Glyphosate sorption to soils of Argentina. Estimation of affinity coefficient by pedotransfer function

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ABSTRACT

Argentine agricultural production is fundamentally based on a technological package that combines direct seeding and glyphosate with transgenic crops (soybean, maize and cotton), which makes glyphosate the most widely employed herbicide in the country. Glyphosate is strongly sorbed to soil in a reversible process that regulates the half-life and mobility of the herbicide, with the resulting risk of contaminating surface and groundwater courses. However, this behavior may vary depending on the characteristics of the soil on which it is applied. Sorption coefficients are thus the most sensitive parameters in models used for environmental risk assessment. The aim of this work was to study the affinity of glyphosate to 12 different soils of Argentina and create a model to estimate the glyphosate Freundlich sorption coefficient (K_f) from easily measurable soil properties. Batch equilibration adsorption data are shown by Freundlich adsorption isotherms. Principal component analysis and multiple linear regressions were used to correlate the effects of soil properties on glyphosate adsorption coefficients. Results indicate that pH and clay contents were the major soil parameters governing glyphosate adsorption in soils. The Freundlich (K_f) pedotransfer function obtained by stepwise regression analysis has 97.9% of the variation in glyphosate sorption coefficients that could be attributed to the variation of the soil clay contents, pH, P_{Bray} and Al_{in}.

1. Introduction

Glysophate (*N*-[phosphonomethyl] glycine) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. It is absorbed by the foliage, with rapid translocation throughout the plant. Glyphosate interferes in the biosynthesis of aromatic amino acids phenylalanine, tyrosine and tryptophan by inhibiting the enzyme 3-enol-pyruvylshikimate-5-phosphate synthase (EPSP Synthase), located in the chloroplast, which forms part of metabolic pathway of the shikimic acid (Roberts et al., 1998). Biosynthesis pathway inhibition only occurs in plants, bacteria and fungi and does not exist in animals; due to this fact acute toxicity in animals is low. Nevertheless, some studies have reported adverse effects on aquatic and terrestrial species (Contardo-Jara et al., 2009; Paganelli et al., 2010) and concern about potential environmental impacts has risen due to its widespread use and the large amounts annually applied (Schuette, 1998). Glyphosate is the most commonly used herbicide in Argentina, both in frequency of use and intensity, associated with transgenic crops (soybean, maize and cotton) and direct seeding (Aapresid, 2012), where weed control is only performed chemically during cultivation and fallow periods.

After its application, glyphosate is strongly sorbed to soil through a reversible process that regulates the half-life and mobility of the herbicide, with the resulting risk of contaminating surface and groundwater courses. Despite the low mobility that glyphosate presents in soil and its microbiological degradation, it has been found in natural water courses (Peruzzo et al., 2008; Battaglin et al., 2009), where it is principally bound to the suspended particulate matter and deposited in the sediment (Aparicio et al., 2013). Transport of the glyphosate molecule strongly bound to soil colloids to other environmental compartments is the result of runoff or leaching (Kjær et al., 2005; Scribner et al., 2007) or air pollution (Neary et al., 1993).

Sorption to soil depends on the physicochemical properties of the pesticide and soil (Gevao et al., 2000; Aparicio et al., 2013). The glyphosate molecule is a zwitterion with three polar functional groups (amine, carboxylate, and phosphonate) that can bind to metal polyvalent cations (Morillo et al., 1997; de Jonge and de Jonge, 1999; Borggaard and Gimsing, 2008). It is known that glyphosate is adsorbed to soil mineral fractions such as clay and amorphous iron and aluminum oxides (Vereecken, 2005; Borggaard and Gimsing, 2008) and that it is released from these sites by competition with inorganic phosphates (Schuette, 1998; Prata et al., 2003). Although the role played by

organic matter in glyphosate adsorption mechanisms is as yet unclear, glyphosate seems to be adsorbed on humic substances in soil (Albers et al., 2009). Soil pH is the major factor governing glyphosate adsorption because its net charge is pH-dependent (McConnell and Hossner, 1985). With increasing pH, the net charge of the glyphosate molecule becomes more negative; simultaneously the negative charge of clay minerals, iron and aluminum oxide can be increased as well. Therefore, the adsorption of glyphosate decreases by electrostatic repulsion with the negative charge surfaces (Morillo et al., 1997, 2000; Wauchope et al., 2002; Damonte et al., 2007).

The affinity of the molecule to soil is the most sensitive input parameter in pesticide fate models (Farenhorst et al., 2008). This parameter depends on the nature of the pesticide molecule and selected soil properties such as organic carbon, pH, clay, CEC and texture (Wauchope et al., 2002; Weber et al., 2004). Because of such complex and interactive processes, it is essential to identify a set of soil properties that can predict location-specific pesticide sorption and thereby mobility. Several mechanisms have been proposed to explain the sorption of glyphosate to soils. 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 (Nicholls and Evans, 1991; Piccolo et al., 1994; Morillo et al., 1997; de Jonge et al., 2001; Dideriksen and Stipp, 2003; Mamy and Barriuso, 2005; Wang et al., 2006; Borggaard and Gimsing, 2008).

