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STUDY OF TRANSPORT OF FLUOROQUINOLONES AND SULFONAMIDES IN SOILS OF VOLCANIC SOURCE OF THE CENTER AND SOUTH OF CHILE: EXPERIMENTAL FRAMEWORK, SIMULATION AND MODELING [View project](#)

Adsorption of Glyphosate on Variable-Charge, Volcanic Ash–Derived Soils

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Glyphosate (*N*-phosphonomethylglycine) is widely used due to its broad spectrum of activity and nonselective mode of action. In Chile it is the most used herbicide, but its adsorption behavior in the abundant and widespread variable charge soils is not well understood. In this study, three volcanic ash–derived soils were selected, including Andisols (Nueva Braunau and Diguillin) and Ultisols (Collipulli), to evaluate the adsorption kinetics, equilibrium isotherms, and the effect of pH in glyphosate adsorption. The influence of glyphosate on soil phosphorus retention was also studied. Glyphosate was rapidly and strongly adsorbed on the selected soils, and adsorption isotherms were well described by the Freundlich relationship with strong nonlinearity ($n_{\text{fads}} < 0.5$). The n_{fads} values were consistently higher than n_{fdes} values, suggesting strong hysteresis. Adsorption (K_{ads}) increased strongly when pH decreased. The presence of glyphosate ($3200 \mu\text{g mL}^{-1}$) changed the adsorption behavior of phosphate at its maximum adsorption capacity. Andisol soils without the addition of glyphosate had similar mean K_{ads} values for Nueva Braunau (5.68) and Diguillin (7.38). Collipulli had a mean K_{ads} value of 31.58. During the successive desorption steps, glyphosate at the highest level increased K_{ads} values for phosphate in the Andisol soils but had little effect in the Ultisol soil. This different behavior was probably due to the irreversible occupation of some adsorption sites by glyphosate in the Ultisol soil attributed to the dominant Kaolinite mineral. Results from this study suggest that in the two types of volcanic soils, different mechanisms are involved in glyphosate and phosphate adsorption and that long-term use of glyphosate may impose different effects on the retention and availability of phosphorus. Volcanic ash–derived soils have a particular environmental behavior in relation to the retention of organic contaminants, representing an environmental substrate that may become highly polluted over time due to intensive agronomic uses.

GLYPHOSATE (*N*-phosphonomethylglycine) is widely used due to its broad spectrum of activity and nonselective mode of action. The use of this herbicide increased more than sixfold in the USA with an increasing adoption of glyphosate-resistant crops (Cerdeira and Duke, 2006). The extensive use of glyphosate has stimulated numerous studies on its behavior under different environmental conditions (Sheals et al., 2003; Kogan et al., 2003; Mamy and Barriuso, 2005; Barrett and McBride, 2006). In Chile, glyphosate is the most used herbicide; however, little is known about its fundamental processes (e.g., adsorption) in volcanic ash–derived Chilean soils.

Glyphosate (Fig. 1) is a multicharged compound and bears functional groups that are positively (secondary amino group) or negatively (phosphonic and carboxylic group) charged in solutions (Dzygiel and Wiczorek, 2000; Stalikas and Konidari, 2001). It can be adsorbed in soil by ligand exchange through the phosphonic acid moiety, similar to that of phosphate (Cheah et al., 1997). This property determines that soil factors such as clay mineral type and content, organic matter content, soil pH, and cation exchange capacity can greatly affect glyphosate adsorption in soil (Zhou et al., 2006). Moreover, it has been proposed that in soils with a mineralogy dominated by crystalline compounds, glyphosate likely competes with phosphate for the same adsorption sites (Jonge et al., 2001; Gimising and Borggaard, 2001, 2002a; Gimising et al., 2004a, 2004b; Strange-Hansen et al., 2004). Several studies show that phosphate plays an important role in determining the bioavailability and leaching potential of glyphosate in soil, and in some cases phosphate is able to completely desorb glyphosate (Gimising et al., 2002a; Strange-Hansen et al., 2004). However, the reversal of this interaction (i.e., long-term glyphosate use on adsorption and availability of phosphate) has not been investigated.

In the central and southern regions of Chile where most of the country's population centers are situated, soils derived from volcanic materials are abundant and widespread. These soils are derived from parent materials of volcanic origin, and their areas account for approximately 69% of the nation's arable land (Escudey et al.,

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Published in *J. Environ. Qual.* 38:1449–1457 (2009).

doi:10.2134/jeq2008.0146

Received 27 Mar. 2008.

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Abbreviations: OC, organic carbon.

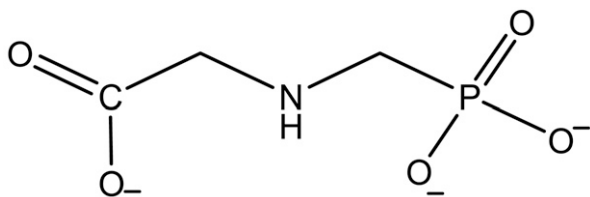


Fig. 1. Structure of glyphosate.

2001, 2007). Andisols are rich in organic matter, have high specific surface area, and contain short-range ordered minerals such as allophane. In comparison, Ultisols have lower organic matter and higher total iron oxide contents, and, being more developed than Andisols, contain more crystalline minerals, such as halloysite and kaolinite (Escudéy et al., 2007). Volcanic ash-derived soils possess surface charge that may change rapidly with pH (Escudéy et al., 2004, 2007). In addition, Andisols have higher total phosphorus (P) concentrations than Ultisols, but both generally have low available P and poor fertility. At their original acidic pH range (4.5–5.5), these soils require frequent adjustments of soil pH, replenishment of exchangeable Mg, and heavy P applications to remain productive. For these soils, it is critical to understand the adsorption of glyphosate and how its adsorption affects P retention and availability.

