr>
<td>pH 6</td>
<td>1.4 ± 0.1</td>
<td>0.91 ± 0.02</td>
<td>0.993</td>
<td>0.9</td>
<td>10</td>
</tr>
<tr>
<td>With urea (pH 4.9)</td>
<td>2.6 ± 0.2</td>
<td>0.83 ± 0.01</td>
<td>0.996</td>
<td>2.9</td>
<td>34</td>
</tr>
<tr>
<td>pH 4.9</td>
<td>2.7 ± 0.2</td>
<td>0.82 ± 0.03</td>
<td>0.999</td>
<td>2.9</td>
<td>34</td>
</tr>
<tr>
<td><strong>MCPA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 4</td>
<td>16.3 ± 0.3</td>
<td>0.80 ± 0.01</td>
<td>0.990</td>
<td>18.1</td>
<td>208</td>
</tr>
<tr>
<td>pH 5</td>
<td>7.4 ± 0.3</td>
<td>0.80 ± 0.02</td>
<td>0.996</td>
<td>7.7</td>
<td>88</td>
</tr>
<tr>
<td>pH 6</td>
<td>4.2 ± 0.2</td>
<td>0.82 ± 0.02</td>
<td>0.995</td>
<td>3.9</td>
<td>45</td>
</tr>
<tr>
<td>With urea (pH 4.7)</td>
<td>5.1 ± 0.2</td>
<td>0.71 ± 0.03</td>
<td>0.997</td>
<td>5.4</td>
<td>63</td>
</tr>
<tr>
<td>pH 4.7</td>
<td>8.5 ± 0.2</td>
<td>0.70 ± 0.03</td>
<td>0.990</td>
<td>8.5</td>
<td>98</td>
</tr>
</tbody>
</table>

† $K_v$ values were obtained for a 1.0 mg L$^{-1}$ herbicide solution.
‡ Mean ± standard deviation ($n = 4$).
with that of flumetsulam (Table 1) could produce more urea hydrolysis, increasing the amount of NH$_4^+$ in the solution and consequently leading to a higher pH. Similar results have been found in adsorption studies performed with atrazine and urea (Liu et al., 1995) and pendimethalin and urea (García-Varcárcel and Tadeo, 2003), showing an increase in soil pH, resulting in decreased herbicide adsorption. Those researchers indicated that the initial increase in pH resulted in the release of DOC into the soil, which favors herbicide desorption or competition for soil adsorption sites. We evaluated the effect of urea on the change in soil pH and DOC content without herbicide addition. Urea increased the soil solution pH from 5.70 to 6.22, and the DOC concentration increased by about 48%, from 30.8 to 45.8 mg L$^{-1}$ at 2 d. After 10 d, the pH and DOC began to decrease below the initial soil values. The pH value after 2 mo was 4.66, showing a final soil acidification.

### pH Effect on Adsorption

The effect of pH on the speciation of both herbicides is shown in Table 1. This relationship is fundamental to understanding the sorption processes of these acidic herbicides. Within the range of studied pH values, the neutral form of the flumetsulam molecule makes up approximately 80 to 4% of the total flumetsulam, while the neutral form of MCPA comprises approximately 33 to 0.5% of all MCPA (Schwarzenbach et al., 2003). The soil used is relatively acidic and has a net negative charge based on the pH difference in water and CaCl$_2$ ($\Delta$pH = pH$_{\text{CaCl}_2}$ - pH$_{\text{H}_2\text{O}}$ = -0.92) (Báez et al., 2013).

The $K_d$ values for both herbicides are pH dependent, and they increased as the pH of the solution decreased (Fig. 2). Because the isotherms were not linear ($1/n < 1$), $K'_d$ and $K_w$ were determined for a concentration of 1.0 mg L$^{-1}$ for both herbicides. This concentration is approximately equivalent to the field dose of both herbicides.