The identification of the soil properties that govern sorption makes it possible to establish a pedotransfer function (Weber et al., 2004; Vinther et al., 2008), which is very important for understanding pesticide leaching, modeling their fate, and implementing best management to limit groundwater contamination. Pedotransfer functions have been commonly developed to estimate soil hydraulic properties (Medina et al., 2002) and have potential in agronomy to study management practices, especially irrigation and chemical application. Pedotransfer functions were developed for different soil properties such as prediction of the oxygen-diffusion coefficient in soils (Bakker et al., 1987), the cation exchange capacity (CEC) of different soil horizons (Breeuwsma et al., 1986), the yearly pyrite oxidation rate (POR) (Bronswijk et al., 1995) and to predict the potential supply of soil nitrogen (SN), phosphorus (SP), and potassium (SK) for maize (Janssen et al., 1990). For adsorption studies, an early pedotransfer function was presented for heavy metal sorption to soil (Chardon, 1984; van der Zee and van Riemsdijk, 1987) that was later adapted by other authors (Anderson and Christensen, 1988; Reinds et al., 1995; Streck and Richter, 1997; Wilkens et al., 1998; Elzinga et al., 1999; Ingwersen et al., 2000). In a similar way, pedotransfer function it has been developed for estimating sorption soil capacity of phosphate (Breeuwsma et al., 1986; Borggaard et al., 2004), sodium (Rashidi and Seilsepour, 2008) and ammonium (Li et al., 2006; Vogeler et al., 2011).

There is not much information on the current literature about pedotransfer functions applied to sorption parameters of pesticides to soil.

Mathematical equations that correlate the pesticide soil/solution distribution coefficients (Kd) reported in the literature with the respective soil properties were developed for 57 pesticides in order to estimate Kd values based on some soil parameters (Weber et al., 2004). In another study, dinoseb pesticide sorption was studied exploring the relationship between adsorption parameters and soil factors using a pedotransfer function regression (Guan et al., 2013). Regarding glyphosate, a pedotransfer function that allows the prediction of sorption parameters (Kd, Kf and n) was built for a wide range of soils and sediments (Dollinger et al., 2015). Additionally, adsorption of the herbicide glyphosate and its main metabolite AMPA was investigated on 17 different agricultural soils, in this case, using a nonlinear multiple regression equation (Sidoli et al., 2016). Accordingly, the objectives of the present work were (i) to identify the soil properties responsible for the glyphosate adsorption in various Argentinean agricultural soils; (ii) to use PCA and stepwise regression analysis to relate the glyphosate sorption coefficient with the soil physical and chemical properties; and (iii) to build pedotransfer functions for the estimation of sorption parameters (K_f, n) from the currently available soil properties. This function allowed us to identify the most significant explanatory variables of adsorption and, through a sensitivity study of these variables, to evaluate to what extent the pedotransfer rules can be used when certain soil property data are missing.

2. Materials and methods

2.1. Chemicals

Glyphosate reference standard was purchased from Seasinglab (Tandil, Argentina).Isotope-labeled glyphosate (1, 2-^{13}C, ^{15}N), used as internal standard (IS), was purchased from Sigma (Bs. As., Argentina). Analytical reagent-grade disodium tetraboratedecahydrate, ammonium acetate (NH_4Ac, reagent grade), and 9-fluorenmethylcho3coroformate (FMOC-Cl) were supplied by Seasinglab. HPLC-grade methanol, HPLC-grade acetonitrile and dichloromethane (CH_2Cl_2) were purchased from Seasinglab. HPLC-grade water was obtained by purifying demineralized water in ELGA purelab ultra (Illinois, USA).

2.2. Soil samples

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

The sampling depth was 0–5 cm. The samples were dried at 30 °C, ground and sieved to 2 mm. The physicochemical and granulometric characteristics of the studied soils are shown in Table 1.

2.3. Glyphosate adsorption isotherms

Glyphosate sorption isotherms were performed by shaking 1 g of soil sample with 10 mL of 0.01 M $CaCl_2$ solution (to minimize changes in ionic strength and avoid dispersion) containing different concentrations of glyphosate (0, 1, 2, 5, 10, 20, 30 and 50 mg L^{-1}). The samples were incubated with agitation at 25 °C during 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 equilibrium glyphosate concentration in the solution (Aparicio et al., 2013).

The amount of glyphosate adsorbed on the soil was calculated as the difference between the amount initially present in solution and the amount remaining at the end of the experiment. Blanks of each sample did not reveal the presence of glyphosate in the soils before the experiments.

The experimental data were fitted to the Freundlich model

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

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

2.4. Instrumental analysis

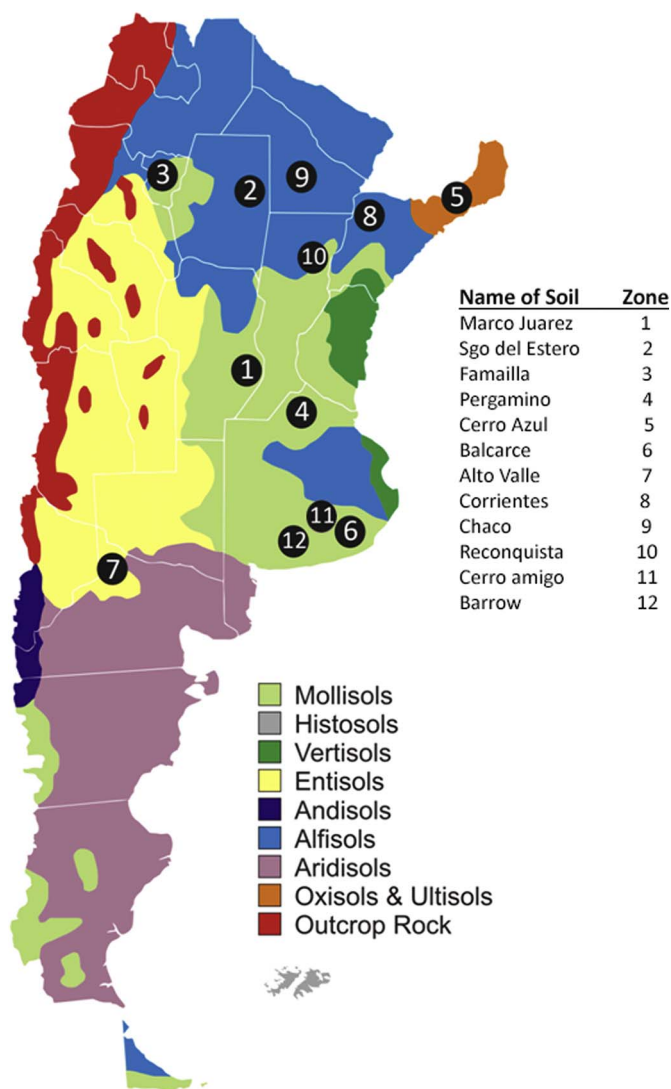The glyphosate concentration in the centrifuged solution was