The purposes of this study were to characterize adsorption and desorption of glyphosate in variable charge Chilean soils, to evaluate the effect of pH on its adsorption in these soils, and to understand the effect of its excessive use on P retention and availability in soil.

Materials and Methods

Soils

The three volcanic soils used in this study were taken from the 0- to 15-cm layer in the agricultural regions of the south-central Chile. One Ultisol soil (Collipulli: 36°58' S; 72°09' W) and two Andisol soils (Nueva Braunau: 41°19' S; 73°06' W and Diguillin: 36°53' S; 72°10' W) were collected. Collipulli (Fine, mesic, Xeric, Paleumult) is an old volcanic ash-derived soil, and Nueva Braunau (Ashy, mesic Hydric Dystrandep) and Diguillin (Medial, thermic, typic, haploxerand) are modern volcanic ash-derived soils.

The soil organic carbon (OC) content was determined by the Walkley-Black method (Allison, 1965). The pH and electrical conductivity were measured in soil suspensions with a soil to water ratio of 1:2.5 (w/v). The bulk density and cation exchange capacity were determined by methods outlined by Blake (1965). The bulk density was determined by the average air-dried weight of soil in an undisturbed soil core in a 5 cm (diameter) × 5 cm (height) brass ring. Cation exchange capacity was determined as the sum of concentrations of Na, K, Mg, and Ca in ammonium acetate extracts (Peech, 1965).

Adsorption Kinetics Experiments

Batch equilibration experiments were first conducted to determine the adsorption kinetics of glyphosate in the selected

soils. A 10-mL aliquot of the aqueous stock solution of glyphosate (99%; Chem Service, West Chester, PA) at 800 $\mu\text{g mL}^{-1}$ (in 0.01 mol L^{-1} KCl) was mixed with 2.0 g of soil in 50-mL plastic centrifuge tubes. The soil suspensions were shaken mechanically at 60 rpm for 10, 30, 60, 90, 120, 240, and 1440 min at room temperature ($20.0 \pm 2.0^\circ\text{C}$) and centrifuged for 15 min at 3200 rpm. Blanks without pesticide were included and handled using the same procedure. After centrifugation, 5 mL of the supernatant was removed and filtered through a 0.45- μm glass fiber membrane (Whatman, Florham Park, NJ) using a syringe, and the filtrate was used for analysis of glyphosate. The amount of adsorbed herbicide was calculated as the difference between the initial herbicide concentration in solution and that in the sample supernatant.

Quantitative analysis was performed by ion chromatography using a Dionex DX-500 ion chromatograph (Dionex, Sunnyvale, CA) with a Dionex IonPac AS 11 HC column (2 × 250 mm) and a Dionex IonPac AG11-HC guard column (2 × 50 mm). Glyphosate was eluted with 30 mmol L^{-1} KOH solution over 20 min at a flow rate of 0.3 mL min^{-1} and monitored with an electrochemical detector. An injection volume of 20 μL was used. Analytical sensitivity, detection, and quantification limits were 0.03, 0.06, and 0.64 $\mu\text{g mL}^{-1}$, respectively. These values were calculated from a calibration curve performed at four concentration levels (0.01, 0.10, 0.50, and 1.00 $\mu\text{g mL}^{-1}$). The chromatographic response was found to be linear in the concentration range considered for these purposes, with an r^2 value of 0.99.

The adsorption kinetic was better fit with the second-order model:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad [1]$$

where q_t is the amount adsorbed at time t ($\mu\text{g g}^{-1}$), q_e is the amount adsorbed at equilibrium ($\mu\text{g g}^{-1}$), and k_2 is a rate constant for the pseudo-second order model. The integration of Eq. [1] for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad [2]$$

Equation [2] can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{1}{q_e} \cdot t \quad [3]$$

Rate parameters, k_2 and q_e , can be directly obtained from the intercept and slope of a plot of (t/q_t) against t .

Glyphosate Adsorption-Desorption Isotherm Experiments

The batch equilibration method was used to obtain adsorption and desorption isotherms of glyphosate. The conditions were the same as described above, and the solution concentrations were 100, 200, 400, 800, 1600, 2400, and 3200 $\mu\text{g mL}^{-1}$. Three replicates were used for each concentration. The soil slurries were mechanically shaken for 24 h to ensure equilibrium. Desorption

was performed using the samples treated at 3200 $\mu\text{g mL}^{-1}$. After the adsorption equilibrium was reached, 5 mL of the supernatant solution was replaced with 5 mL of herbicide-free 0.01 mol L^{-1} KCl solution, and the samples were mixed again for 2 h, followed by centrifugation. The same step was repeated for four consecutive times, and each time an aliquot of the centrifuged supernatant was removed for analysis of glyphosate.

Adsorption and desorption isotherms were fitted to the Freundlich model:

$$C_s = K_f C_e^{n_{\text{fads}}} \quad [4]$$

where C_s is the concentration of adsorbed herbicide ($\mu\text{g g}^{-1}$), C_e is the concentration in the supernatant solution ($\mu\text{g mL}^{-1}$), K_f is the empirical Freundlich adsorption coefficient ($\text{mL } \mu\text{g}^{-1}$), and n_{fads} is a linearity factor.