For flumetsulam, the $K_d$ values at pH 5 and 6 were low (<4 L kg$^{-1}$) and the $K_w$ values ranged from 74 to 10 (Table 2). These values are comparable to those obtained by Shaw and Murphy (1997), who reported $K_w$ values <35 in soils with low OM content (<4%) and pH values ranging from 5 to 8. At higher pH values, flumetsulam is anionic and thus is not adsorbed on the surfaces of negatively charged soil colloids. At pH 4, flumetsulam exists predominantly in its neutral form and is weakly adsorbed by soil OM. The adsorption of the neutral form of flumetsulam is largely influenced by OM and occurs through hydrophobic and van der Waals interactions (Fontaine et al., 1991; Shaw and Murphy, 1997; Strebe and Talbert, 2001).

The $K_w$ values for MCPA were in the range of 18.1 to 3.9 L kg$^{-1}$, while the $K'_w$ values ranged from 208 to 45 (Table 2). While $K'_w$ values ranging from 14 to 50 have been reported for soils with pH values near 6 and low OM content (<6%) (Hiller et al., 2006; Piwowarczyk and Holden, 2013), no studies have reported $K'_w$ values for Andisols, although the dependence of the adsorption of acidic herbicides on OM content and pH were discussed by Kah and Brown (2006, 2007), who established that adsorption is negatively correlated with pH and positively correlated with OM content.

MCPA exhibits a greater affinity for OM than flumetsulam, although a lower fraction of neutral MCPA molecules exists in solution compared with flumetsulam. Phenoxyacetic herbicides such as MCPA exhibit hydrophobic interactions and carboxylic group H bonding (Hyun and Lee, 2005). In Andisols, which are characterized by high OM contents, anionic adsorption is not
a likely mechanism because a high ratio of clay minerals to OM (>30) is necessary (Cáceres et al., 2010b) and the ratio for the soil used in our study was 2.1. At the highest experimental pH, the $K_d$ values in this study were higher than expected considering the low proportions of neutral herbicide molecules. However, it has been suggested that the surface pH of OM could be 0.2 to 0.5 pH units lower than the pH of the liquid phase, increasing the number of neutral molecules present (Kah and Brown, 2006). Additionally, in Andisols, high $K_d$ values could be attributed to Ca bridging due to the high selectivity for Ca in Andisols. On the other hand, Andisols have a high content of amorphous minerals, mainly allophane and oxides of Fe and Al, which are reactive species that could explain the greater adsorption of MCPA, contributing to a certain extent to the anionic pesticide sorption through electrostatic interactions (Cáceres et al., 2010b; Hyun and Lee, 2005; Paszko, 2007).

**Kinetic Studies**

Figure 3 shows the sorption kinetics of flumetsulam and MCPA at pH 4, 5, and 6. The percentages of adsorbed flumetsulam during the initial phase (1 h) with respect to the sorbed percentages at 24 h at pH 4, 5, and 6 were 88, 83, and 86%, respectively. For MCPA, the percentages adsorbed were 99, 90, and 86%, respectively. The sorption of both herbicides increased quickly during the first hour of contact between the herbicide solution and soil; subsequently, a much slower stage progressed toward an apparent equilibrium. Kinetic studies performed with metolachlor (Cáceres et al., 2010a), atrazine (Baez et al., 2013), and diuron [3-(3,4-dichlorophenyl)-1,1-dimethyleurea; Cáceres-Jensen et al., 2013] in Andisols indicated similar behavior, with a rapid initial stage followed by a slower second stage to reach an apparent equilibrium with time.

Different kinetic models were applied to the experimental data to determine the kinetic parameters and the involved sorption mechanisms (Table 3). For the hyperbolic model, the determination coefficients ($R^2$) used to evaluate the model fit were <0.858 for both herbicides and were influenced by pH. For flumetsulam, $R^2$ decreased from 0.811 to 0.690 at higher pH values. For the pseudo-first-order model, the $R^2$ values were >0.925 for both herbicides, indicating that this model provided a good fit. However, the $q_{max}$ value given by the model differed greatly from the experimental value ($q_{max,exp}$) at 24 h (Table 3). At pH 4, 5, and 6, the $q_{max}$ values for flumetsulam were 4.80, 3.56, and 1.77 mg kg$^{-1}$, respectively, while those for MCPA were 7.34, 5.18, and 3.21 mg kg$^{-1}$, respectively.