take place overnight at room temperature. After that, 5 mL of dichloromethane (CH_2Cl_2) was added to the derivatized sample by shaking vigorously, and then centrifuged at 3000 rpm for 10 min. Finally, the supernatant was filtered through a 0.22 μm nylon filter, and 20 μL of the final extract was injected into the UPLC-ESI-MS/MS system.

To perform the chromatographic separation, the mobile phases were water (phase A) and methanol (phase B), both modified with ammonium acetate 5 mM. The flow rate for the mobile phase was 0.4 mL min^{-1}. The percentage of organic modifier (B) was changed linearly as follows: 0 min, 0%; 0.2 min, 0%; 2.5 min, 70%; 3.5 min, 100%; 4.5 min, 100%; 5.0 min, 0%; and 6 min, 0%. The column was kept at 60 °C. Drying as well as nebulizing gas was nitrogen, obtained from a nitrogen generator. The cone gas and desolvation gas flows were optimized at 2 L h^{-1} flow and 600 L h^{-1}, respectively. For operation in MS/MS mode, collision gas was Argon 99.995% with a pressure of 4.04×10^{-3} mbar in the T-Wave cell. Positive ionization mode was performed using capillary voltage of 3.0 kV. The desolvation gas temperature was set to 400 °C and the source temperature to 120 °C. Dwell times of 0.10 s/scan were chosen. Masslynx NT v 4.1 (Waters) software was used to process quantitative data obtained from calibration standards and from samples.

2.5. Statistical analyses

The statistical analysis was performed using version 3.2.2 of the R statistical computing software (Cran R organization 2015). The individual and combined influence of the physical and chemical properties of soils on glyphosate adsorption was elucidated using principal component analysis (PCA).

Afterward, stepwise multiple linear regression analysis was applied to obtain a relationship between the sorption parameters and soil properties (K_f, CEC, sand, silt, clay, OC, pH, Fe$_{ox}$, P$_{Bray}$ and Al$_{in}$). For this purpose, we made the simplest assumption of a linear dependence of K_f on the combinations of the measured properties. The stepwise multiple regression analysis was performed using the default "step" function of the R software.

Predictive K_f values were obtained from the equation:

$$K_f = a_0 + \sum_{i=1}^{n} (a_i X_i)$$

where a_i is the regression coefficient associated with the X_i soil physicochemical property (i = 1 to n number of considered soil properties).

Internal model validation was carried out using residual bootstrap method (Fox and Weisberg, 2017). Boostrapt analysis was performed using the **Boot** function of the R package 'car'. Number of bootstrap samples was set in 1000 replicates.

Fig. 1. Geographic location of the soil samples.

Name of Soil	Zone
Marco Juarez	1
Sgo del Estero	2
Famailla	3
Pergamino	4
Cerro Azul	5
Balcarce	6
Alto Valle	7
Corrientes	8
Chaco	9
Reconquista	10
Cerro amigo	11
Barrow	12

Legend:
- Mollisols
- Histosols
- Vertisols
- Entisols
- Andisols
- Alfisols
- Aridisols
- Oxisols & Ultisols
- Outcrop Rock

determined by Ultra-high-performance liquid chromatography (ACQUITY UPLC™) coupled to tandem mass spectrometry (Quattro Premier™ XE), using an Acquity UPLC BEH C18 column (1.7 μm, 50 × 2.1 mm) (Waters). At first, 2 mL supernatant content of glyphosate was spiked with 10 μL of isotope-labeled glyphosate (1,2-^{13}C,^{15}N) stock solution (10 mg L^{-1}). The sample was derivatized by adding 1 mL of KH_2PO_4/$Na_2B_4O_7$ buffer (0.1 M, pH = 9) followed by 2 mL of FMOC-Cl reagent in acetonitrile (1 mg mL^{-1}), and allowing the reaction to

Table 1
Physical and chemical properties of soils.