The hysteresis coefficient, H , for the desorption isotherms was calculated according to the following relationship (Mamy and Barriuso, 2007):

$$H = n_{\text{fdes}} / n_{\text{fads}} \quad [5]$$

where n_{fdes} is the desorption Freundlich linearity factor.

pH Effect Experiment

The effect of soil pH on glyphosate adsorption was evaluated in a separate experiment. The initial glyphosate concentration was 800 $\mu\text{g mL}^{-1}$, and an experimental design similar to that described above was used. Different volumes of 0.01 mol L^{-1} NaOH or 0.01 mol L^{-1} HCl solutions were added to the centrifuge tubes to adjust the solution pH to 4, 6, 7, and 8. Blanks without herbicide were included as the control. Three replicates were used for each soil type–pH combination. After centrifugation, 5 mL of the centrifuged supernatant was filtered through a 0.45- μm membrane and used for analysis.

Phosphate Adsorption-Desorption Experiment

Adsorption isotherms of phosphate were measured for the selected soils using a range of phosphate concentrations (4750, 9500, 23,750, 47,500, and 95,000 $\mu\text{g mL}^{-1}$) and a procedure similar to that for glyphosate. Adsorption isotherms of phosphate were fitted to the Langmuir model:

$$C_s = C_m \frac{K_l C_e}{1 + K_l C_e} \quad [6]$$

where C_s is the concentration of adsorbed phosphate in soil at equilibrium ($\mu\text{g g}^{-1}$), C_e is the phosphate concentration in the supernatant solution ($\mu\text{g mL}^{-1}$), C_m is the maximum adsorption capacity ($\mu\text{g g}^{-1}$), and K_l is the empirical Langmuir coefficient ($\text{mL } \mu\text{g}^{-1}$).

The same batch equilibration procedure was used to characterize the effect of glyphosate on phosphate adsorption. Herbicide concentrations of 100, 200, 400, 800, 1600, 2400, and 3200 $\mu\text{g mL}^{-1}$ were used. Different solutions of phosphate (KH_2PO_4), depending on the maximum adsorption capacity determined for each soil, were equilibrated together with the corresponding glyphosate solution. Three replicates were used for each soil

type–concentration step combination. After centrifugation, 5 mL of the supernatant was removed, filtered through a 0.45- μm membrane filter, and analyzed for phosphate.

Quantitative analysis of phosphate was conducted under the same conditions as given for glyphosate by ion chromatography using a Dionex DX-500 ion chromatograph with a Dionex IonPac AS 11 HC column (2×250 mm) and a Dionex IonPac AG11-HC guard column (2×50 mm). The calibration curve was made with six concentration levels (475, 4750, 9500, 23,750, 47,500, and 95,000 $\mu\text{g mL}^{-1}$). The chromatographic response was found to be linear in the concentration range considered, with an r^2 value of 0.99.

The samples with the highest level of glyphosate (3200 $\mu\text{g mL}^{-1}$) were subjected to desorption steps to obtain the phosphate desorption isotherms using a procedure similar to that described above. Blanks without glyphosate added but with the same adsorbed phosphate for each soil were included as the control.

Results and Discussion

Glyphosate Adsorption Kinetics

Adsorption of glyphosate occurred very rapidly in all three Chilean soils, with an apparent equilibrium reached in 10 to 120 min (Fig. 2). The results also showed that adsorption was faster in Nueva Braunau and Diguillin soils than in Collipulli soil, which may be due to their specific physical and chemical properties (i.e., high soil OC content) (Table 1). The slower adsorption kinetic for Collipulli soil may suggest a process controlled by molecular diffusion to the interior pores of the soil. The time-dependent adsorption of glyphosate was fitted to a pseudo first-order and a pseudo second-order model. A better fit was found with the second-order model.

The values of k_1 for the pseudo first-order model, k_2 for the second-order model, and r^2 values are listed in Table 2. Also, the time required for the adsorbent to take up half as much glyphosate as at equilibrium (i.e., $t = t_{1/2}$ as $q_t = q_e/2$) is shown. The difference in the kinetic constants suggests different adsorption sites in the soils used in this study. Some studies show that glyphosate adsorption in soils is fast on pure minerals. Differences in crystallinity of the adsorbing minerals in soils may result in kinetic differences (Gimsing and Borggaard, 2002b). In this study, after the first 10 min of equilibration, the adsorbed amounts of glyphosate were 98.8% in Nueva Braunau, 91.0% in Diguillin, and 83.1% in Collipulli of the amount adsorbed at equilibrium (q_e). For the subsequent adsorption experiments, it was estimated that the amounts adsorbed at 24 h were 99.8, 99.2, and 98.4% in Nueva Braunau, Diguillin, and Collipulli soils, respectively.

Glyphosate Adsorption and Desorption

Our first approach to study glyphosate adsorption was through the determination of isotherms at concentration values near normal agronomic application rates. Consequently, different concentrations ranging between 5 and 100 $\mu\text{g mL}^{-1}$ were equilibrated with 2 g of soils. However, due to the ex-

