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Glyphosate sorption and desorption in soils of Argentina

**SORPTION AND DESORPTION OF GLYPHOSATE IN MOLLISOLS AND  
ULTISOLS SOILS OF ARGENTINA**

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**Abstract**

In Argentina, glyphosate use has increased exponentially in the past years due to the widespread adoption of no-till management combined with genetically modified glyphosate-resistant crops. This massive use of glyphosate has created concern about its potential environmental impact. Sorption-desorption of glyphosate was studied in three Argentinean soils with contrasting characteristics. Glyphosate sorption isotherms were modeled using the Freundlich equation to estimate the sorption coefficient ( $K_f$ ). Glyphosate sorption was high and the  $K_f$  varied from 115.6 to 1612 mg<sup>1-1/n</sup>L<sup>1/n</sup>/Kg. Cerro Azul soil had the highest glyphosate sorption capacity due to a combination of factors such as higher clay content, CEC, total Fe, Al oxides and lower available phosphorous and pH. Desorption isotherms were also modeled using the Freundlich equation. In general, desorption was very low (<12%). The low values of hysteresis coefficient (H) confirm that glyphosate strongly sorbs to the soils and that it is almost an irreversible process. Anguil soil had a significant higher desorption coefficient ( $K_{fd}$ ) than the other soils, associated with its lower clay content and higher pH and phosphorous. Glyphosate high sorption and low desorption to the studied soils may prevent groundwater contamination. However, it may also affect its bioavailability increasing its persistence and favoring its accumulation in environment. Results of this study contribute to the knowledge and characterization of glyphosate retention in different soils. This article is protected by copyright. All rights reserved

**Keywords:** Sorption; Desorption; Glyphosate; Soil properties

## INTRODUCTION

Glyphosate [N-phosphonomethyl glycine] is a post-emergent non-selective broad-spectrum herbicide extensively used in agriculture for the control of most annual and perennial weeds. The main uses of glyphosate are in genetically modified (GM) glyphosate-resistant crops (i.e. soybean, corn, cotton) [1] and during the fallow period in no-till practices. At present, glyphosate-based herbicides represent 60 % of the total sold pesticides in Argentina [2]. Glyphosate can be applied from 3 to 6 times in an annual cycle, which leads to its accumulation in agricultural soils [3]. This has raised great concern in the population and in the scientific community, regarding the possible negative impacts on soil, water resources, biota and human health. In this context, it is important to identify and understand the mechanisms that control the fate of glyphosate in the environment.

Sorption and desorption processes to the soil matrix are key factors that influence the mobility and bioavailability of pesticides. Once a pesticide reaches the soil, its behavior will depend on the intrinsic properties of the molecule (e.g. sorption, solubility, and persistence), combined with the physico-chemical and biological properties of the soil (e.g. organic content, humidity, biomass, pore connectivity, and pH) [4]. A number of soil properties can affect pesticide retention, such as organic matter content, soil acidity and soil texture (e.g. [5,6,7,8,9]).

In general, glyphosate sorption cannot be related to one soil property, but to several interactions with the soil components. For example, glyphosate has four dissociation constants ( $pK_a$ : 2, 2.6, 5.8 and 10.8; [10]), therefore pH affects its sorption to the charged molecules of the mineral phase [11]. For example, Mamy and Barriuso [12] and Glass [13] related glyphosate sorption to the clay content and CEC of the adsorbent. Piccolo et al. [14]

suggested that glyphosate binds to humic substances through its phosphonic acid moiety reacting with polyvalent cations adsorbed on clays and organic matter. Previous studies on sorption of glyphosate and phosphate by pure soil minerals revealed a high capacity of sorption by iron and aluminum oxides for both compounds, whereas limited amounts were adsorbed by 2:1-layer clay silicates minerals [11,15]. However, phosphate affinity to oxides is higher and it can desorb pre-adsorbed glyphosate [11].

In the last 20 years, Argentina suffered an intensification of agriculture with an increase in the cultivated areas in detriment of livestock production and pastures. This situation has generated a decrease in the organic matter levels as well as changes in other soil properties and an increase in soil degradation. Furthermore, most of the cultivated lands are under no-till management, which implies a greater use of herbicides for weed control. These changes on the edaphic properties along with the crop sequences and land-use may have an influence on the sorption-desorption of glyphosate posing a potential environmental risk. Since glyphosate behavior is dependent on various soil properties, it is important to study the sorption-desorption process for each particular soil in order to predict its bioavailability and leaching potential. Therefore, the objective of this work was to study glyphosate sorption-desorption in three contrasting soils from agricultural areas in Argentina under no-tillage management.

