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Changes in soil pH and addition of inorganic phosphate affect glyphosate adsorption in agricultural soil

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Abstract

Glyphosate is the most widely used herbicide in Argentina. The strong sorption of glyphosate to the mineral fraction of the soil can be affected by environmental conditions and agricultural management, such as the application of fertilisers. This work aimed to study the effect of pH and the presence of inorganic phosphate on the affinity of glyphosate for nine different surface soils of Argentina. The effect of pH on glyphosate sorption was investigated by batch experiments with pH adjusted between 3 and 12. The greatest glyphosate adsorption occurred at a certain pH value and then adsorption decreased with increasing or decreasing pH. The effects of pH on adsorption could be described by a model that includes changes in electrical potential. The effect of inorganic phosphate on glyphosate adsorption was studied by batch experiments in the presence of 0.5 or 1 mM phosphate. The results showed a significant competition between phosphate and glyphosate in all soils. The Freundlich glyphosate coefficients decreased by 40%–65% with phosphate in solution, and the amount of glyphosate adsorbed decreased between 1% and 5%, depending on the particular characteristics of the soil. For the glyphosate-phosphate competition, the competition terms were not reciprocal with each other because the competition between ions for adsorption sites also involves electrical effects.

Highlights

- There is a pH at which glyphosate shows a higher affinity for the soil.
- The presence of phosphate significantly reduces the adsorption of glyphosate to the soil.
- The effects of pH can be explained by rather small changes in the estimated surface potential.

KEYWORDS
electric potential, glyphosate, phosphate, soil variability, sorption coefficient

1 | INTRODUCTION

Glyphosate (*N*-[phosphonomethyl] glycine) is the main broad-spectrum herbicide used in Argentina. Its use has increased drastically in the last years due to the weed control in fallows and genetically modified crops (Aapresid, 2012). Once it reaches the soil, glyphosate is strongly adsorbed to soil particles (Aparicio et al., 2013; Gevao et al., 2000). Different works have shown the importance of amorphous iron and aluminium oxides in

glyphosate adsorption (Borggaard & Gimsing, 2008; Vereecken, 2005). However, in typical agricultural soils of Argentina, adsorption to clay minerals appears to be one of the most important factors affecting the behaviour and fate of the herbicide (De Gerónimo et al., 2018).

Phosphorus is one of the essential elements for crops. Plants absorb phosphorus from the soil solution mainly as orthophosphate ion (HPO_4^{2-} or $H_2PO_4^-$). However, due to the high adsorption of phosphate to the soil and the ability to form complex ions and insoluble compounds with common metal ions, the availability of phosphate uptake for microbes and plants is limited, so agricultural soils are often supplemented with phosphate fertilisers to maintain crop production (Holford, 1997; Tiessen, 1995). Therefore, long-term phosphate fertiliser applications result in the build-up of phosphate in agricultural soils (de Jonge et al., 2001), which has caused great environmental concern since phosphate is largely responsible for the eutrophication in nearby water bodies (Klapper, 1991; Zhou et al., 2001).

The amount of variable charge surfaces present in the soil and the magnitude of this charge on the surface are the main factors governing glyphosate and phosphate adsorption (Barrow, 1999). The charge and the electric potential of the variable charge are sensitive to soil pH because these charges arise from the protonation and deprotonation of functional groups exposed on the soil surface, mainly non-crystalline aluminium silicates, oxides and hydroxides of iron and aluminium, and organic matter present in the soil (Barrow et al., 2015; Parfitt, 1980).

With increasing pH, the net charge of the molecules becomes more negative; simultaneously, the negative charge of clay minerals and iron and aluminium oxides can be increased as well. Therefore, the adsorption of both compounds decreases by electrostatic repulsion with the negative charge surfaces (Damonte et al., 2007; Morillo et al., 1997; Morillo et al., 2000; Wauchope et al., 2002). However, due to the differences in charge and molecular size between glyphosate and phosphate, the interaction affinity of these compounds with the soil is different (Gimsing et al., 2007; Gimsing & Borggaard, 2001).

It has been widely discussed that the amount of adsorbed glyphosate greatly depends on pH. There is a consensus that glyphosate adsorption decreases with increasing pH (De Gerónimo et al., 2018; Pereira et al., 2019; Pessagno et al., 2005). However, there are conflicting reports about the effect of acidic pH (Barja & dos Santos Afonso, 2005; Gimsing, Borggaard, & Bang, 2004; Pessagno et al., 2008; Zhao et al., 2009).

Several mechanisms have been proposed to explain the sorption of glyphosate to soils. Minerals with a pH-dependent charge probably adsorb glyphosate by an anion-exchange mechanism (Gimsing & dos Santos Afonso, 2005). The formation of strong adsorbent–cation–P(glyphosate) bonds by ligand exchange between the glyphosate phosphonate group and singly coordinated Al—OH and Fe—OH groups on the surfaces of variably charged soil minerals has been proposed as a possible sorption mechanism (Borggaard & Gimsing, 2008; de Jonge et al., 2001; Dideriksen & Stipp, 2003; Jonsson et al., 2008; Mamy & Barriuso, 2005; Morillo et al., 1997; Nicholls & Evans, 1991; Piccolo et al., 1994; Sheals et al., 2002; Wang et al., 2006). The experimental evidence shows that the three functional groups (phosphonic acid, carboxylic acid, secondary amine) can interact with the clay mineral surface, although the carboxyl group may be important at low pH values, and not at near-neutral and higher pH values (Dideriksen & Stipp, 2003). Several studies have shown that the pH, clay content and iron oxides are the most important factors playing a role in glyphosate adsorption on soils (De Gerónimo et al., 2018; Dion et al., 2001; Glass, 1987). The clays appear to have two well-defined glyphosate adsorption sites, a first adsorption site being on the external surface and a second one on the interlayer space. In both types of sites, adsorption would occur via inner-sphere surface complexation through a ligand exchange mechanism similar to that suggested for glyphosate adsorption on iron oxides (Barja & dos Santos Afonso, 2005). In this sense, if the glyphosate concentration is low, adsorption would only occur on the edge surface. As glyphosate concentration increases, these sites become saturated and other sites probably located at the siloxane layer contribute significantly to adsorption. In the swelling clays, it was found that glyphosate is bound to the external surface sites, like in iron oxides, but it is also bound through the positively charged amino group to the surface interlayer sites (de Santana et al., 2006). An important factor in the interaction of glyphosate with the clay surface is the point zero charge (pzc), as studies on montmorillonite have shown. If the pH values of the solution are higher than the pzc of the edges, the clay mineral surface becomes deprotonated and the negatively charged ligand can hardly reach the surface adsorption sites, with the main mechanism of adsorption in these cases being the ligand exchange where edge surface hydroxyl groups are exchanged by ligands (Lagaly et al., 2006). Studies carried out on goethite showed that the phosphonate group bonds monodentately or bridges bidentately to the surface of iron oxide in an inner sphere mode (Barja & dos Santos Afonso, 2005; Gimsing & Borggaard, 2001). The tendency of glyphosate to form coordination compounds with metal ions is also well known. Different studies have shown that glyphosate forms a 1:1 chelate complex with copper ions involving the carboxylate, amino and phosphonate groups (Glass, 1987). Also, in the solid-state

complexes, cobalt, aluminium (III) and iron (III) ions are chelated by the phosphonate and carboxylic acid of glyphosate whereas the amino group remains protonated.

Like in any ligand exchange reaction, glyphosate adsorption competes with other ligands to bind to the metal ion. In this sense, different anions, such as phosphate and sulphate, among others, potentially compete with glyphosate for adsorption sites.