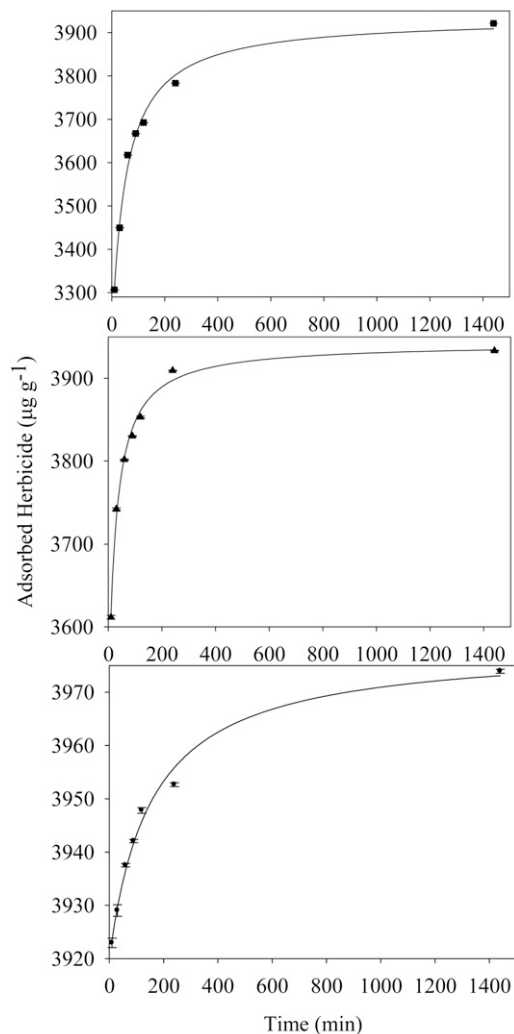


Fig. 2. Adsorption kinetics of glyphosate on Collipulli (squares), Diguillin (triangles), and Nueva Braunau (circles) soils. Data are mean of triplicate, and error bars show SD.

Table 1. Physical and chemical properties of selected Chilean soils.

Soils	pH	Bulk					CEC
		density	Sand	Silt	Clay	OC†	
		g mL ⁻¹	%			cmol kg ⁻¹	
Collipulli	5.2	1.36	13.7	40.7	45.7	1.5	8.7
Diguillin	6.2	1.12	35.5	45.1	19.4	5.8	11.8
Nueva Braunau	5.1	0.82	6.2	66.2	27.6	9.5	10.3

† CEC, cation exchange capacity; OC, organic carbon.

ceptionally strong adsorption of glyphosate by these soils, glyphosate concentrations in the equilibrated solutions were not detectable, in spite of the low limit of detection of the employed analytical method. Adsorption of glyphosate in the selected soils over the extended range of concentrations was well described by the Freundlich equation ($r^2 \geq 0.99$) (Fig. 3; Table 3). The obtained n_{fads} values ranged from 0.34 to 0.41, suggesting significant nonlinearity and strong concentration dependence of adsorption in these soils. The values of the estimated Freundlich adsorption coefficient K_f were very high (range, 1464–3764), which was in good agreement with other studies (Cheah et al., 1997; Kogan et al., 2003). According to the

Table 2. Rate constants and regression coefficients obtained from treatment of adsorption kinetics data according to pseudo first and second-order models.

Soils	First order		Second order		
	k_1	r^2	k_2	r^2	$t_{1/2}$ (min)
Collipulli	0.0035 ± 0.03	0.59	0.00006 ± 0.02	1.00	5.00
Diguillin	0.0047 ± 0.01	0.84	0.00018 ± 0.01	1.00	1.66
Nueva Braunau	0.0053 ± 0.01	0.74	0.00045 ± 0.02	1.00	1.50

K_f values, adsorption decreased in the order Nueva Braunau > Diguillin > Collipulli.

The soil organic carbon–water partition coefficient (K_{OC}) values were 987, 253, and 396 (mL g⁻¹) for Collipulli, Diguillin, and Nueva Braunau, respectively. The relatively high K_{OC} value obtained for Collipulli soil may be attributed to the fact that glyphosate was not only adsorbed on the organic matter but also on the inorganic soil constituents that influenced the adsorption kinetic.

The ratio of Freundlich exponents for desorption and adsorption gives an indication of desorption hysteresis. The hysteresis coefficient H was calculated by using Eq. [2] for the highest pesticide concentration in the desorption experiments. The H values for all three soils were <1, with values of 0.7, 0.2, and 0 for Collipulli, Diguillin, and Nueva Braunau soils, respectively, which indicates “positive hysteresis” (Table 3). The low H value for Nueva Braunau soil suggests that reincorporation of glyphosate to the soil solution during desorption was practically negligible. The hysteresis phenomena have been explained as the result of entrapment of adsorbed molecules on microporous mineral surfaces, on soil organic matter within soil aggregates due to slow rates of desorption, and pore structure heterogeneity (Mamy and Barriuso, 2007).

The adsorption of glyphosate in soils may include mechanisms such as precipitation reactions, coordination bonding, and less specific sorption interactions (Jonge et al., 2001). The cation exchange capacity, electrical conductivity, OC, and P content of the clay size fractions were reported to be responsible for the majority of the chemical activities of these soils (Escudey et al., 2001). The organic matter, broken bonds of clay minerals, amorphous Fe/Al oxides, and ferric oxides have potentially active sites for glyphosate adsorption (Yu and Zhou, 2005). In the soils used in this study, significant amounts of Fe were present as organic matter complexes (Fe_{PYRO}), amorphous iron oxide (Fe_{OX}), and free iron oxides (Fe_{DCB}). The respective Fe_{PYRO} , Fe_{OX} , and Fe_{DCB} values were determined to be 0.7, 0.9, and 6.2%, for Collipulli, 0.4, 1.9, and 3.4% for Diguillin, and 1.8, 3.3, and 5.1% for Nueva Braunau (Pizarro et al., 2003). Soil containing large amounts of iron oxides was found to have a great adsorption capacity for glyphosate and phosphate (Gimsing and Borggaard, 2001, 2002b; Strange-Hansen et al., 2004; Borggaard et al., 2005).

Gerritse et al. (1996) reported that adsorption of glyphosate decreased when soil OC content increased. Gimsing and Borggaard (2002b) and Yu and Zhou (2005) concluded that a close correlation existed between glyphosate adsorption and the amount of organic matter with variable charges. In this study, K_{OC} values for Andisols were lower than that for the

Ultisol (Table 3). Nueva Braunau soil, with the highest OC content (Table 1), showed the highest adsorption capacity for glyphosate. In contrast, the lowest adsorption was found for Collipulli soil, which also had the lowest OC content. The fact that Collipulli soil had the highest K_{OC} suggested the presence of other adsorption sites in this soil.