Soil	K_f	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	239.1	32.9	12.9	53.4	33.7	4.7	5.94	4082.2	23.2	12.2
Santiago del Estero	129.7	19.9	21.3	54.9	23.8	4.5	6.99	1804.3	112.9	14.5
Famaillá	172.4	38.3	8.5	57.1	34.4	8.5	6.10	3758.2	39.8	22.9
Pergamino	265.2	16.5	19.9	53.5	26.6	2.7	5.41	3330.6	24.5	13.3
Cerro azul	397.4	27.3	5.7	24.8	69.5	6.0	4.80	16,121.7	3.1	58.8
Balcarce	174.1	37.4	43.8	26.9	29.3	10.3	5.75	3588.2	28.3	14.4
Alto valle	58.7	26.2	43.1	35.6	21.2	2.7	7.20	12,147.1	53.6	14.5
Corrientes	24.9	9.0	90.3	3.3	6.4	0.5	5.63	560.5	4.18	17.7
Chaco	310.4	23.5	13.5	49.0	37.5	4.0	6.10	1567.1	154.3	13.3
Reconquista	110.3	19.0	24.9	50.4	24.7	5.1	6.28	1671.7	16.6	13.8
Cerro amigo	167.5	30.0	38.1	32.5	29.4	6.9	6.02	5917.8	28.5	15.0
Barrow	151.6	40.5	29.7	33.2	37.1	7.3	6.84	5335.5	39.0	12.7

3. Results and discussion

3.1. Soil properties

The values of the selected soil properties are listed in Table 1. The soils used in the glyphosate sorption measurements displayed great variability in their origins and properties. The combination of the soils used in this work provides a wide range of clay content for studying glyphosate sorption. Clay content values ranged from 6 to 69.5%, with Corrientes soil presenting the lowest value (6%) and Cerro Azul soil the highest (69.5%).Sand content was inversely correlated to the clay content, that is, 90.3% in Corrientes soil and 5.7% in Cerro Azul soil. Most of the soil pH was acidic except in Alto Valle and Santiago del Estero soils, whose pH was neutral or slightly alkaline. P_{Bray} concentrations ranged from 3.1 to 154.3 mg kg^{-1}, with the highest value in Chaco soil. The highest amounts of Fe_{ox} were present in Cerro Azul and Alto Valle soils (16.1 and 12.1 g kg^{-1}, respectively), ranging from 0.6 to 5.9 g kg^{-1} in the rest of studied soils. There were no significant differences in the Al_{in} content between the soils, except in the case of Cerro Azul, which presented 58.8 mg kg^{-1}. Al_{in} content was correlated with clay, pH and Fe_{ox} content. The OC also showed great variations, with the highest amount found in Balcarce soil (10.3%) and the lowest in Corrientes soil (only 0.5%).

Some basic soil properties showed highly significant correlations. The OC content was correlated with CEC (0.845), and the clay content was correlated with sand (−0.711), iron oxides (0.655) and aluminum (0.774) (Table 2).

3.2. Adsorption isotherms

Fig. 2 presents the adsorption isotherms for glyphosate on the different soils. The isotherms obtained for all the soils were of the "L" isotherm type without strict plateau, where the ratio between the concentration of the glyphosate remaining in solution and adsorbed on the soil decreases when the analyte concentration increases. Freundlich mathematical model was applied to simulate glyphosate adsorption isotherms on the soils and estimate the sorption parameters (Table 1). This model fitted the adsorption isotherms with high correlation coefficients (0.991–0.998), except in Cerro Azul soil where the fit was not so good ($r^2 = 0.975$). The Freundlich coefficient (K_f) is an indicator of sorption strength. The K_f obtained for the different soils employed in this work ranged between 24.9 and 397.4 (Table 1). The highest adsorption of glyphosate was observed for Cerro Azul soil and then adsorption decreased in the following order: Chaco > Pergamino > Marco Juárez > Balcarce > Famaillá > Cerro Amigo > Barrow > Santiago del Estero > Reconquista > Alto Valle > Corrientes.

Experimental values of the n coefficients were significantly lower than 1, varying between 0.44 and 0.65. These low n values indicate the saturation of sorption sites at high concentrations, in agreement with some previous studies (Sidoli et al., 2016).

3.3. Principal component and multiple linear regression analysis

When K_f is analyzed in terms of each soil property, glyphosate sorption seems to show a clearly positive linear dependence on the clay content and a negative linear dependence on soil pH (Fig. 3). These results are consistent with those of earlier adsorption studies on herbicides of widely different chemical character (Sprankle et al., 1975), which demonstrated the importance of clay content in the glyphosate-soil interaction.

PCA was applied to the adsorption data to view the interrelation among the studied soil variables and their influence on glyphosate adsorption (Table 3). This procedure reduced the number of independent variables to two or three principal component factors (PCs), which were independent linear combinations of the original variables. These PCs are linear combinations of all of the original variables, and therefore they capture more information than any one of the original variables. The resulting factor scores were used as independent variables during the multiple regression analysis while the K_f parameters were used as dependent variables. The earlier values indicated that adsorption data could be satisfactorily presented using only three PCs, which captured 81.3% of variances in the original adsorption data. To identify which soil variables were most highly correlated with K_f, the PC1–PC2 and PC1–PC3 loading plots (Fig. 4a and b, respectively) were examined. Considering that the variable vectors formed by linking the origin point with the variable position in a given two-PC-space loading plot and by checking the angle between two variable vectors, the correlation between two variables can be ascertained. Thus, from the PC1–PC2 plot (Fig. 4a) it was deduced that a high positive correlation existed between K_f and clay component (0.855), whereas moderate positive correlations among K_f, MO, CEC, Fe_{ox} and Al_{in} were also evidenced. In addition, in the PC1–PC3 space (Fig. 4b), an angle close to 180° between the K_f vector and the vectors of pH and sand indicated a high negative correlation between K_f and these variables (−0.615 and −0.725, respectively).

From a single linear regression analysis for each soil variable considered independently, it was observed that clay content was the parameter that provided the best correlation with K_f ($R^2 = 0.854$). Moreover, K_f was negatively associated with pH ($R^2 = 0.615$) and sand content ($R^2 = 0.521$) (Fig. 3). Glyphosate affinity to clay was one of the first glyphosate sorption studies reported in the literature (Sprankle et al., 1975) that showed that the herbicide sorption was stronger in a clay loam soil than in a sandy soil. Later studies confirmed the importance of clay content in glyphosate soil sorption (Glass, 1987; Farenhorst et al., 2009).