Competition for soil binding sites between phosphate and glyphosate has been under discussion since the introduction of glyphosate-based herbicidal formulations into the market. This discussion stems from the considerable molecular similarity between inorganic phosphate and the highly reactive phosphonomethyl functional group of the glyphosate molecule (Borggaard & Gimsing, 2008; de Jonge & de Jonge, 1999; Dion et al., 2001; Gimsing & Borggaard, 2002; Sprankle et al., 1975; Zhao et al., 2009). The phosphate ion reacts with soil by adsorbing on variable-charge surfaces, causing the surface to acquire a 'semi-permanent' negative charge that change the electric potential of the variable-charge surfaces (Barrow, 1974; Barrow & Debnath, 2014; Bolland & Allen, 2003). Several studies demonstrated that glyphosate sorption by soils decreased in the presence of inorganic phosphate. Batch equilibrium experiments in soils that have been fertilised with phosphate for many years show significantly less sorption of glyphosate in comparison with untreated soils (de Jonge et al., 2001; Munira et al., 2016; Munira & Farenhorst, 2017). In this sense, it has been observed that the Freundlich partitioning coefficients decrease by up to 50% in soils with the greatest Olsen P contents, relative to soils with the lowest concentrations of Olsen P (de Jonge et al., 2001). Similar results have been reported in other soils with high concentrations of Olsen P, where the linear partition coefficients were reduced by 25%–44% relative to control soils (Kanissery et al., 2015; Munira et al., 2016, 2018). Although it has been shown that phosphate can displace previously adsorbed glyphosate, there are questions about the ability of glyphosate to desorb phosphate (Gimsing & Borggaard, 2001; Gimsing, Borggaard, & Bang, 2004). In this sense, previous studies showed that glyphosate has the potential to release phosphate adsorbed to the soil, but the glyphosate concentrations used were much higher than those commonly employed (Gimsing, Borggaard, & Sestoft, 2004). The importance of the enhanced mobility of glyphosate by phosphate competition has grown in recent years due to possible phytotoxic effects after the application of phosphate in sensitive crops such as tomato (*Solanum lycopersicum* L.; Cornish, 1992) and soy.

Direct soil studies are required to estimate the environmental consequences of the strong competition between glyphosate and phosphate for adsorption sites. Identifying the soil properties that govern sorption makes it possible to establish a pedotransfer function (Vinther et al., 2008; Weber et al., 2004), which is essential for understanding pesticide leaching, modelling its fate and implementing better management practices to limit groundwater contamination. Although the adsorption of glyphosate in typical agricultural soils of Argentina has already been studied (De Gerónimo et al., 2018), the influence that the application of phosphate fertilisers and their possible concomitant change in pH exerts in glyphosate–soil interaction has never been studied in these soils. These studies are of special importance in a country like Argentina where approximately 1.6 million tons of phosphorus and 200 million litres of glyphosate are applied each year (CIAFA, 2020).

Accordingly, the objectives of the present work were (i) to study the effect of pH on glyphosate adsorption in various Argentinean agricultural soils and (ii) to evaluate the competitive adsorption of glyphosate and phosphate on several agricultural soils with different physical and chemical properties.

2 | MATERIALS AND METHODS

2.1 | Chemicals

The glyphosate reference standard and Isotope-labelled glyphosate (1, 2-^{13}C, ^{15}N), used as internal standard (IS), were purchased from Sigma (Bs. As., Argentina). Analytical reagent-grade disodium tetraborate decahydrate, ammonium acetate (NH$_4$Ac, reagent grade), 9-fluorenmethylchoroformate (FMOC-Cl), sodium acid phosphate (Na$_2$HPO$_4$), HPLC-grade methanol, HPLC-grade acetonitrile and dichloromethane (CH$_2$Cl$_2$) were purchased from Sigma-Aldrich. HPLC-grade water was obtained by purifying demineralized water in ELGA purelab ultra.

2.2 | Soil samples

Nine representative soils were selected from different regions of Argentina, with no history of glyphosate and phosphate application within the last 10 years, corresponding to different taxonomic orders (Figure 1): Marcos Juárez (Córdoba province), Famaillá (Tucumán province), Cerro Azul (Misiones province), Balcarce (Buenos Aires province), Alto Valle (Río Negro province), Barrow (Buenos Aires province), Santiago del Estero (Santiago del Estero province), Corrientes (Corrientes province) and Reconquista (Santa Fe province).

The sampling depth was 0–5 cm. The samples were dried at 30°C, ground and sieved to 2 mm. The physico-chemical and granulometric characteristics of the studied soils are shown in Table 1. Texture (Robinson pipette method, Soil Conservation Service 1972), organic carbon (OC; chromic acid method; Walkley & Black, 1934), cation exchange capacity (CEC; determined by displacement with ammonium acetate at pH 7; Chapman, 1965), pH (measured in soil-water solution [1:2.5] with Orion Expandable Ion Analyzer EA 940) and electrical conductivity (EC; measured in Orion Thermo Conductivity Meter, model 150+) were determined.
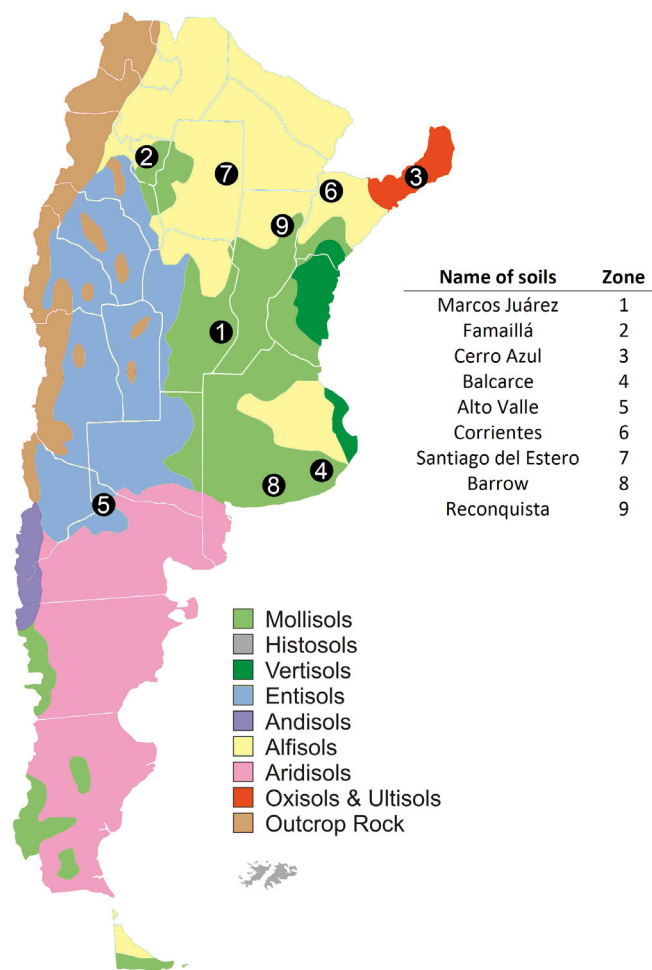
2.3 | Glyphosate adsorption isotherms

Glyphosate sorption isotherms were performed at different pH and in the presence or absence of phosphate with a batch equilibration technique. Detailed information regarding experimental conditions is provided in a previous study (De Gerónimo et al., 2018). Briefly, 1 g of soil sample was mixed with 10 ml of 0.01 M $CaCl_2$ solution containing different glyphosate concentrations (0, 0.1, 1, 2, 5, 10, 20, 30, and 50 mg L^{-1}). The samples were incubated with agitation at 25°C for 24 h to reach equilibrium. They were then centrifuged at 3000 rpm for 10 min and the supernatants were filtered through a 0.22 μm nylon membrane to determine the equilibrium glyphosate concentration in the solution by ultra-high-performance liquid chromatography (ACQUITY UPLC™) coupled to tandem mass spectrometry (Quattro PremierTM XE). Phosphate sorption was measured in batch system at 25°C. Soil sample of 1 g was mixed with 10 ml of 0.01 M $CaCl_2$ solution containing 40 mg L^{-1} of phosphate (as KH_2PO_4). The sample was shaken for 24 h in a reciprocating shaker and the supernatant solution was separated by centrifuging. Phosphate concentration in the solution was measured by the ascorbic acid method (Murphy & Riley, 1962).