A close relationship between the adsorbing capacity of humic substances and the content of aliphatic C, molecular size, chemical structure, and stereo-chemical properties has been shown (Piccolo et al., 1996). Binding of glyphosate to soil was attributed to the phosphonic acid moiety reacting with polyvalent cations adsorbed on soil organic matter (Wang et al., 2006). Some authors further attributed binding to the formation of an organic matter–metal–glyphosate complex and the formation of glyphosate- H_2 species with one net negative charge (Miles and Moye, 1988; Gerritse et al., 1996; Babic et al., 2005; Yu and Zhou, 2005). Other studies established hydrogen bonding as the primary mechanism for the adsorption to humic substances (Jonge et al., 2001). The hydrogen bonding between glyphosate and humic substances is likely controlled also by the molecular size and stereochemical flexibility of the humic material (Gerritse et al., 1996). Therefore, given the multiple processes and variables contributing to the interaction with soil humic substances, there may not be a linear relationship between glyphosate adsorption and soil OC content for different soils.

Glyphosate has also been suggested to adsorb to iron and aluminum oxides and non-crystalline materials by ligand exchange through its phosphonic acid moiety in a way similar to the adsorption of phosphate or by hydrogen bonding to the clay surface (Gimsing and Borggaard, 2002a; Babic et al., 2005). The soils in this study were formed from volcanic materials under different climatic conditions and have been under different native vegetations. For the Andisol (Nueva Braunau), the main mineral is allophane (50–90%). Diguillin has minerals such as halloysite and plagioclase (1–5%), whereas Collipulli contains kaolinite as the main clay crystalline mineral (>95% of the clay content) (Besoain, 1985; Escudey et al., 2001; Escudey et al., 2004). Some researchers have shown that glyphosate has strong and specific adsorption to kaolinite (Gerritse et al., 1996; Yu and Zhou, 2005; Zhou et al., 2006). Consequently, kaolinite probably plays an important role in the adsorption of glyphosate in this soil. Glyphosate is able to strongly coordinate to clay minerals, and its binding to soil is highly influenced by the nature of the saturating cations associated with soil particles and by soil pH (Miles and Moye, 1988; Haney et al., 2000; Morillo et al., 2000; Yu and Zhou, 2005; Barrett and McBride, 2006). In this

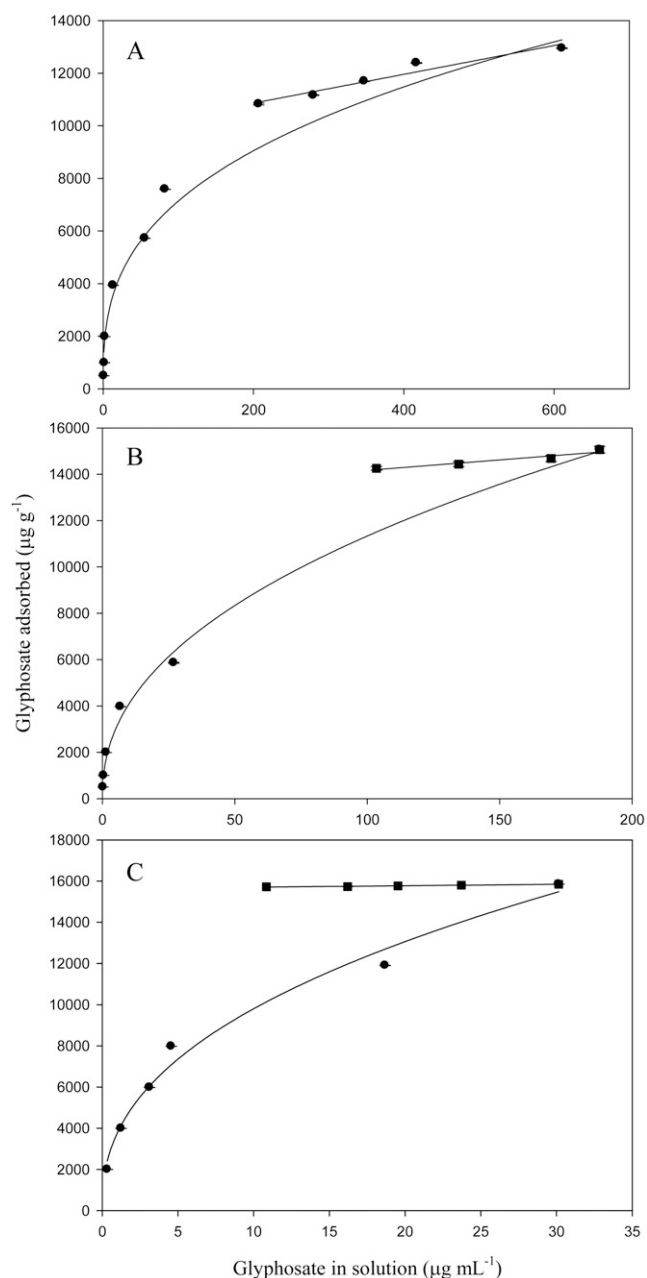


Fig. 3. Adsorption (circles) and desorption (squares) isotherms of glyphosate on (A) Collipulli, (B) Diguillin, and (C) Nueva Braunau soils. Data are mean of triplicate, and error bars show SD.

study, the contribution of clay minerals or cations to the overall glyphosate adsorption was less predominant than that of organic matter, with the exception of the Ultisol soil.