Stepwise multiple linear regression analysis was used to examine which set of measured soil properties could explain K_f best using as few assumptions as possible. This procedure makes decisions based on a statistic called AIC (Akaike's Information Criterion), which is a measure of the relative quality of statistical models for a given set of data, allowing one to minimize the problem of multicollinearity among soil properties (Bowerman and O' Connell, 1990; Jagadamma et al., 2008). In this work the forward procedure was performed starting with no variables in the model and adding one variable at a time, testing the

Table 2
The Pearson correlation coefficients matrix among soil properties.

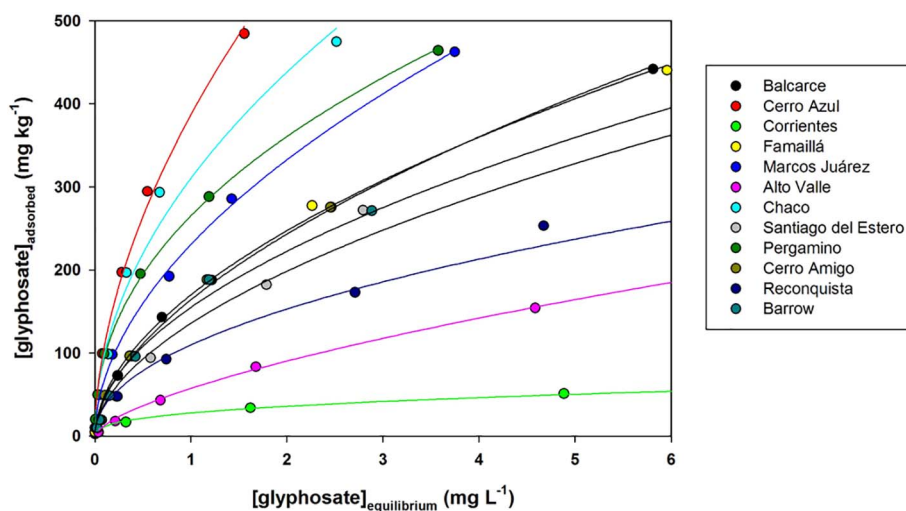| Parameters	Sand (%)	Silt (%)	Clay (%)	OC (%)	pH	Fe_{ox} (mg Kg^{-1})	P_{Bray} (mg Kg^{-1})	Al_{in} (mg Kg^{-1})
CEC (cmol Kg^{-1})	−0.416	0.183	0.448	0.845	0.163	0.264	−0.042	0.036
Sand (%)		−0.772	−0.711	−0.379	0.074	−0.251	−0.284	−0.288
Silt (%)			0.104	0.146	0.293	−0.237	0.434	−0.292
Clay (%)				0.432	−0.442	0.655	−0.035	0.774
OC (%)					−0.038	0.102	−0.088	0.121
pH						−0.172	0.469	−0.603
Fe_{ox} (mg Kg^{-1})							−0.284	0.725
P_{Bray} (mg Kg^{-1})								−0.313

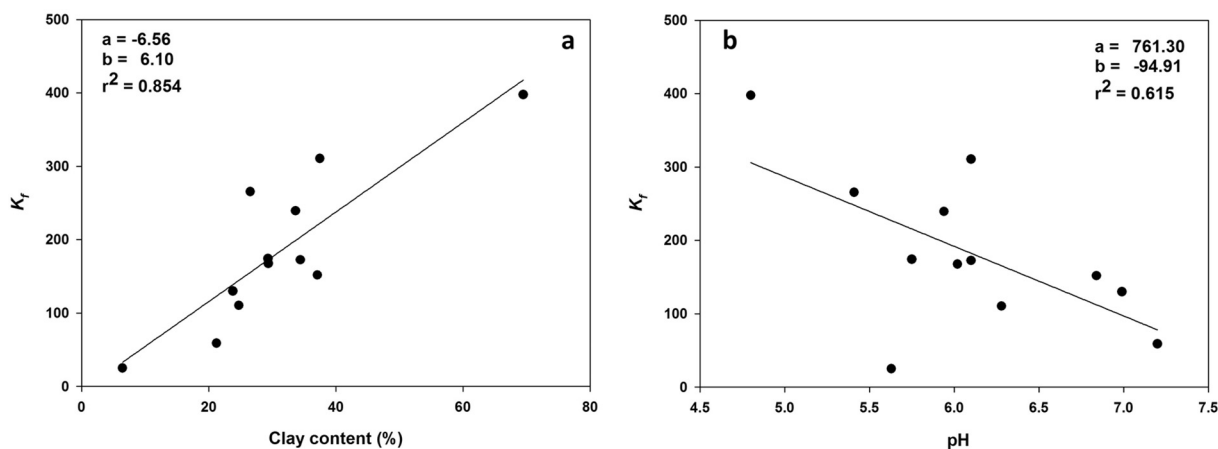Fig. 2. Adsorption isotherms for glyphosate on the different soils.

Fig. 3. K_f as a function of clay content (a) and pH (b).

Table 3
Principal component analysis of the physicochemical soil properties.