FIGURE 1 Geographic location of the soil samples [Color figure can be viewed at wileyonlinelibrary.com]

Name of soils	Zone
Marcos Juárez	1
Famaillá	2
Cerro Azul	3
Balcarce	4
Alto Valle	5
Corrientes	6
Santiago del Estero	7
Barrow	8
Reconquista	9

TABLE 1 Physical and chemical properties of soils

Soil	CEC (cmol kg^{-1})	Sand (%)	Silt (%)	Clay (%)	OC (%)	pH	Fe$_{ox}$ (mg kg^{-1})	P$_{Bray}$ (mg kg^{-1})	Al$_{in}$ (mg kg^{-1})
Marco Juárez	32.9	12.9	53.4	33.7	4.7	5.94	4082.2	23.2	12.2
Famaillá	38.3	8.5	57.1	34.4	8.5	6.10	3758.2	39.8	22.9
Cerro Azul	27.3	5.7	24.8	69.5	6.0	4.80	16,121.7	3.1	58.8
Balcarce	37.4	43.8	26.9	29.3	10.3	5.75	3588.2	28.3	14.4
Alto Valle	26.2	43.1	35.6	21.2	2.7	7.20	12,147.1	53.6	14.5
Corrientes	9.0	90.3	3.3	6.4	0.5	5.63	560.5	4.18	17.7
Santiago del Estero	19.9	21.3	54.9	23.8	4.5	6.99	1804.3	112.9	14.5
Barrow	40.5	29.7	33.2	37.1	7.3	6.84	5335.5	39.0	12.7
Reconquista	19.0	24.9	50.4	24.7	5.1	6.28	1671.7	16.6	13.8

To study the effect of pH, isotherms were made by adding different volumes of NaOH (0.1 M) or HCl (0.1 M). All solution pH values after equilibrium were measured by a pH meter. To study the effect of phosphate on glyphosate adsorption, isotherms were performed in the presence of 0.5 or 1 mM phosphate. The adsorption experiments were done in triplicate.

The experimental data were fitted to the Freundlich model

$$C_s = K_f C_{aq}{}^n$$

where C_{aq} is the concentration of glyphosate in the aqueous phase (mg L^{-1}), C_s is the concentration of glyphosate in the soil (mg kg^{-1}), K_f is the Freundlich sorption coefficient and n is the non-linearity parameter.

The equation proposed by Bowden et al. (1977) was applied to explain the effects of pH on glyphosate and phosphate sorption, where sorption is related not to concentration but to the surface activity function (S_a):

$$S_a = K_i c \alpha \gamma \exp\left(\frac{-z_i F \psi}{RT}\right)$$

where K_i is the binding constant for the reacting ion (i), α is the degree of dissociation of the ion i, c is the solution concentration of the compound, γ is its activity coefficient, z_i is its valency, ψ is the electric potential in the plane of adsorption, F is the Faraday constant, R is the universal gas constant and T is the temperature (K) (Barrow & Debnath, 2015). Using this assumption, the effects of pH on sorption of a wide range of ions can be comprehensively described (Barrow, 1999; Barrow et al., 2015, 2017). In the case of polyprotic acids, it was described that one ion species dominates the sorption reactions, and the α values can be calculated using the dissociation constants.

The relationship between the electric potential and the obtained Freundlich constants can be obtained as follows (Barrow & Debnath, 2015):

$$K_f = K_i \alpha \gamma \exp\left(\frac{-z_i F \psi}{RT}\right)$$

At given pH values, the values of K_f can be estimated by fitting the Freundlich equation to the experimental data. Then,

$$\psi = -\ln\left(K_f / K_i \alpha \gamma\right)/0.078$$

because $Z_i F/RT$ is equal to 0.078. To calculate the relevant values for ψ, we assumed that K_i and γ were 1. Choosing different values causes the curves to move up or down but do not change their slope.

To study the competition between glyphosate and phosphate, the equation described by Roy et al. (1986a, 1986b) was used:

$$S_{gly} = \frac{a_{gly} c_{gly}}{\left(c_{gly} + k_{gly,P} c_P\right)^{1-b_{gly}}}$$

and

$$S_P = \frac{a_P c_P}{\left(c_P + k_{P,gly} c_{gly}\right)^{1-b_P}}$$

where S_{gly} is the adsorbed glyphosate, S_p is the adsorbed phosphate, c_{gly} is the concentration of glyphosate in the aqueous phase, c_P is the concentration of phosphate and a_{gly}, $k_{gly,P}$, a_P, $k_{P,gly}$, b_{gly} and b_P are the fitting coefficients. It has been shown that ions compete not only via ordinary chemical competition for adsorption sites, but also via their effects on the surface charge and therefore the electric potential of the surface (Barrow, 1992). In this case, the a term decreases with increasing levels of sorption of the competing ion:

$$a_{gly} = a_{gly,0} - m_{gly,P} S_P$$

The minimization of the sum of the square of the difference between the predicted and observed concentrations was used as a goodness-of-fit criterion for the ability of the model to adjust to the experimental values.

3 | RESULTS

### 3.1 | Influence of pH on glyphosate and phosphate adsorption

The relative Freundlich coefficient (relative K_f) of glyphosate for each soil as a function of pH is shown in Figure 2. It clearly demonstrates that the affinity of glyphosate for the soil greatly depends on the pH. For most of the studied soils, there was a pH for which the K_f had a maximum value, and then adsorption decreased with increasing or decreasing pH. The behaviour of Alto Valle soil differed from the rest of the soils,

(a)

(b)
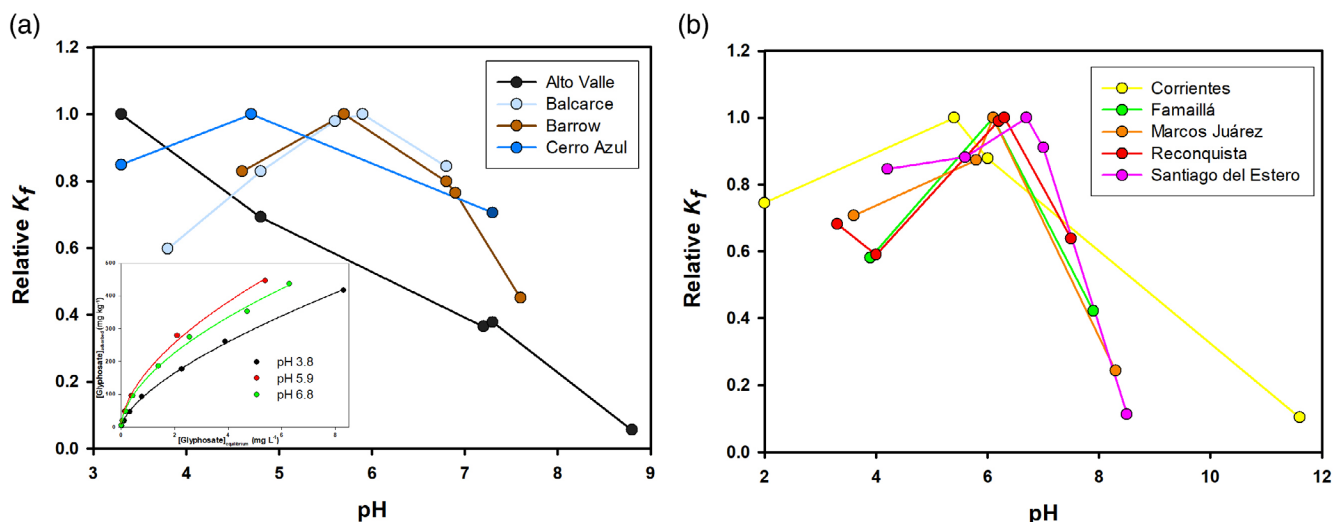
FIGURE 2 Effect of solution pH on Freundlich coefficient of glyphosate for the different soils. Relative K_f is defined as the ratio of K_f value at a given pH with respect to the maximum value of K_f obtained (glyphosate K_fpH/glyphosate $K_f$maximun). (Inlet: Example of adsorption isotherms for glyphosate at different pH for Balcarce soil) [Color figure can be viewed at wileyonlinelibrary.com]

showing an increase in the Freundlich coefficient (K_f) as the pH became lower. In this soil, for a pH value of 3, the K_f was approximately 2 and 12 times larger than for pH values of around 7.2 and 8.8, respectively. On the other hand, for Cerro Azul soil the highest K_f was obtained for a pH value of 4.7, decreasing by approximately 18% and 32% at pH values of 3.3 and 7.3, respectively. Similarly, for Balcarce soil, the highest K_f value was observed at a pH of 5.9, decreasing by almost 40% when the pH decreased to 3.8 and by 16% when the pH increased to 6.8. The soils of Famaillá, Marcos Juarez and Barrow showed a decrease of between 60% and 75% in the value of K_f when the pH increased to values close to 8. The most marked effect on the K_f value at alkaline pH was found in Corrientes and Santiago del Estero soils with decreases of up to 90%. By contrast, the acidic pH had a minor effect on the K_f of these two soils, with decreases between 15% and 45%. Experimental values of the non-linearity coefficient (n) were significantly lower than 1 for all the soils at the different pHs (Figure S1). The soil of Corrientes presented a lower value of n compared to the rest of the soils, varying between 0.36 and 0.56. For each soil, there seems to be a minimum n value at pH around 6 with a slight tendency to increase at more acidic or alkaline pHs.