Table 3. Freundlich parameters and K_{OC} values estimated from adsorption and desorption isotherms of glyphosate on Collipulli, Diguillin, and Nueva Braunau soils.

Soils	$K_f \dagger$ mL μg^{-1}	n_{fads}	r^2	K_{OC}	K_{fdes}	n_{fdes}	r^2	H
Collipulli	1480 ± 123	0.3 ± 0.01	0.99	987	4007 ± 421	0.2 ± 0.02	0.99	0.7
Diguillin	1464 ± 87	0.4 ± 0.01	0.99	253	9400 ± 536	0.1 ± 0.01	0.97	0.2
Nueva Braunau	3764 ± 186	0.4 ± 0.00	0.99	396	15336 ± 51	0.0 ± 0.00	0.86	0.0

† H, desorption hysteresis coefficient; K_f , empirical Freundlich adsorption coefficient; K_{fdes} , Freundlich coefficient for desorption; K_{OC} , carbon–water partition coefficient; n_{fads} , linearity factor; n_{fdes} , Freundlich nonlinearity constant for desorption.

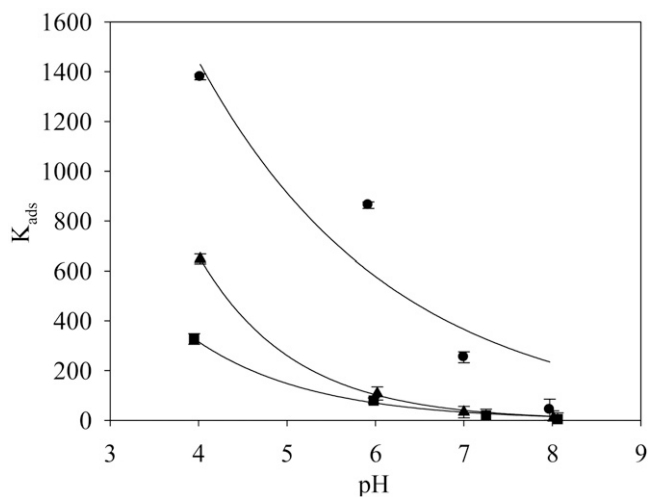


Fig. 4. Effect of pH on K_{ads} value during adsorption of glyphosate on Collipulli (squares), Diguillin (triangles), and Nueva Braunau (circles) soils. Data are mean of triplicate, and error bars show SD.

Effect of pH on Glyphosate Adsorption

Glyphosate is an amino acid that has a strongly ionized phosphate group; as a result, its dissociation constants, pK_{a1} , pK_{a2} , pK_{a3} , and pK_{a4} , are 2.0, 2.6, 5.6, and 10.6, respectively (Stalikas and Konidari, 2001). To further understand the importance of pH in glyphosate adsorption, the pH of the soil slurries was artificially adjusted before glyphosate addition. It is evident that glyphosate adsorption for each soil showed a nonlinear dependence on pH (Fig. 4). The K_{ads} values increased as the pH decreased in all three soils. It is well known that the variable charge surfaces of the oxides become more protonated at lower pH, reducing the negative charge on the oxides and increasing the overall positive charge on the soil surface. This shift may have resulted in the enhanced adsorption of the negatively charged glyphosate species.

The decrease of glyphosate adsorption with pH was steeper for Nueva Braunau than for Collipulli or Diguillin. Therefore, the differences in glyphosate adsorption observed in the unadjusted soils cannot be solely attributed to the inorganic portion of the soils. When pH was changed from 6.5 to 7.6 in Collipulli and Diguillin soils, only a small decrease in K_{ads} occurred (Fig. 4). At the same pH, significant differences in K_{ads} were present among the different soils. For instance, at pH 4, K_{ads} for Nueva Braunau was twice that for Diguillin and about five times that for Collipulli (Fig. 4). The strong effect of pH observed for Nueva Braunau soil may also be attributed to its high OC content; as pH decreased, a decrease in the number of ionized functional groups could affect the adsorption of glyphosate.

Effect of Glyphosate Adsorption on Soil Phosphorus Retention

The adsorption isotherms of phosphate in the selected soils in the absence of glyphosate were adequately described by the Langmuir equation, with an r^2 value close to 1.0 (Fig. 5; Table 4). From the maximum adsorption capacity, adsorption of phosphate in the selected soils followed the order Nueva

Braunau > Diguillin > Collipulli, which was similar to that for glyphosate. The soils Nueva Braunau and Diguillin have higher OC contents. In a previous study, total P in Ultisols was found to be lower than that in Andisols, with the values being 2216 and 3000 $mg\ kg^{-1}$ for Diguillin and Nueva Braunau, respectively, and 1108 $mg\ kg^{-1}$ for Collipulli (Escudey et al., 2001). The soils derived from volcanic ashes exhibit a strong capacity to retain phosphate, and significant amounts of the accumulated P are from the organic forms, similar to allophanic soils in other parts of the world.

The effect of glyphosate adsorption on the retention of phosphate was evaluated in soils over a wide range of concentrations near the maximum capacity of phosphate adsorption (Table 5). Statistical differences between mean K_{ads} values for each concentration of glyphosate were not significant (hypothesis test concerning the difference between the means; $p > 0.05$). Both Andisols had similar K_{ads} values when glyphosate was added, with mean K_{ads} values of 5.68 for Nueva Braunau and 7.38 for Diguillin. Collipulli showed the highest phosphate adsorption, with a mean K_{ads} value of 31.58. All these values were lower than those for soils without the addition of glyphosate under the same experimental conditions (i.e., the blank samples). Furthermore, the addition of glyphosate significantly changed the phosphate desorption pattern in each soil (Table 5).