	Eigen value	Proportion of variance (%)	Cumulative proportion of variance (%)
Principle component			
PC1	4.025	40.25	40.25
PC2	2.546	25.46	65.71
PC3	1.559	15.59	81.30

	PC1	PC2	PC3
K_f	**0.428**		0.318
pH	−0.253	**0.367**	−0.201
Clay	**0.487**		
Silt		**0.526**	0.246
OC	0.251	0.220	**−0.546**
Fe_{ox}	**0.323**	−0.211	−0.111
P_{Bray}		**0.417**	0.327
Sand	−0.366	**−0.370**	−0.200
Al_{in}	**0.380**	−0.324	
CEC	0.246	0.269	**−0.574**

Bold values: the highest loadings of principal components on the physicochemical soil properties.

addition of each variable using AIC values. The regression coefficients of each prediction model of K_f values depending on soil properties are presented in Table 4. The standardized coefficients (beta values) indicate the strength of the effect of the respective soil properties on K_f values, that is, a greater absolute value shows a stronger effect.

The best model obtained includes seven soil variables (Clay, pH, P_{Bray}, Al_{in}, OC, Sand, Fe_{ox}) and explains 99.7% of the variation in K_f values. However, the standardized coefficients indicate that some of the
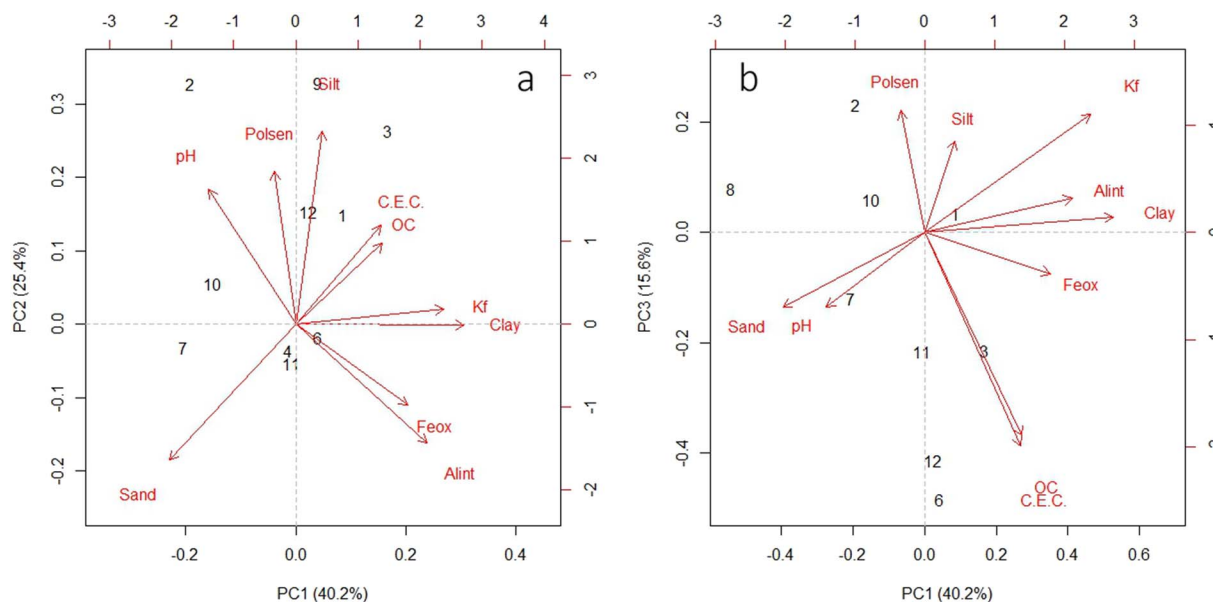
Fig. 4. Loadings plot of PC1–PC2 space (a) and PC1–PC3 space (b).

Table 4
Glyphosate K_f coefficients calculated by multiple linear regressions.

| Soil variables X_n		Clay (%)	pH	P_{Bray} (mg Kg^{-1})	Sand (%)	Al_{in} (mg Kg^{-1})	OC (%)	Fe_{ox} (mg Kg^{-1})	Silt (%)	CEC (cmol Kg^{-1})	R^2
Regression coefficients	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	
7 variables (Clay, pH, P_{Bray}, Al_{in}, OC, Sand, Fe_{ox})	735.2	5.2	−104.2	0.7	−1.0	−3.8	−5.1	0.0036	–	–	0.994
6 variables (Clay, pH, P_{Bray}, Al_{in}, OC, Sand)	631.4	6.2	−89.6	0.5	−0.8	−3.3	−6.6	–	–	–	0.988
5 variables (Clay, pH, P_{Bray}, Al_{in}, OC)	565.2	7.8	−87.9	0.6	–	−4.2	−7.0	–	–	–	0.979
4 variables (Clay, pH, P_{Bray}, Al_{in})	572.3	6.5	−92.5	0.7	–	−3.2	–	–	–	–	0.958
3 variables (Clay, pH, P_{Bray})	482.9	4.6	−79.2	0.9	–	–	–	–	–	–	0.913
3 variables (Clay, pH, Sand)	566.1	2.5	−65.9	–	−2.0	–	–	–	–	–	0.884
2 variables (Clay, pH)	299.1	5.2	−45.5	–	–	–	–	–	–	–	0.801
1 variables (Clay)	−6.6	6.1	–	–	–	–	–	–	–	–	0.731
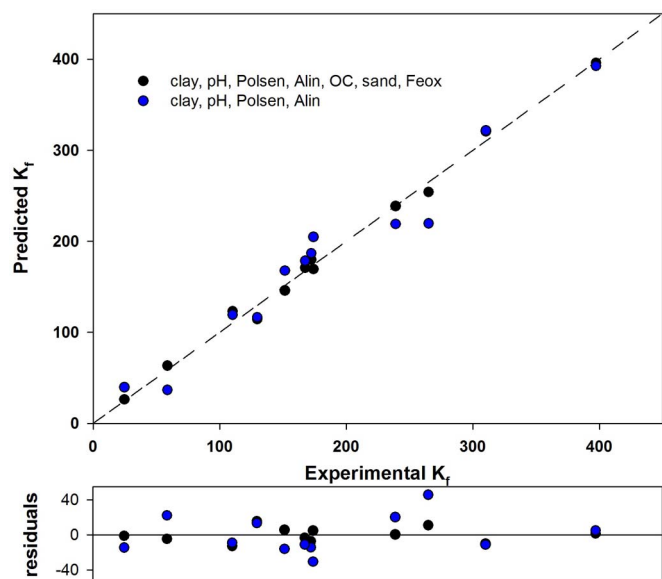
Fig. 5. Comparison between measured and predicted Kf coefficients with the multiple linear regression model. The dotted lines represent a 1 to 1 straight line.