Balcarce and Alto Valle soils were tested to investigating the effects of pH on phosphate sorption (Figure 3). As in the case of glyphosate, phosphate adsorption is higher in Balcarce soil than in the Alto Valle soil. The highest phosphate liner distribution coefficient (K_d) value was observed at a pH between 9 and 10, then adsorption
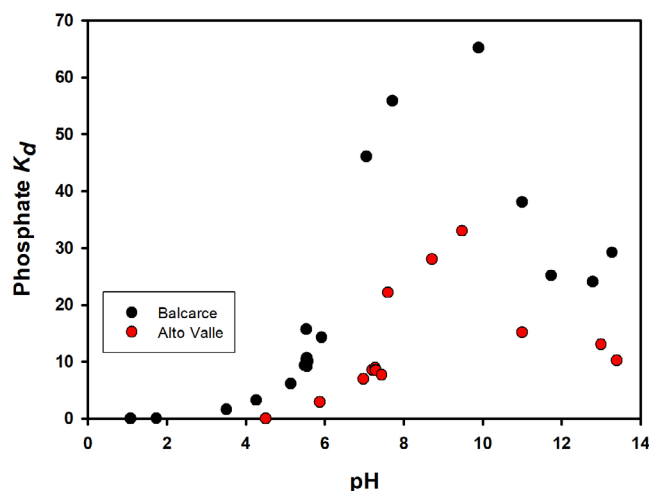
FIGURE 3 Effect of solution pH on distribution coefficient of phosphate for Balcarce and Alto Valle soils [Color figure can be viewed at wileyonlinelibrary.com]

tends to decrease with increasing or decreasing pH. The decrease in the amount of phosphate adsorbed is more pronounced below a particular pH, being negligible at pH less than 4.5 for Alto Valle soil and pH below 3 for Balcarce soil.

The estimated electric potential (ψ) of glyphosate for each soil and phosphate for two of the soils as a function of pH is shown in Figure 4. Adsorption of phosphate produced an increase in the electric potential with a maximum value around pH between 8 and 11. As has already been reported, infrared studies have shown that most of the links between phosphate and goethite are bidentate

from pH 3.5 to 8, and at higher pH there is an increasing abundance of monodentate species (Hiemstra & van Riemsdijk, 1996). Nevertheless, the effects of pH on phosphate sorption can be modelled assuming that all bonds are bidentate and can be related to the concentration of divalent ions in solution (Barrow, 1999; Bowden et al., 1980; Hiemstra & van Riemsdijk, 1996; Strauss et al., 1997). In the same way as for phosphate, we can assume that the glyphosate ion mainly involved in the interaction with the soil is the one that has two negative charges, being the data modelled based on the assumption that bidentate links were formed between glyphosate

and soil components. Unlike what is observed for the Freundlich constant, the estimated electric potential shows the same behaviour as a function of pH for all studied soils.

3.2 | Effect of inorganic phosphate addition on the sorption of glyphosate

The effect of the presence of phosphate on K_f, the Freundlich non-linearity coefficient (n) and glyphosate adsorption on different soils is presented in Figure 5
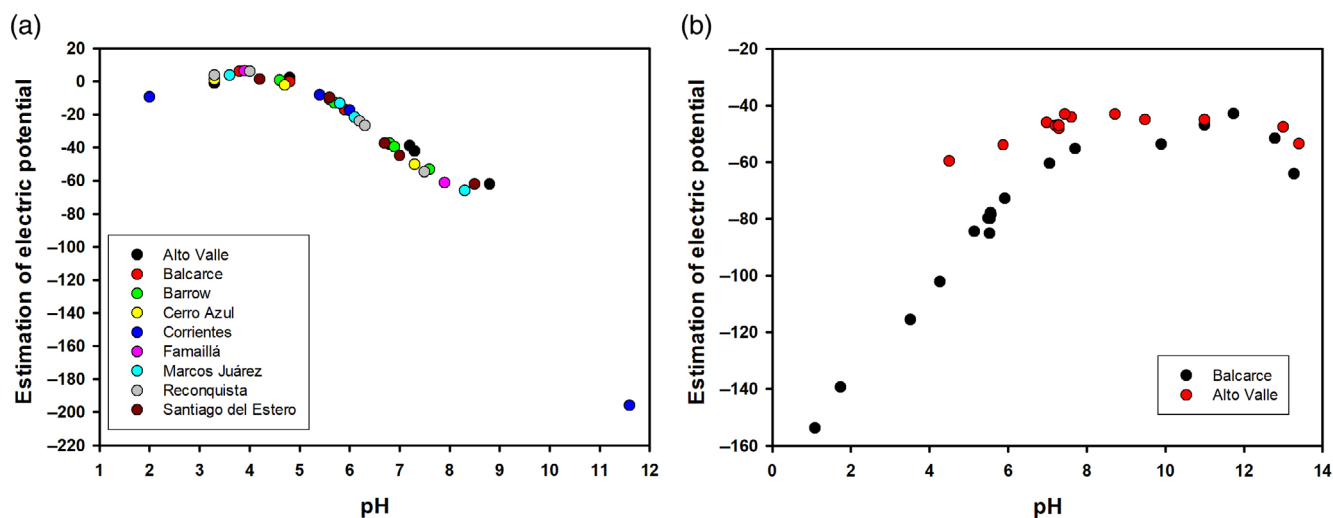

FIGURE 4 Effects of pH on the estimated values for the electric potential for glyphosate (a) for the different soils and phosphate (b) for the different pH [Color figure can be viewed at wileyonlinelibrary.com]
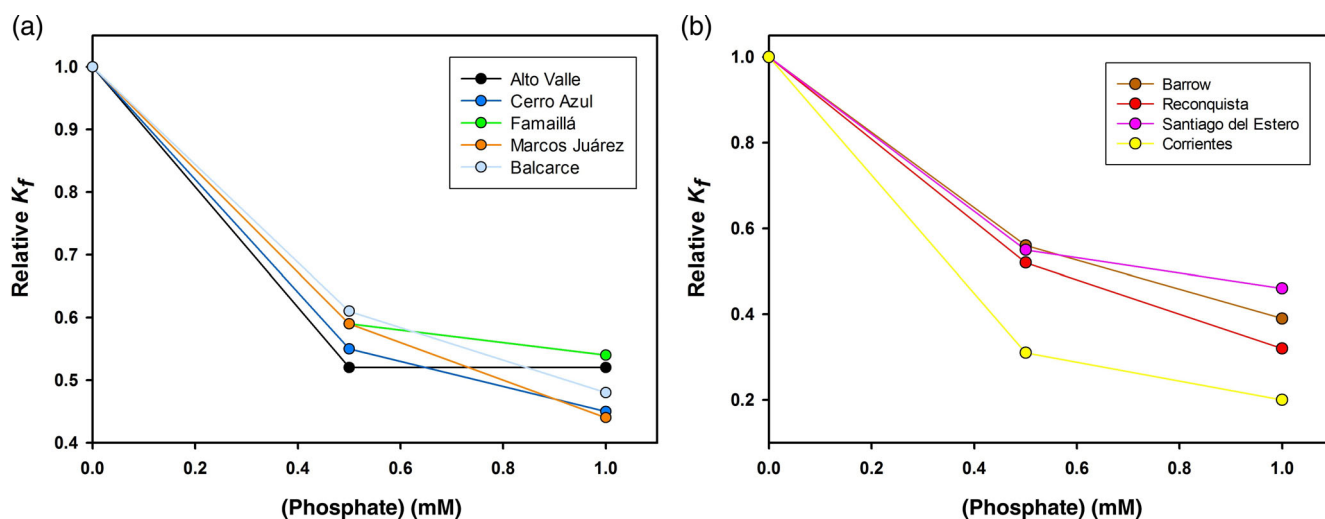