At maximum capacity of phosphate adsorption, the corresponding equilibrium solutions showed an increase in pH higher than 8. These pH changes can be explained by the adsorption of phosphate on clay minerals such as kaolinite, producing the OH ion. This is especially true for Collipulli because of its high content of kaolinite (>50% of total mineral content). On the other hand, the isoelectric point values were 2.0, 2.8, and 5.5 for Collipulli, Diguillin, and Nueva Braunau soils, and the original pH values were 5.2, 6.2, and 5.1, respectively. At pH above 7, P is mainly in the form of HPO_4^{2-} . This divalent ion, with two nucleophilic centers and the potential to act as a bidentate ligand, may have a greater affinity for the adsorbent surfaces in spite of the effect of alkalinity on the increasing negative net charge in soils, which could produce electrostatic repulsion toward the P anions (Pardo et al., 1992).

Competition between glyphosate and phosphate adsorption was assessed by simultaneously adding both sorbates to soils. In spite of the high concentration of phosphate in relation to the concentration of glyphosate used in this study, the latter influenced adsorption of phosphate. The behavior of phosphate in the presence of glyphosate can be a result of the mineralogical composition of soils offering the same types of active sites for the two adsorbates. Nueva Braunau and Diguillin soils are dominated by allophane (>50% of total mineral content), and crystalline minerals, such as gibbsite and plagioclase, are found at the 1 to 5% range (Escudey et al., 2001). Competitive adsorption and desorption between glyphosate and phosphate on oxides and clay silicates have been studied, but in all cases adsorption of one of them was performed 5 to 7 d before the addition of the second adsorbate (Gimsing and Borggaard, 2002a, 2002b; Gimsing et al., 2007). As a result, gibbsite and goethite adsorbed glyphosate and phosphate in comparable

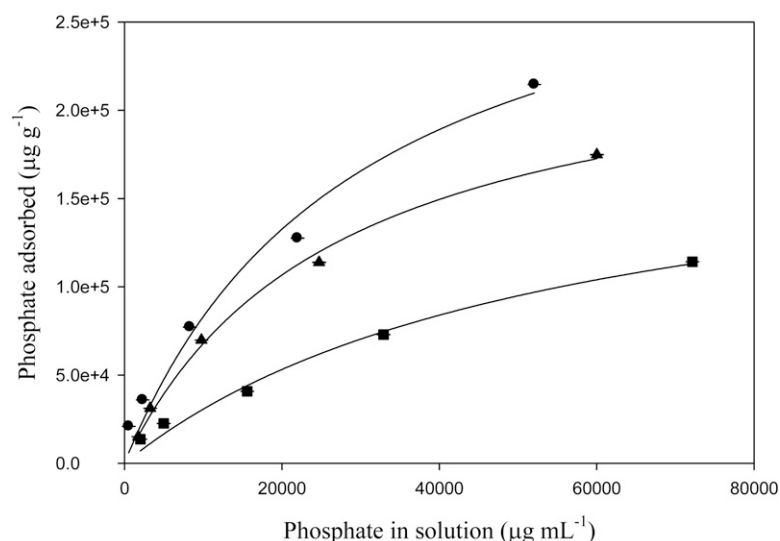


Fig. 5. Adsorption isotherms of phosphate on Collipulli (square) Diguillin (triangles), and Nueva Braunau (circles) soils. Data are mean of triplicate, and error bars show SD.

amounts and much greater than montmorillonite and illite. Significant competition occurred between phosphate and glyphosate for adsorption sites on the oxides. When phosphate was applied to oxide suspensions containing adsorbed glyphosate, glyphosate was desorbed by phosphate, whereas phosphate desorbed phosphate only to a limited extent; however, on the clay silicates, the effect of phosphate on glyphosate adsorption was weaker than on the oxides, and glyphosate had a greater effect on phosphate adsorption (Gimsing and Borggaard, 2002a, 2002b). Adsorption of phosphate and glyphosate on oxides takes place by ligand exchange, where hydroxyl groups at the oxide surface are displaced and inner-sphere complexes are formed (Dideriksen and Stipp, 2002; Gimsing and Borggaard, 2002a; Borggaard et al., 2004; Strange-Hansen et al., 2004). Adsorption on clays takes place by ligand exchange with the hydroxyl groups (Fe-OH and Al-OH) exposed at the edges (Gimsing and Borggaard, 2002a).

The effect of glyphosate on phosphate sorption process was also observed through the successive steps of desorption. In the two Andisols soils, there was an apparent re-adsorption of phosphate over each desorption step as phosphate K_{des} increased. This effect was not observed or was slightly evident when phosphate behavior was studied without the addition of glyphosate. On the other hand, in Collipulli soil, apparent re-adsorption was present only in the blank sample, and K_{des} was practically constant throughout the desorption steps in the corresponding competition experiment. The continued increase of phosphate sorption in Andisols may be due to the formation of an iron or aluminum oxide complex and subsequent precipitation of iron or aluminum phosphate because of the final pH of the equilibrium solution, a mechanism described previously (Borggaard et al., 2005). Andisols contain a higher level of amorphous iron oxides and iron complexed by organic carbon than Ultisols (Pizarro et al., 2003). Thus, it is likely that glyphosate and phosphate were adsorbed directly on these iron oxides or allophane via ligand exchange with surface hydroxyls

Table 4. Langmuir parameters estimated from the adsorption isotherms of phosphate on Collipulli, Diguillin, and Nueva Braunau soils.