soil properties can be removed from the model. In this sense, OC, Sand, Fe_{ox} could be removed and, in this case, the model with the remaining soil properties explains 97.9% of the variation in K_f values (Fig. 5).

Therefore, four factors were selected as the predictors of K_f to build up the regression equation:

$$K_f = 735.2 + 5.2*Clay - 104.2*pH + 0.7*P - 3.8*Al_{in}$$

The R square is 0.958, in which 85.6% of K_f variation can be explained directly by clay contents variation. Bootstrap methods were employed for internal validation of pedotransfer model. Histograms of bootstrap coefficient estimates are shown in Fig. 6. It was observed that kernel density estimates and the normal density based on the bootstrap mean are similar for all the coefficients and confidence intervals are symmetric about the original values.

Combining the results from correlation analysis, PCA, and stepwise regression, we can conclude that clay contents and pH are the most important factors affecting glyphosate sorption to soil. For the glyphosate-soil interaction, various mechanisms controlled by different soil properties have been postulated. The glyphosate molecule is a pH-dependent zwitterion with three donor groups (an amine group, a carboxylate group, and a phosphonate group), which are responsible for complexation reactions with metal ions and mineral surfaces. The dominating sorption mechanism of glyphosate to soil seems to be by a ligand exchange process, resulting in the formation of inner-sphere surface complexes with soil-exchanged polyvalent cations, in which the
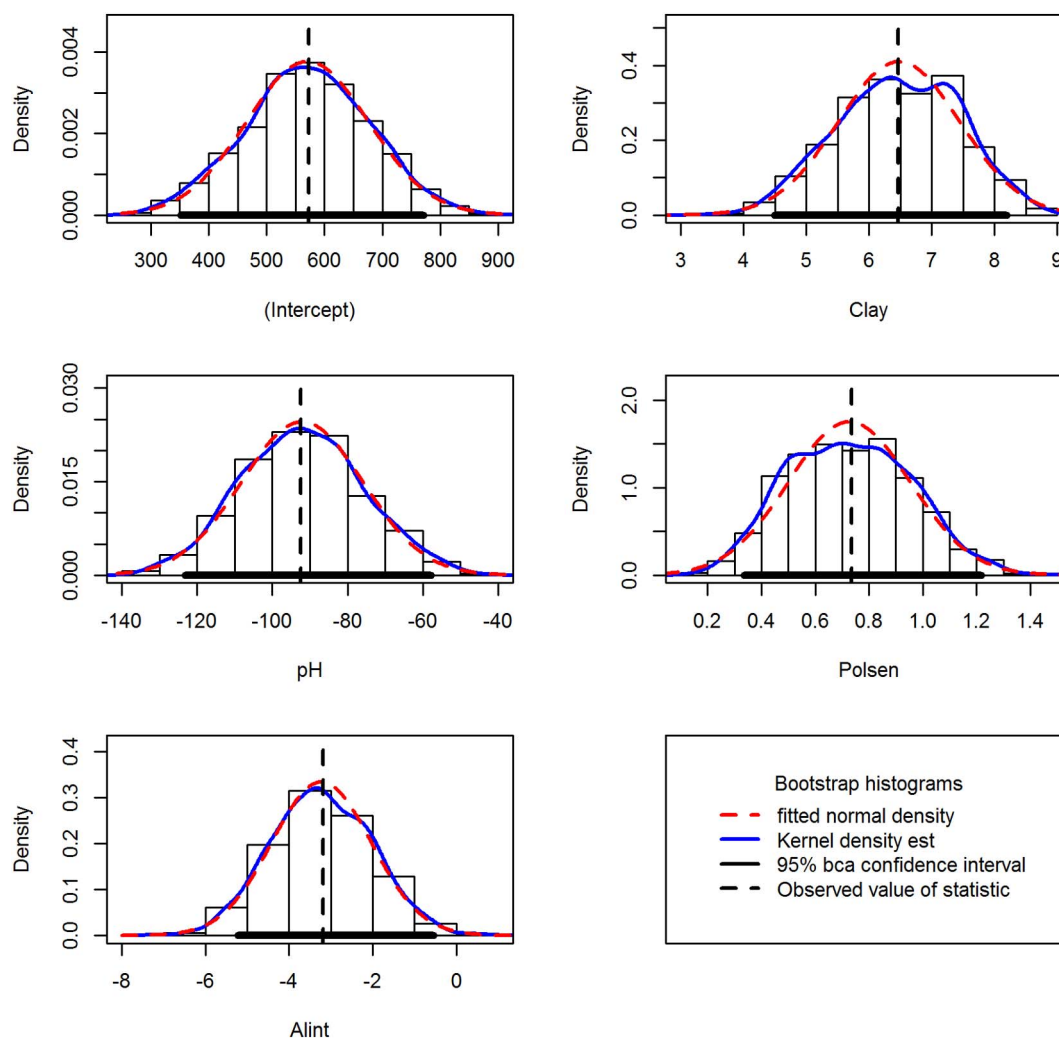
Fig. 6. Bootstrap histograms for each model regression coefficients.

phosphonate group of glyphosate binds to surface ions, displacing co-ordinated water molecules and/or hydroxyl ions (Sheals et al., 2002; Waiman et al., 2013).