FIGURE 5 Effect of inorganic phosphate on Freundlich coefficient of glyphosate for the different soils. Relative K_f is defined as the ratio of K_f in the presence of phosphate (0.5 or 1 mM) with respect to K_f in the absence of phosphate (glyphosate $K_f$phosphate/glyphosate K_f) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Freundlich Constant, Freundlich non-linearity coefficient (n) and glyphosate adsorbed in presence of inorganic phosphate. The values in parentheses are standard errors

Soil	0 mM PO_4^{-3}		0.5 mM PO_4^{-3}		1 mM PO_4^{-3}		$K_f0.5/K_f$	K_f1/K_f [a]	Glyphosate adsorbed (%)			Phosphate
	K_f	n	K_f	n	K_f	n			0 mM PO_4^{-2}	0.5 mM PO_4^{-2}	1 mM PO_4^{-2}	K_d
Marco Juárez	222.5 (4.3)	0.53	130.2 (3.1)	0.58	97.9 (2.7)	0.62	0.59	0.44	98.7 (0.7)	95.5 (0.8)	91.6 (0.9)	20.1
Famaillá	182.3 (3.6)	0.54	107.6 (1.7)	0.66	98.7 (3.2)	0.63	0.59	0.54	97.8 (1.2)	93.6 (1.3)	92.0 (1.1)	20.9
Cerro Azul	386.9 (4.7)	0.61	213.2 (2.4)	0.43	172.3 (5.1)	0.47	0.55	0.45	99.3 (0.4)	98.4 (0.5)	96.4 (0.8)	127.6
Balcarce	179.6 (3.2)	0.56	109.7 (2.8)	0.59	86.2 (3.7)	0.61	0.61	0.48	97.1 (1.1)	92.8 (0.8)	91.4 (1.2)	43.0
Alto Valle	61.2 (5.4)	0.63	32.0 (3.1)	0.68	31.6 (2.6)	0.68	0.52	0.52	86.4 (0.9)	76.7 (1.3)	73.1 (0.7)	14.8
Corrientes	22.2 (2.7)	0.36	6.9 (3.2)	0.68	4.4 (1.3)	0.86	0.31	0.20	64.4 (1.4)	22.1 (1.2)	21.0 (1.1)	1.4
Santiago del Estero	135.8 (2.5)	0.55	74.7 (4.1)	0.58	62.7 (2.3)	0.58	0.55	0.46	95.5 (1.2)	90.8 (0.8)	88.1 (0.7)	25.1
Barrow	154.9 (4.9)	0.52	86.7 (2.6)	0.62	60.8 (1.7)	0.60	0.56	0.39	96.9 (0.7)	93.1 (1.3)	90.3 (1.1)	39.5
Reconquista	109.7 (2.4)	0.48	57.1 (3.5)	0.52	45.7 (2.8)	0.55	0.52	0.42	95.3 (1.3)	90.5 (1.5)	87.9 (1.3)	21.2

[a]$K_f0.5$ and K_f1 are the glyphosate Freundlich constants in presence of 0.5 and 1 mM phosphate, respectively.

and Table 2. The results clearly show that the general effect of the co-presence of phosphate on the system was to decrease the glyphosate adsorption, diminishing the apparent affinity of this molecule for the soil components.

For all soils, the addition of 0.5 mmol L^{-1} phosphate causes a significant decrease in glyphosate sorption. In the case of Cerro Azul soil, this capacity only decreased by 1% in the presence of phosphate (0.5 mM), which would indicate that this soil has a large number of binding sites still available. In this sense, the low phosphorus content of this soil supports this idea since it has been shown that glyphosate sorption decreases with increasing Olsen P concentrations (Gimsing et al., 2007; Munira et al., 2018). However, the K_f value (which is correlated with the affinity of the glyphosate interaction) was reduced by 45% (Table 2). For most of the soils (Famaillá, Marcos Juárez, Barrow, Reconquista, Santiago del Estero and Balcarce soils), a decrease of between 3% and 5% was observed in glyphosate adsorption and the K_f value was between 40% and 58% lower. The application of phosphate significantly reduced glyphosate sorption by 11% in Alto Valle soil, while in Corrientes soil the effect was the most marked, decreasing by approximately 65% and the K_f value obtained was 70% lower than that obtained in the absence of phosphate. An increase of 0.5–1 mM in the phosphate concentration produced only a small decrease in the amount of glyphosate adsorbed in almost all soils (between 1.5% and 2%), while this effect was moderate in the soils of Marcos Juárez, Alto Valle, and Corrientes (around 5%). At the same time, the effect that increasing the glyphosate concentration has on phosphate adsorption, at constant total phosphate concentration, (Figure 6) is to decrease it, indicating that both functional groups are involved in the process.

On the other hand, the addition of phosphate does not significantly modify the value of the non-linearity coefficient (n) for all the tested soils, being always lower than 1. Figure 7 shows the correlation between glyphosate K_f and phosphate K_d for the tested soils.

The model proposed by Roy et al. (1986a, 1986b) was applied to study the competition between glyphosate and phosphate in some selected soils. The effect of considering the electric potential of the surface in Freundlich competition equation was also compared (Barrow et al., 2005). The fit of the competition Model is shown in Figure 8 and the fitted parameters of the prediction model for the selected soils are given in Table 3. These results show that the competition model used allows explaining the experimental data and the correction for the electric potential proposed significantly decreased the residual sums of squares.
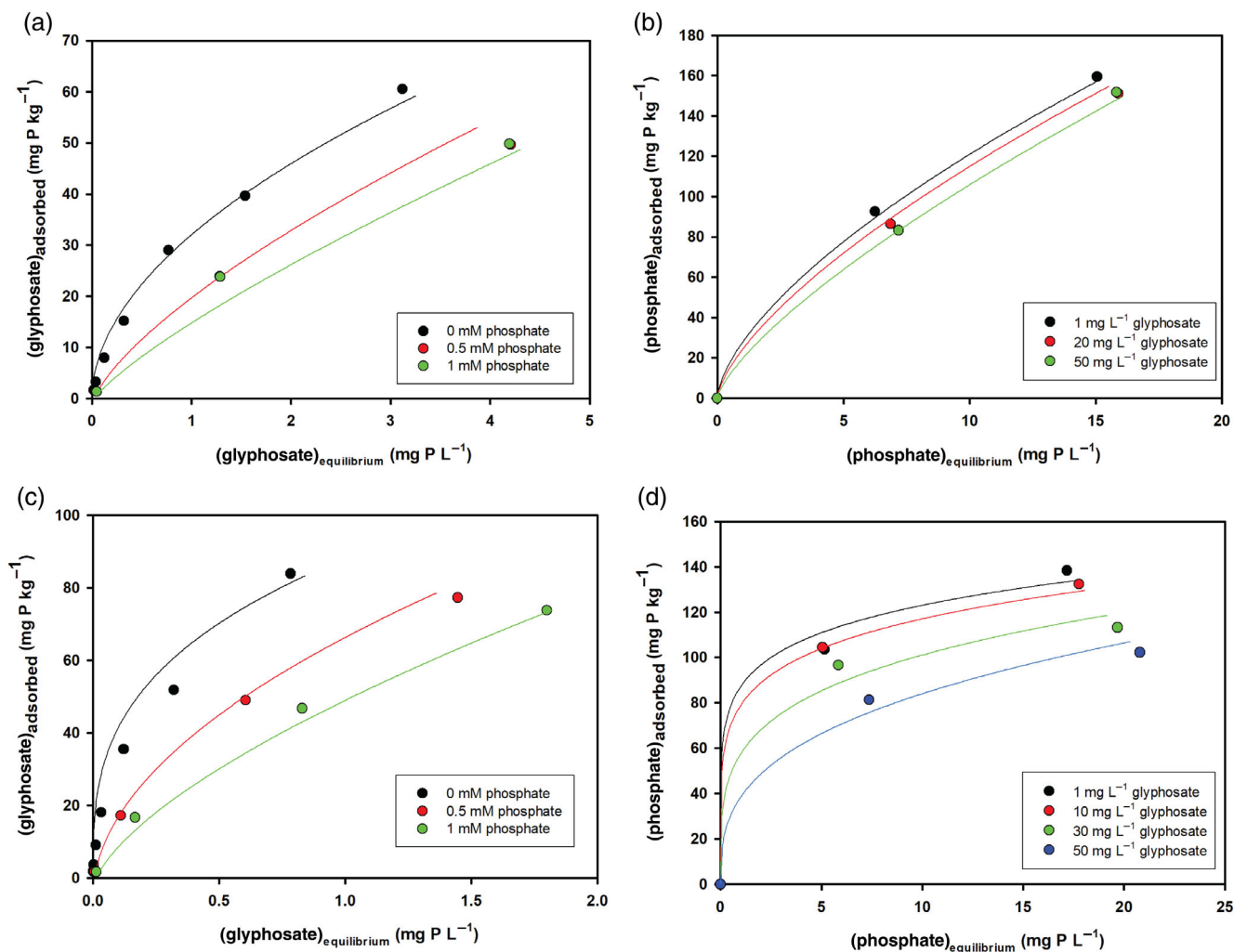
FIGURE 8 Experimental points and fitted lines for competition between glyphosate and phosphate in two selected representative soils, Alto Valle (a, b) and Marcos Juárez (c, d). The summary of the coefficients of the equations is given in Table 3 [Color figure can be viewed at wileyonlinelibrary.com]