Soil	K_l mL μg^{-1}	C_m $\mu\text{g g}^{-1}$	r^2
Collipulli	$1.82 \text{ E}^{-5} \pm 5.48 \text{ E}^{-6}$	$199,282 \pm 32,562$	0.99
Diguillin	$3.72 \text{ E}^{-5} \pm 5.12 \text{ E}^{-6}$	$249,760 \pm 15,376$	0.99
Nueva Braunau	$3.36 \text{ E}^{-5} \pm 1.27 \text{ E}^{-5}$	$329,384 \pm 59,673$	0.98

Table 5. Phosphate adsorption (K_{ads}) values for Collipulli, Diguillin, and Nueva Braunau soils amended with different concentrations of glyphosate and desorption values (K_{des}) at the higher glyphosate concentration (mean values, $n = 3$).

Glyphosate $\mu\text{g mL}^{-1}$	Phosphate adsorption in presence of glyphosate, K_{ads}	Phosphate desorption, blank, K_{des}	Phosphate desorption in presence of glyphosate, K_{des}
<u>Collipulli</u>			
100	33.53 ± 4.51	K_{ads} 48.52 \pm 4.04	29.26 \pm 0.16
200	34.66 ± 4.23	K_{des1} 54.92 \pm 0.77	25.38 \pm 1.15
400	30.13 ± 0.53	K_{des2} 62.89 \pm 0.69	24.42 \pm 1.31
800	29.74 ± 0.74	K_{des3} 93.23 \pm 4.97	26.33 \pm 6.15
1600	30.13 ± 1.30	K_{des4} -	30.42 \pm 0.25
3200	29.26 ± 0.16		
<u>Diguillin</u>			
100	7.12 ± 0.36	K_{ads} 35.60 \pm 1.51	7.58 \pm 0.12
200	7.33 ± 0.28	K_{des1} 35.88 \pm 1.08	7.12 \pm 0.09
400	7.52 ± 0.13	K_{des2} 34.72 \pm 0.49	16.08 \pm 0.88
800	7.35 ± 0.24	K_{des3} 33.00 \pm 0.29	42.72 \pm 7.83
1600	7.35 ± 0.22	K_{des4} -	121.26 \pm 7.75
3200	7.58 ± 0.12		
<u>Nueva Braunau</u>			
400	6.16 ± 0.55	K_{ads} 25.47 \pm 1.96	5.66 \pm 0.20
800	5.84 ± 0.09	K_{des1} 26.24 \pm 0.86	6.03 \pm 0.07
1600	5.48 ± 0.17	K_{des2} 27.10 \pm 1.83	11.68 \pm 0.74
2400	5.28 ± 0.06	K_{des3} 33.25 \pm 1.53	24.71 \pm 2.07
3200	5.66 ± 0.20	K_{des4} -	50.82 \pm 7.40

where inner-sphere complexes were subsequently formed. Alternatively, the observed re-adsorption of phosphate suggests

a previous desorption of glyphosate from oxide species. The last process was not demonstrated because of the complexity to determine the herbicide and phosphate simultaneously under the experimental conditions used. In addition, several studies indicate that the amount of phosphate adsorbed is approximately twice the amount of glyphosate adsorbed under the same conditions (Gimsing and Borggaard, 2001, 2002b). The difference is probably due to the different molecular sizes because the glyphosate molecule is 0.43 nm long, whereas the phosphate molecule is 0.25 nm long, or due to the fact that glyphosate requires more space, reducing the sites available. Therefore, phosphate has more adsorption sites available compared with glyphosate under the same conditions.

The opposite was observed in the Ultisol. Glyphosate has strong and specific adsorption on kaolinite (Gerritse et al., 1996; Yu and Zhou, 2005; Zhou et al., 2006). It is likely that in Collipulli, glyphosate cannot be desorbed by phosphate, resulting in close to constant desorption K_{des} values and, consequently, increasing amounts of phosphate in the equilibrium solution, without any possibility of re-adsorption. In a recent study, glyphosate adsorption on two soils with high levels of kaolinite presented the highest maximum adsorption capacity and K_L values, showing the high affinity for this mineral surface (Pessagno et al., 2008).

Finally, these observations suggest that in Andisols, extensive use of glyphosate may result in enhanced adsorption and, consequently, reduced availability of phosphate. On Ultisols, glyphosate may be immobilized with no effect on the phosphate adsorption process.

Conclusions

In variable-charge Chilean soils, adsorption of glyphosate occurred rapidly, with the kinetics well described by a pseudo second-order model. The adsorption isotherms were well described by the Freundlich model, showing strong adsorption capacities and significant nonlinearity. There was a pronounced hysteresis of glyphosate desorption in these soils. The pH of the equilibrium solution greatly influenced the adsorption of glyphosate, especially in the lower pH range, increasing as pH decreased. The addition of glyphosate changed significantly phosphate desorption pattern in each soil. When the behavior was examined near the maximum phosphate adsorption capacity, adsorption of glyphosate resulted in decreased phosphate adsorption for all soils, as compared with the behavior of blank samples. The increases in phosphate K_{des} in Andisol soils suggest apparent re-adsorption of phosphate or a possible precipitation of iron phosphate, whereas the constant desorption K_{des} values in the Ultisol was likely due to the more favorable competition of glyphosate for adsorption sites than phosphate. The different responses observed between the Andisols and Ultisols suggest that different mechanisms are involved in the adsorption of glyphosate and phosphate in these volcanic soils and that long-term use of glyphosate may therefore have different effects on the retention and availability of soil P.

Acknowledgments

We thank Peggy Resketo and Svetlana Bondarenko for their technical assistance. This study was supported through DICYT-USACH, MECESUP UMCE-0204 (Chile) and FONDECYT 1070116.

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