## **MATERIALS AND METHODS**

### *Soils*

Soil samples were taken from agricultural fields of Cerro Azul (located in the south of the province of Misiones), Tandil (in the southeast of the province of Buenos Aires) and Anguil (northeast of the province of La Pampa) (Fig. 1). The studied soils are located in

areas of high agronomic land use and have different edaphoclimatic conditions. Four composite soil samples from the top 15 cm of topsoil were collected from each field. Samples were homogenized, air-dried, and sieved to a particle size of 2 mm.

A sub-sample of each replicate was used for physico-chemical analysis of the soils. Particle size distribution was measured using the pipette method [16]; organic carbon (OC) content was measured according to the Walkley-Black method [17]; cation exchange capacity (CEC) was determined by displacement with 1M ammonium acetate at pH 7 [18]; soil pH was measured by electrode in a soil:water ratio of 1:2.5; available phosphorous (P-Bray) was determined according to Bray and Kurtz [19], total iron (Fe) was determined by atomic absorption spectrophotometry [20]; exchangeable aluminum (Al) was measured according to the aluminum method [21].

#### *Chemicals*

Stock solutions for the standard curves and the isotherm studies solutions were prepared using analytical pure glyphosate (PESTANAL®, 99.9%) purchased from Sigma-Aldrich. HPLC-grade methanol and HPLC-grade acetonitrile (ACN) for analytical procedures were purchased from Seasinglab. Nanopure water was obtained by purifying demineralized water (ELGA Purelab Ultra ® Illinois, USA).

#### *Sorption isotherms*

The sorption isotherms were performed according to the Batch Equilibrium Method [22]. Two g of soil were shaken with 40 mL of a 0.01 M CaCl<sub>2</sub> solution. After 24 h, glyphosate was spiked at different initial concentrations ( $C_0$ ): 0; 0.5; 1; 5; 10; and 20 mg/L. The suspensions were shaken for another 24 h at constant temperature (20°C). Afterward, tubes were centrifuged and an aliquot (3 ml) of the aqueous solution was analyzed for

glyphosate concentration. Each initial concentration was tested by duplicate for each soil sample. These laboratory duplicates were averaged, finally obtaining data of four replicate isotherms per soil.

#### *Desorption isotherms*

The desorption isotherms were performed using the spiked soil with the  $C_0$ : 5 mg/L solution from the sorption isotherm studies. This concentration is equivalent to the commonly used dose in the field per year (6 L/ha/year) considering 5 cm depth of soil. After the sorption study, the aqueous phase was carefully discarded to avoid any soil loss during manipulation. The volume of the solution that was removed was replaced with 40 mL of 0.01 M  $\text{CaCl}_2$  and the soil was re-suspended and shaken at a constant temperature for another 24 h. Then, samples were centrifuged and glyphosate was measured in the aqueous solution in order to quantify the glyphosate that desorbed from the soil matrix. This procedure was repeated at 48 and 72 h by removing the aqueous solution and adding again 40 ml of  $\text{CaCl}_2$ . The amount of adsorbed glyphosate at each desorption step was calculated as the difference between the initially adsorbed concentration and the desorbed amount.

#### *Glyphosate analysis*

To quantify the remaining glyphosate in the aqueous solution, an aliquot of 3 ml was transferred to a 15 mL polyethylene flask. Afterwards, 0.5 ml of borate buffer solution (0.04 mM  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ , pH= 9) and 0.5 ml of ACN were added. The samples were shaken vigorously and then derivatized with 0.5 ml of 9-fluorenylmethylchloroformate (FMOC-CL) dissolved in ACN (6 g/L), and incubated overnight at room temperature. As a clean-up step, 4.5 ml of  $\text{CH}_2\text{Cl}_2$  were added to the samples to remove any organic

impurities and minimize matrix effects. The aqueous fraction was separated from the organic solvent by centrifuging for 10 min at 664 g. The supernatant was collected and filtered through a 0.22  $\mu\text{m}$  nylon filter, and then analyzed by liquid chromatography (LC) coupled to a tandem mass spectrometer (MS/MS).

The chromatographic analysis was carried out using a Waters® ACQUITY® UPLC (ultra-performance LC) system, with an ACQUITY BEH C18 1.7  $\mu\text{m}$  2.1 x 50 mm column. The injected volume per sample was 20  $\mu\text{L}$ . The flow rate was set at 0.4 mL/min and the column temperature to 60°C. The mobile phase solvents were: A) water + 5 mM  $\text{NH}_4\text{Ac}$  (ammonium acetate), and B) methanol. The liquid chromatography gradient was set as following: from 0 to 0.2 min 100% A, from 0.2 to 2.5 min 30% A:70% B, from 2.5 to 4.5 min 100% B, and from 4.5 to 6 min 100% A. Target molecules were detected by a triple quadrupole (TQD) mass spectrometer (MS/MS) Quattro Premier XE (Waters). The equipment was operated with an electrospray ionization source in positive mode (ESI+). In order to take into account the matrix effect of each soil, the standard curves were prepared using a background solution of each soil obtained after shaking with  $\text{CaCl}_2$  0.01 M. After separating the solid phase from the aqueous phase, the solution was used to prepare each point of the standard curves by adding the corresponding glyphosate concentration. A sample without any glyphosate was also analyzed to check the concentration of pre-sorbed glyphosate. In all cases, the background solution had non-detectable levels of glyphosate. The limit of detection (LD) was 0.1  $\mu\text{g L}^{-1}$  and the limit of quantification (LQ) was 0.5  $\mu\text{g L}^{-1}$ .