4 | DISCUSSION

4.1 | Influence of pH on glyphosate adsorption

The strongly pH-dependent adsorption of glyphosate is due to the different electrical charges that both the components of the soil and the glyphosate molecule present as the pH changes, which has a direct effect on the electrostatic interaction. This increasing attraction is due to an increasing positive charge on the soil surface rather than to the decreasing negative charge of glyphosate molecules, the surface soil charge being strongly correlated with the mineral composition of soils (Gimsing et al., 2007; Pessagno et al., 2005). For this reason, in all tested soils presented in this work, the affinity between glyphosate and soil colloids decreased drastically as the pH became more alkaline. The glyphosate molecules, at

pH 6, where the highest adsorption occurred for most soils, had an average net charge of −1.8 (22.4% H_2G^- and 77.6% HG^{-2} being the predominant species), while at pH 8 the average net charge was −2.0 (99% HG^{-2}, 0.2% H_2G^- and 0.7% G^{-3}) and at pH 10 the average net charge was −2.4 (58% HG^{-2} and 42% G^{-3}).

In all soils except for Alto Valle, the ability to adsorb glyphosate decreased as the pH changed from 5–6.7 to more acidic values. This phenomenon is probably due to the partial decomposition of the clay components at acidic pH, where a substantial dissolution of relatively resistant layer silicates occurs, and to the possible release of cations from the binding sites and the subsequent decrease in the number of exchange sites, limiting adsorption (Komadel, 2003). A factor that can also influence the lower herbicide adsorption at acidic pH is a decrease in the specific surface area due to the Na^+ replacement of ions by protons (Altin et al., 1999).
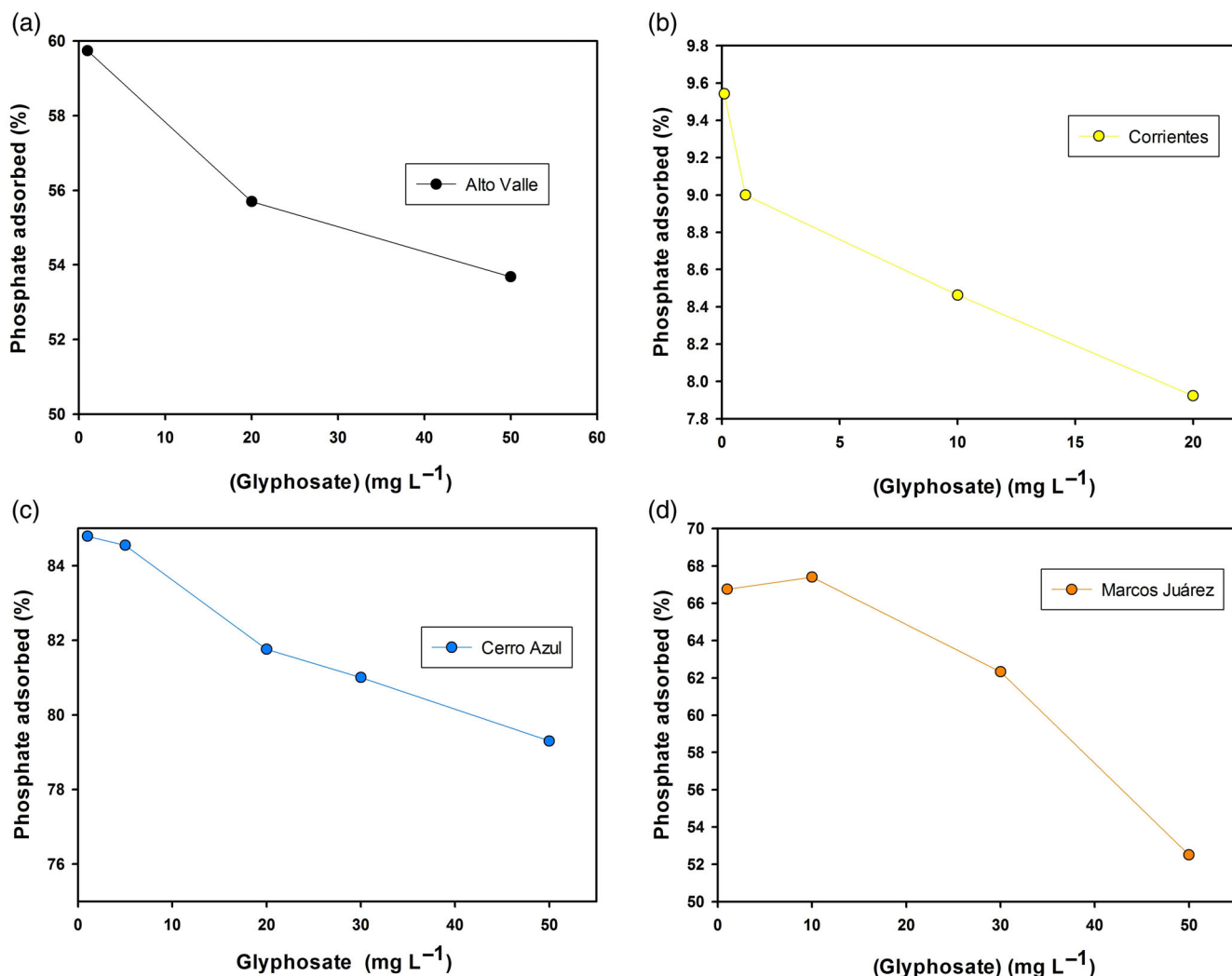
FIGURE 6 Effect of increasing glyphosate concentration on phosphate adsorption in some representative soils. (a) Alto Valle soil; (b) Corrientes soil; (c) Cerro Azul soil and (d) Marcos Juárez soil [Color figure can be viewed at wileyonlinelibrary.com]
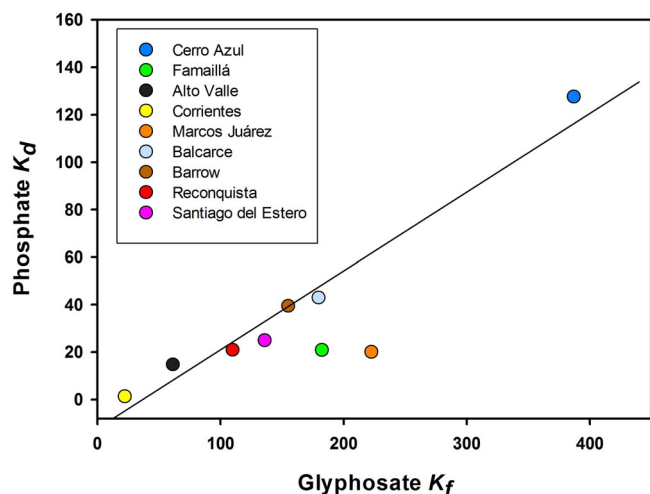

FIGURE 7 Association between phosphate K_d and glyphosate K_f in the different soils [Color figure can be viewed at wileyonlinelibrary.com]

Studies performed on montmorillonite showed a decrease in the critical aggregation concentration with decreasing pH, which could be assigned to the formation of positive charges on the edges of the montmorillonite particles, promoting the edge (+)–face (−) aggregation and leading to an increasing apparent particle size with decreasing pH (Ji et al., 2004). A similar dependence of glyphosate sorption with pH was also found for silty clay and sandy loam soil (Nicholls & Evans, 1991), with the strongest sorption occurring around pH 4.