The pseudo-second-order model showed a good fit with the experimental data, with $R^2 > 0.994$ for both herbicides at all pH values (Table 3). The $q_{max}$ values obtained were consistent with the experimental values (Table 3). For MCPA, the kinetic rate constant ($k_2$) was lower than that of flumetsulam. According to the initial rate constant values ($b = q_{max}^{-1}k_2$) obtained from the intercept of the pseudo-second-order equation (Eq. [6]), this trend was more marked in the first stage of adsorption. In general, the higher $R^2$ values at pH 4, 5, and 6 indicate an almost instantaneous sorption equilibrium.

Additionally, the Weber–Morris model, which relates $q_t$ with $t^{1/2}$, should produce a straight line with slope $k_4$ that passes through the origin when intraparticle diffusion (Eq. [8]) controls the sorption process. The $C$ intersect values indicate the thickness of the boundary layer, meaning that a larger value of $C$ corresponds to a greater boundary layer effect. Table 3 shows the kinetic parameters obtained using this model. The model showed a good fit for flumetsulam ($0.877 < R^2 < 0.945$) and a lower fit for MCPA ($0.750 < R^2 < 0.784$); however, the linear fits did not pass through the origin, and the $C$ values were non-zero. Thus, the boundary layers surrounding the soil particles have an important effect on the initial sorption kinetics for both herbicides, being greater for MCPA. These results are in accordance with those
obtained by Cáceres et al. (2010a), who reported that the high Andisol OM content is the governing factor for this soil, with mass transfer across the boundary layer and intraparticle diffusion playing lesser roles.

Conclusions

The adsorption of acidic herbicides on Andisols treated with urea fertilizer is strongly affected by the acidic character of the herbicide and the magnitude of the pH change resulting from urea hydrolysis. The higher acidic character of MCPA than that of flumetsulam produced a greater hydrolysis of urea, leading to a higher pH. Urea reduced the adsorption of MCPA but not that of flumetsulam, which was attributed to an increase in DOC due to the greater increase in soil pH. The investigation of the effect of pH on herbicide adsorption revealed that the adsorption of both herbicides is inversely related to pH. Despite the fact that fewer neutral MCPA molecules are present in solution compared with flumetsulam, MCPA has a greater affinity for OM than flumetsulam due to the different mechanisms that contribute to its adsorption. The results of kinetic studies indicated that large amounts of both herbicides are adsorbed in a rapid, initial, pH-dependent stage followed by much lower rates of adsorption in a slower second stage in which pH does not have marked effect. For the Andisol characterized by high OM content studied here, mass transfer across the boundary layer and, to a lesser extent, intraparticle diffusion were also active mechanisms, as indicated by the pseudo-second-order kinetic equation and the Elovich and Weber–Morris models. These results suggest that pH changes caused by the application of urea to the soil along with the effects of acidic herbicides on urea mineralization can strongly affect their bioavailability in soil.

Acknowledgments

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References


Table 3. Kinetic parameters from linear fitting with the hyperbolic, pseudo-first-order, pseudo-second-order, Weber–Morris, and Elovich kinetic models for flumetsulam and MCPA on an Andisol soil at pH 4, 5, and 6.