As indicated above, in early studies it was suggested that clay minerals were responsible for sorption (Sprankle et al., 1975; Glass, 1987). This interaction seems to be governed by H-bonding and ion-exchange mechanisms in the case of cation-saturated clays (Miles and Moye, 1988). In this mechanism, complexation of glyphosate by cations released from the clays via a cation-exchange reaction with solution protons has been proposed as an adsorption mechanism (Hance, 1976). The K_f obtained for the soils of Argentina studied are consistent with reported evidence that suggests that glyphosate adsorbs within the interlayer spaces of the clay minerals (Glass, 1987). In contrast, other authors found that the adsorption of glyphosate to different Danish soils is not influenced by the clay content but only by the pH (Gimsing et al., 2004).

In our results, the content of iron and aluminum was not significant in the affinity of glyphosate, this is probably due to the high influence of clay content in the soils employed in our work, which caused the influence of Fe_{ox}–Al_{ox} to be masked. In contrast, others authors concluded that clay and Fe_{ox}–Al_{ox} play an even more important role (Wang et al., 2005; Bergström et al., 2011; Rampazzo et al., 2013).

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.

There is a negative correlation of K_f with soil pH, which means that the sorption of glyphosate to the soil is favored at a lower pH. This behavior is due to the different electrical charge 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. At pH 4.80 (Cerro Azul soil), glyphosate molecules have an average net charge of -1.2 (81.9% H_2G^- .17.9% HG^{-2} and 0.2% H_3G), while at pH 7.20 (Alto Valle soil) the average net charge is -2.0 (98% HG^{-2}, 1.8% H_2G^- and 0.1% G^{-3}). The increase in the negative charge with soil pH involves not only the glyphosate molecule but also the increase in the amount of negatively charged soil colloids, favoring the repelling forces between these compounds and, consequently, reducing the interaction drastically (McConnell and Hossner, 1985; Wang et al., 2004).

Previous studies have provided experimental evidence for the influence of soil hydroxides on the soil sorption of glyphosate (Nomura and Hilton, 1977; Piccolo et al., 1994; Gerritse et al., 1996). A study performed in four typical European soils demonstrated that glyphosate mainly interacted with the iron and aluminum hydroxides (Piccolo et al., 1994). In the same way, Gerritse et al. (1996) found that the adsorption of glyphosate in sandy soils of Australia increased strongly with increasing iron and aluminum content of soils, whereas it decreased with increasing soil organic matter. In another study developed in Danish soils, a fast adsorption of glyphosate to iron and aluminum oxides was observed (Gimsing et al., 2004). In addition, these authors found that soil pH was the main factor determining the amount of

glyphosate that was sorbed to the soil. A strong dependence of glyphosate sorption on the pH was also found for a silty clay and sandy loam soil (Nicholls and Evans, 1991), with the strongest sorption occurring around pH 4. Based on the information currently available, it is generally accepted that phosphonic moiety controls glyphosate adsorption in terms of hydrogen bonding through complexation, while soil organic matter only seems to have an indirect effect by blockage of sorption sites.

Different studies employing goethite (α-FeOOH) showed that glyphosate is easily accommodated at the goethite surface from pH 3 to pH 6, indicating that glyphosate adsorbs via predominantly monodentate complexation (Sheals et al., 2002), while the phosphonate group of glyphosate binds directly to the goethite component of soil to form predominantly monodentate inner-sphere complexes. The carboxylate group remains relatively "free" from complexation with goethite, leaving it subject to degradation and/or complexation with metal ions present in the environment. A minor quantity of bidentate complexes is thought to form both at near-neutral pH and when the surface concentration of glyphosate is low.

Although there are studies showing the importance of humic substances isolated from different soils in the adsorption of glyphosate (Albers et al., 2009), in our results the influence of organic matter was not significant. It has been suggested that the acidic functions of the humic substances could play a role in the adsorption of glyphosate, which would be able to form hydrogen bonds with the corresponding glyphosate functions (Piccolo and Celano, 1994; Piccolo et al., 1996). However, there is a general consensus that the influence of organic matter on the adsorption of glyphosate is weak compared to other soil components, such as clay, iron and aluminum oxides (Vereecken, 2005). The ability of the organic matter to adsorb glyphosate has been studied by comparing the interaction of this herbicide with solely humic acids and with iron-humic acid complexes. These authors observed that this interaction was stronger in the complex than in the isolated humic acid, suggesting that the presence of mineral-organic complexes may explain why glyphosate would adsorb in soil organic matter (Piccolo et al., 1992).

4. Conclusions

The influence of soil physical and chemical properties on glyphosate sorption was studied across twelve soils of Argentina. Glyphosate sorption appeared to be mainly controlled by pH and clay content and, to a lesser extent, interchangeable aluminum and P_{Bray}. The best-four set of parameters selected gives an acceptable prediction of Freundlich constants (K_f) compared to using all parameters measured in our soils. These four key soil parameters combined in a multiple linear regression equation provide a robust pedotransfer function for K_f prediction, which enables prediction of glyphosate sorption for a wide range of soils of Argentina with a limited number of properties and with reasonable accuracy for most environmental conditions.

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