The particular behaviour of the Alto Valle soil may be due to the different mechanism that governs the glyphosate adsorption. The soils with the highest iron content were those of Alto Valle and Cerro Azul, although the K_f in Cerro Azul soil was almost seven times greater. This substantial difference demonstrates the great influence that clay content has on herbicide adsorption (69.5% in Cerro Azul and 21.2% in Alto Valle). In view of these

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TABLE 3 Values of the coefficients calculated of the equations fitted to data for competition between glyphosate and phosphate for the selected representative soils

Soil	Parameters	a_{gly}	b_{gly}	$K_{gly,P}$	a_P	b_P	$K_{P, gly}$	'm' term	rss glyp	rss P	sum rss
Alto Valle	5	31.62	0.55	0.36	23.71	0.71			0.2161	0.7444	0.9605
	6	32.52	0.50	0.25	26.92	0.65	1.28		0.2131	0.2765	0.4896
	7	32.05	0.52	0.28	27.90	0.64	1.08	5.98×10^{-6}	0.2191	0.2521	0.4712
Cerro Azul	5	148.04	0.40	0.43	158.04	0.35			0.2704	0.9885	1.2589
	6	153.12	0.44	0.10	146.44	0.39	5.44		0.0011	0.1666	0.1677
	7	111.14	0.20	0.15	153.56	0.34	1.50	1.32×10^{-4}	0.1668	0.7876	0.9544
Corrientes	6	8.64	0.40	0.19	6.21	0.38	3.88		0.0508	0.0939	0.1447
	7	8.68	0.41	8.13×10^{-4}	13.67	0.07	2.17	0.26	0.0362	0.0897	0.1259
Famailla	5	83.65	0.51	0.11	44.79	0.48			0.0342	2.2711	2.3053
	6	80.46	0.42	0.07	44.69	0.47	8.31		0.0199	2.2408	2.2607
	7	80.36	0.42	0.06	44.69	0.47	8.24	1.24×10^{-5}	0.0201	2.2405	2.2606
Marcos Juarez	5	101.74	0.54	0.25	91.99	0.14			0.0833	2.0809	2.1642
	6	88.19	0.33	0.07	88.06	0.15	3.79		0.0362	1.6581	1.6943
	7	147.23	0.37	1.10×10^{-5}	81.16	0.18	4.15	0.86	0.5863	0.7868	1.3731

results, since Alto Valle soil has a relatively high content of iron oxides with respect to clay, it is reasonable to infer that the predominant mechanism in the adsorption of glyphosate in this soil would be the interaction with iron oxides and not with clays, which enhances the ligand adsorption as the pH becomes more acidic. This effect is well known for anion adsorption onto iron oxides and has been reported in several studies (Antelo et al., 2005; Hiemstra & van Riemsdijk, 1996; Tadanier & Eick, 2002). In addition, different works performed on the surface of goethite (R-FeOOH) as a function of pH show this behaviour, with an increase in the extent of glyphosate adsorption as the pH decreases (Barja & dos Santos Afonso, 2005; Dideriksen & Stipp, 2003; Sheals et al., 2002, 2003). Then, the high influence of clay content on the other soils employed in our work may have masked the influence of Fe_{ox}–$Al_{ox.}$ The values of the n coefficient were less than 1 for all soils, being lowest in the soil of Corrientes, which would mean that the saturation of the sorption sites in this soil would occur at lower concentrations of glyphosate. There is no clear trend respect to the variation of the value of n with the change of pH, although a lower value is hinted at a pH around 6 (Figure S1). More studies will be needed to clarify this behaviour.

The type of clay is also a factor to be considered as it can affect glyphosate adsorption. Although the differences may be due to the different clay types, they may also be due to different surface areas (Gimsing & Borggaard, 2002; Motekaitis & Martell, 1985). A previous work showed that glyphosate would have a higher affinity for kaolinite than for illite at low or close to neutral pH. By contrast, quartz has the lowest surface area and showed a very low affinity for glyphosate (Beltran et al., 1998; de Jonge & de Jonge, 1999; dos Santos Afonso et al., 2003).

The observed behaviour of glyphosate sorption in the soils at different pH also provides evidence of its interaction with variable surface charges. Unlike the permanent charges commonly associated with the presence of isomorphous ions in the clay mineral network, the variable charges on the surface are changed by the presence of potential determining ions such as H^+ or anions such as phosphate, among others. The effect of pH on the adsorption of inorganic phosphate in two of the soils used was studied to compare with the behaviour shown by glyphosate. As Figure 3 shows, the maximum adsorption of phosphate occurs when the average net charge is around −1.8 and −2. In this sense, both glyphosate and phosphate have the same average net charge when adsorbed to the soil with the highest affinity which, according from the values of the relevant pKa, correspond to a pH 6 and 8, respectively. This result is in agreement with numerous publications that show that inorganic phosphate forms mostly bidentate bonds to an oxide surface (Kwon & Kubicki, 2004; Kim et al., 2011; Li et al., 2013; Wang et al., 2013) being possible to relate the adsorption with the concentration of divalent phosphate ions in solution (Bowden et al., 1980).

The changes in the surface concentration of specifically adsorbed ions induce slow penetration of the ions

and consequent changes in the surface electric potential (Barrow et al., 2015). The model of Bowden et al. (1977) is very useful in these cases since it can be adapted to soils. In this case, the effect of pH is determined by the balance between the fraction of the reacting species present in solution (α) and the value of the electrical potential—which decreases with increasing pH (Barrow et al., 2017). In these sense, it is necessary to assume which of the glyphosate ions is involved in the interaction with soil. As previously mentioned, glyphosate has four dissociations, according to the pH range studied; the species which seems to most closely match the observed behaviour is the one that has two negative charges. These negative charges are well separated occurring at opposite ends of the molecule and, if the link to the reacting surfaces is via the phosphate moiety, the negative charge on the carboxyl group would be expected to 'drag' the position of the mean charge away from the 'surface' so that the effect of potential will be smaller than it would be otherwise. The estimated surface electric potential obtained (Figure 4) shows that, on the one hand, these assumptions do seem to quantitatively describe the effects of pH and, on the other, that quite different behaviours in soils can be explained by rather small changes in the surface potential with pH. This seems to be different for inorganic phosphate adsorption in these soils, where the effect of α value increase is larger than the potential term. Although the increase in pH generates a less favourable potential for anions adsorption, this is opposed to a significant increase in the proportion of the relevant ions at pH values below the relevant pKa. The net effect is a marked increase in sorption with increasing pH showing optimum pH at a value of around 9, where the concentration of the HPO_4^{-2} species is greater than 99%.

With respect to the adsorption of glyphosate on variable charges, the herbicide would form mostly stable bidentate structures in which the anion is bound to two metal atoms of the oxide, such as inorganic anions (Hiemstra & van Riemsdijk, 1996). The same assumption that bidentate links were formed has been used in studies using organic compounds that have a phosphate group (Barrow et al., 2015).