#### *Sorption modeling*



Following the experimental design proposed by the OECD [22], the measured glyphosate in the aqueous solution was used to estimate the remaining glyphosate sorbed to the soil ( $C_s$ ) with the following equation:

$$C_s = M_s/M_{soil} = (C_o - C_w)V_o/M_{soil} \quad (1)$$

where  $C_s$  is the concentration of glyphosate adsorbed to the soil at equilibrium (mg/Kg),  $M_s$  is the mass of glyphosate sorbed to the soil at sorption equilibrium (mg),  $M_{soil}$  is the dry mass of the soil sample (Kg),  $C_o$  is the initial tested concentration of glyphosate in contact with the soil sample (mg/L).  $C_w$  is the analytically measured mass concentration of glyphosate in the aqueous phase at sorption equilibrium (mg/L) and  $V_o$  is the initial volume of the aqueous phase in contact with the soil sample (mL).

The Freundlich equation was used to describe sorption and desorption isotherms:

$$C_s = K_f C_w^{1/n} \quad (2)$$

where  $K_f$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} / \text{Kg}$ ) is the Freundlich sorption coefficient and  $1/n$  is the Freundlich exponent ( $K_f$  and  $1/n$  will hereafter refer to sorption, and  $K_{fd}$  and  $1/n_d$  to desorption). The  $K_f$  indicates the affinity of the substance to the soil matrix and  $1/n$  indicates the degree of linearity between the amounts adsorbed and the concentration in the solution.

The hysteresis coefficient (H) for the sorption/desorption isotherms was calculated according to the equation:

$$H = (1/n_d)/(1/n)$$

(3)

where  $1/n$  and  $1/n_d$  are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively.

#### *Statistical analysis*

For the isotherms sorption and desorption studies, each soil sample was analyzed by duplicate. The laboratory duplicate samples were averaged and the isotherm curves were then modeled using the NLIN procedure of SAS software [23]. The statistical analysis of the soil properties and of the estimated sorption and desorption parameters were performed using a completely randomized design with four replicates per soil. Analysis of variance (ANOVA) was performed using the PROC GLM procedure to evaluate differences in the Freundlich parameters at a significance level of 5% [23].

## **RESULTS AND DISCUSSION**

### *Soil characteristics*

Table 1 shows the physicochemical properties of the studied soils. Tandil and Anguil soils correspond to a loam texture, while Cerro Azul is classified as clay. The contents of sand, silt and clay, as well as the OC, pH, and CEC, differed significantly between soils. Cerro Azul soil had a significantly higher clay content, followed by Tandil and then Anguil ( $p < 0.05$ ). On the other hand, the OC content and CEC were significantly higher in Tandil,

followed by Cerro Azul and Tandil soil ( $p < 0.05$ ). Anguil soil had had significantly higher pH and P-Bray values than Tandil and Cerro Azul ( $p < 0.05$ ). This is in agreement with Sainz Rosas et al. [24], who reported that soils located to the West of the Pampa region have a high phosphorous content. Regarding the exchangeable cations, only significant differences were observed for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , following the order Tandil > Cerro Azul > Anguil ( $p < 0.05$ ). The highest  $\text{Al}^{3+}$  and Fe content were found in Cerro Azul soil, denoting its Ultisol origin [25,26].

#### *Sorption isotherms*

Glyphosate sorption and desorption isotherms are shown in Fig. 2. The Freundlich sorption coefficients for glyphosate were very high and ranged from 115.6 to 1612 (Table 2), being generally higher than those usually reported in the literature [12,27,28,29,30]. Glyphosate  $K_f$  parameter was significantly higher in Cerro Azul, compared to Tandil and Anguil soil ( $p < 0.05$ ) (Table 2).