<table>
<thead>
<tr>
<th>Model parameter†</th>
<th>Fluometulam pH 4</th>
<th>Fluometulam pH 5</th>
<th>Fluometulam pH 6</th>
<th>MCPA pH 4</th>
<th>MCPA pH 5</th>
<th>MCPA pH 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_{max}, mg kg⁻¹</td>
<td>4.48 ± 0.20‡</td>
<td>3.00 ± 0.20</td>
<td>1.54 ± 0.18</td>
<td>7.25 ± 0.30</td>
<td>4.95 ± 0.20</td>
<td>3.14 ± 0.15</td>
</tr>
<tr>
<td>R²</td>
<td>0.811</td>
<td>0.789</td>
<td>0.690</td>
<td>0.858</td>
<td>0.850</td>
<td>0.790</td>
</tr>
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<td>Hyperbolic model</td>
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</tr>
<tr>
<td>q_{max}, mg kg⁻¹</td>
<td>1.06 ± 0.14</td>
<td>1.37 ± 0.08</td>
<td>0.51 ± 0.03</td>
<td>0.48 ± 0.03</td>
<td>1.05 ± 0.10</td>
<td>0.62 ± 0.03</td>
</tr>
<tr>
<td>k₁, h⁻¹</td>
<td>0.17 ± 0.00</td>
<td>0.15 ± 0.01</td>
<td>0.15 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.28 ± 0.01</td>
<td>0.11 ± 0.00</td>
</tr>
<tr>
<td>R²</td>
<td>0.990</td>
<td>0.943</td>
<td>0.981</td>
<td>0.960</td>
<td>0.974</td>
<td>0.925</td>
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<tr>
<td>Pseudo-first-order model</td>
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</tr>
<tr>
<td>q_{max}, mg kg⁻¹</td>
<td>4.83 ± 0.01</td>
<td>3.55 ± 0.01</td>
<td>1.77 ± 0.00</td>
<td>7.35 ± 0.01</td>
<td>5.18 ± 0.01</td>
<td>3.21 ± 0.04</td>
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<tr>
<td>k₁, mg kg⁻¹ h⁻¹</td>
<td>0.86 ± 0.02</td>
<td>0.48 ± 0.02</td>
<td>1.46 ± 0.02</td>
<td>2.30 ± 0.03</td>
<td>1.00 ± 0.02</td>
<td>2.49 ± 0.04</td>
</tr>
<tr>
<td>h, mg kg⁻¹ h⁻¹</td>
<td>20.00</td>
<td>6.02</td>
<td>4.59</td>
<td>125.00</td>
<td>27.00</td>
<td>25.60</td>
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<tr>
<td>R²</td>
<td>0.999</td>
<td>0.994</td>
<td>0.998</td>
<td>1.00</td>
<td>0.999</td>
<td>0.999</td>
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<tr>
<td>Pseudo-second-order model</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1/Y)ln(XY), mg kg⁻¹</td>
<td>4.10 ± 0.04</td>
<td>2.54 ± 0.01</td>
<td>1.41 ± 0.02</td>
<td>6.93 ± 0.2</td>
<td>4.49 ± 0.03</td>
<td>2.87 ± 0.02</td>
</tr>
<tr>
<td>1/Y, mg kg⁻¹</td>
<td>0.26 ± 0.02</td>
<td>0.27 ± 0.02</td>
<td>0.10 ± 0.00</td>
<td>0.16 ± 0.01</td>
<td>0.22 ± 0.00</td>
<td>0.12 ± 0.00</td>
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<tr>
<td>R²</td>
<td>0.988</td>
<td>0.952</td>
<td>0.861</td>
<td>0.958</td>
<td>0.934</td>
<td>0.862</td>
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<tr>
<td>Elovich model</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>k_{int}, mg kg⁻¹ h⁻¹/2</td>
<td>0.25 ± 0.02</td>
<td>0.28 ± 0.02</td>
<td>0.10 ± 0.00</td>
<td>0.19 ± 0.01</td>
<td>0.21 ± 0.00</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>C, mg kg⁻¹</td>
<td>3.73 ± 0.16</td>
<td>2.23 ± 0.10</td>
<td>1.29 ± 0.08</td>
<td>6.72 ± 0.34</td>
<td>4.27 ± 0.64</td>
<td>2.76 ± 0.10</td>
</tr>
<tr>
<td>R²</td>
<td>0.877</td>
<td>0.945</td>
<td>0.944</td>
<td>0.750</td>
<td>0.784</td>
<td>0.759</td>
</tr>
</tbody>
</table>

† q_{max}, maximum sorbed amount; k₁, first-order rate constant; k₂, second-order rate constant; h, initial adsorption rate; (1/Y)ln(XY), intercept (the sorbed quantity in the fast phase); 1/Y, slope (the duration of the second phase); k_{int}, intraparticle diffusion rate constant; C, constant related to the thickness of the boundary layer.

‡ Mean ± standard deviation (n = 4).