4.2 | Effect of inorganic phosphate addition on the sorption of glyphosate

Regarding the value of the Freundlich constant, the increase in phosphate concentration produced a decrease of only 1% in Alto Valle soil, while in the most affected soil (Corrientes soil) the Freundlich constant was 36% lower. The results obtained in this work are in agreement with numerous previous reports on soils and clay minerals, indicating that the adsorption sites would be common for both molecules (Dion et al., 2001; Gimsing, Borggaard, & Sestoft, 2004; Munira et al., 2016; Waiman et al., 2016).

Figure 6 shows the positive correlation between glyphosate K_f and phosphate K_d, in agreement with previous studies suggesting that phosphate and glyphosate have similar sorption patterns in soil (Gimsing & Borggaard, 2002; Gimsing & Borggaard, 2007; Munira et al., 2016, 2018; Waiman et al., 2016). There seems to be a simple linear tendency between glyphosate K_f and phosphate K_d values; however, Famaillá and Marcos Juárez soils showed a relatively poor correlation between these affinity parameters. This negative deviation could indicate that inorganic phosphate has a lesser impact on glyphosate affinity for these soils. This behaviour could be indicating glyphosate-specific adsorption sites that involve another binding mechanism. In this sense, a factor to be taken into account is the adsorption capacity of the silt due to its strong presence in these soils, which could expose adsorption sites in addition to those already mentioned in clays and iron oxides, masked in other soils. Further studies are required to clarify this hypothesis.

The modified Freundlich equation was applied to investigate the competition between glyphosate and phosphate (Roy et al., 1986a). Table 3 presents the values of the parameters of each prediction model, and Figure 8 shows the predicted values against those measurements for glyphosate and phosphate. For the glyphosate–phosphate data, the competition was not 'symmetrical' and the competition terms ($K_{gly,P}$ and $K_{P,gly}$) were not reciprocals of each other. This result could be due to the fact that competition between ions is not only competition for adsorption sites, but also involves electrical effects that follow penetration of the surface. A further improvement in the model was obtained when sorption of one ion was allowed to directly decrease sorption of the other ion via the linear term of the Freundlich equation (a term). As other authors have previously discussed, these effects would arise because the sorption of ions, and their subsequent penetration into the surface, produces a separate competition effect through a change in charge and, therefore, in the electrical potential of the surface (Barrow, 1992; Barrow et al., 2005).

Thus, by combining the results, we can conclude that glyphosate and phosphate compete for the same sorption sites in the soil. Similar observations have been reported in several studies (de Jonge et al., 2001; Dion et al., 2001; Munira et al., 2016, 2018; Padilla & Selim, 2018; Waiman et al., 2016). In turn, there is evidence that phosphate is preferentially sorbed over glyphosate in soil (de Jonge

TABLE 4 Distribution of glyphosate and phosphate species as a function of pH

pH	GH_4^+ (%)	GH_3 (%)	GH_2^- (%)	GH^{-2} (%)	G^{-3} (%)	Average net charge	H_3PO_4 (%)	$H_2PO_4^-$ (%)	HPO_4^{-2} (%)	PO_4^{-3} (%)	Average net charge
3	0.1	14.5	85.2	0.3	0.0	−0.86	11.6	88.3	0.0	0.0	−0.88
4	0.0	1.6	95.1	3.3	0.0	−1.02	1.3	98.6	0.1	0.0	−0.99
5	0.0	0.1	74.2	25.7	0.0	−1.26	0.1	99.3	0.6	0.0	−1.00
6	0.0	0.0	22.4	77.6	0.0	−1.78	0.0	94.2	5.8	0.0	−1.06
7	0.0	0.0	2.8	97.1	0.1	−1.97	0.0	61.9	38.1	0.0	−1.38
8	0.0	0.0	0.3	99.0	0.7	−2.00	0.0	14.0	86.0	0.0	−1.86
9	0.0	0.0	0.0	93.2	6.8	−2.07	0.0	1.6	98.4	0.0	−1.98
10	0.0	0.0	0.0	58.0	42.0	−2.42	0.0	0.2	99.6	0.2	−2.00
11	0.0	0.0	0.0	12.1	87.9	−2.88	0.0	0.0	97.9	2.1	−2.02
12	0.0	0.0	0.0	1.4	98.6	−2.99	0.0	0.0	82.4	17.6	−2.18
13	0.0	0.0	0.0	0.1	99.9	−3.00	0.0	0.0	31.9	68.1	−2.68

TABLE 5 Clay type distribution of some of the soils employed

Soil	Quartz (%)	Kaolinite (%)	Ilite (%)	Chlorite (%)
Marco Juárez	17.0	1.3	36.4	45.3
Famaillá	41.5	10.6	42.4	5.5
Cerro Azul	30.0	34.6	7.9	27.5
Balcarce	39.2	9.8	51.0	0
Alto Valle	45.5	7.1	21.5	25.9

et al., 2001; Munira, 2018; Munira et al., 2016, 2018; Padilla & Selim, 2018). As indicated above, clay minerals are the preferred sites for the adsorption of these molecules (Glass, 1987; Sprankle et al., 1975). This interaction seems to be governed by H-bonding and ion-exchange mechanisms in the case of cation-saturated clays (Miles and Moye, 1988). Specific adsorption under formation of mono- or binuclear, mono- or bidentate surface complexes is the most likely adsorption mechanism for the two compounds (Borggaard, 1990; Dion et al., 2001; Piccolo et al., 1994; Sheals et al., 2002).

In this mechanism, the complexation of both compounds by cations released from the clays via a cation-exchange reaction with solution protons has been proposed as an adsorption mechanism (Hance, 1976). In this sense, an important factor to be taken into account is the different net electrical charges that these molecules present at the same pH, which would be a determining factor in the different degrees of affinity that these compounds have for the soil. Due to the different acid constants (Table 4), glyphosate has a higher negative charge than phosphate at pH above 3.5, favouring phosphate sorption on the soil surfaces due to less electrostatic repulsion. In addition, it has been postulated that the sorption of phosphate potentially increases the net negative charge on the clay and oxide surfaces, thereby increasing the electrostatic repulsion between glyphosate and soil (Gimsing et al., 2007). Another factor to be considered is the difference in the size of the molecules. The glyphosate molecule is significantly larger than the phosphate molecule, and therefore, it requires more space than phosphate, thereby reducing the number of adsorption sites available to glyphosate in comparison with phosphate (Liu et al., 1999; Martin et al., 1999). Different clays show a specific affinity for glyphosate depending on their structures. For example, the K_f constants reported for montmorillonite and illite clay minerals (Glass, 1987) were significantly lower than those found in all soils studied in this work, except for Corrientes soil. In our work, we did not find a clear relationship between the type of clay and the glyphosate or phosphate adsorption, but this may be due to the low number of soils characterised (Table 5). More studies are required in this respect.

There is a general consensus that the influence of organic matter on the adsorption of glyphosate is weak in comparison with other soil components, such as clay and iron and aluminium oxides (Vereecken, 2005). In this sense, organic matter would not be relevant in phosphate adsorption either due to the content of clays and iron oxides that these soils present.

5 | CONCLUSIONS

The influence of pH changes and the presence of inorganic phosphate on glyphosate sorption were studied across nine different soils of Argentina. The pH has a primary influence on glyphosate–soil interaction because it affects the electrical charges of both glyphosate and soil components. There is a pH at which the Freundlich coefficient presents a maximum value, which is related to a higher affinity of the molecule for the soil. Then, this parameter decreases to more acidic or alkaline pH, suggesting that the electrostatic interaction is decreased mainly by the modification of the electric charges of the soil components, although a soil with a greater amount of iron relative to the clay content shows a different behaviour at acidic pH. The effects of pH in the different soils can be explained by rather small changes in the estimated surface potential. The presence of inorganic phosphate significantly reduces the adsorption of glyphosate to the soil, which shows a competition between these molecules for adsorption sites. The competition between ions could be due to not only competition for adsorption sites, but also involves electrical effects that follow penetration of the surface.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

AUTHOR CONTRIBUTIONS

Study concept and design: Virginia Aparicio and Eduardo de Gerónimo. Acquisition, analysis and interpretation of data, and drafting the manuscript: Eduardo De Gerónimo. Critical revision of the manuscript: Virginia Aparicio.

DATA AVAILABILITY STATEMENT

The data used to support the findings of this study are available from the corresponding author upon request.

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