The values of  $1/n$  ranged from 0.4 to 0.8 (Table 2). Isotherms exhibited an L-type ( $1/n < 1$ ) curve according to the classification of Giles et al. [31]. This indicates that sorption is not constant as the concentration of the herbicide increases and that the sorption sites become saturated with increasing glyphosate concentration [31]. In the case of Tandil and Anguil soils, glyphosate was almost completely sorbed to the soil at low initial concentrations and as the concentration increased, sorption became less efficient (Fig. 2). Isotherms of this type occur when the adsorbent has a high initial affinity for the herbicide until the sorption sites become saturated. In contrast, the Cerro Azul isotherm exhibits an almost linear relationship between the amount of sorbed glyphosate and its concentration at equilibrium in the solution (Fig. 2), with  $1/n$  values closer to 1 (Table 2). Therefore, it can

be assumed that the number of sorption sites remains almost constant even at high concentrations [31]. The reason glyphosate sorption was significantly higher in Cerro Azul soil can be explained by the soils textural composition. Cerro Azul soil is an Ultisol, characterized by a high proportion of clay content composed of a mixture of kaolinite and Fe and Al oxides [32]. Clay content plays a major role in glyphosate sorption [9,33,34]. At the soil's pH, the negatively charged glyphosate molecule can be complexed with cations released from the clays, via a cation exchange reaction with solution protons [13]. On the other hand, iron and aluminum oxides also play an important role in glyphosate sorption [12,28,35,36], since the phosphonate group of glyphosate establishes coordination links with the interchangeable surfaces of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  cations. In this sense, the lower soil pH of Cerro Azul could also be favoring sorption via Fe and Al oxides, since as the pH decreases these oxides become more protonated, increasing the affinity towards the negatively charged glyphosate molecule [35,37,38]. Therefore, aside from cation exchange reactions, glyphosate may strongly bond through ligand exchange with the metal ions (Fe or Al) at the surface of the clay minerals. This mechanism has been proposed for other organic weak acids [39] and hence it can be applied to glyphosate. Ligand exchange is stronger than anion exchange or cation bridging [40] and therefore, causes a strong retention to the soil matrix.

Another important factor that influences glyphosate sorption is pre-sorbed phosphate. Phosphate competes strongly for the same sorption sites as glyphosate since phosphorous bonds by ligand exchange to the Al and Fe oxides [15]. Also, pre-adsorbed phosphate can inhibit glyphosate sorption since it increases the negative charges of the soil, in turn increasing the repulsion of the negative glyphosate molecule [37,41,42]. Hence, the

higher levels of pre-sorbed glyphosate in Tandil and Anguil soils might be another factor for the lower retention capacity of these soils compared to Cerro Azul.

#### *Desorption isotherms*

The Freundlich desorption coefficients of the studied soils ranged from 101.2 to 117.5  $\text{mg}^{1-1/n} \text{kg}^{-1} \text{L}^{1/n}$  (Table 2). Anguil soil had the highest  $K_{fd}$ , while Cerro Azul had a significantly lower desorption coefficient than the rest ( $p < 0.05$ ). The total desorbed glyphosate at the end of the desorption study was 1.6 and 1.9% for Cerro Azul and Tandil, respectively; while in Anguil soil desorption reached 12% (Table 2). The values of  $1/n_d$  ranged from 0.01 to 0.2 (Table 2). The irreversibility of glyphosate sorption was confirmed by the lower values of  $1/n_d$  with respect to  $1/n$ . The more pronounced slope of the desorption isotherms suggests that more energy is required to desorb the molecules than the needed for the sorption process [43]. In consequence, H values were low ranging from 0.01 to 0.4 (Table 2). When comparing the three soils, desorption and H were significantly higher in Anguil. This can be explained by the lower clay content and lower CEC, as well as to the significantly higher pH and available phosphorus, that affect glyphosate sorption mechanisms in an inverse way, as explained before. Nevertheless, desorption hysteresis can be considered significant in all the studied soils since  $H < 0.7$  [44], indicating that glyphosate sorption is nearly an irreversible process.

The fact that glyphosate binds strongly to the studied soils and that desorption was very low has a major implication in glyphosate bioavailability [45]. Glyphosate's biological degradation is strongly limited in soils that have high glyphosate affinity and low desorption [46].

The results obtained in this study indicate that sorption of glyphosate increases in soils with high contents of  $\text{Al}^{3+}$ , Fe and clays as well as with low pH and P content. This situation favors greater glyphosate retention and therefore, lower desorption which would reduce the likelihood of leaching and therefore the potential risk of groundwater contamination. However, glyphosate bioavailability can also be reduced, increasing its persistence and therefore contributing to its accumulation in the environment. These results contribute to the knowledge about glyphosate retention in soils and allows the identification of behavior patterns of this extensively applied herbicide in different edaphic scenarios. This is of major importance for the development of decision-making tools and criteria to reduce the potential negative impacts on soil and groundwater resources.

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*Data Availability*—Readers should contact the corresponding author:

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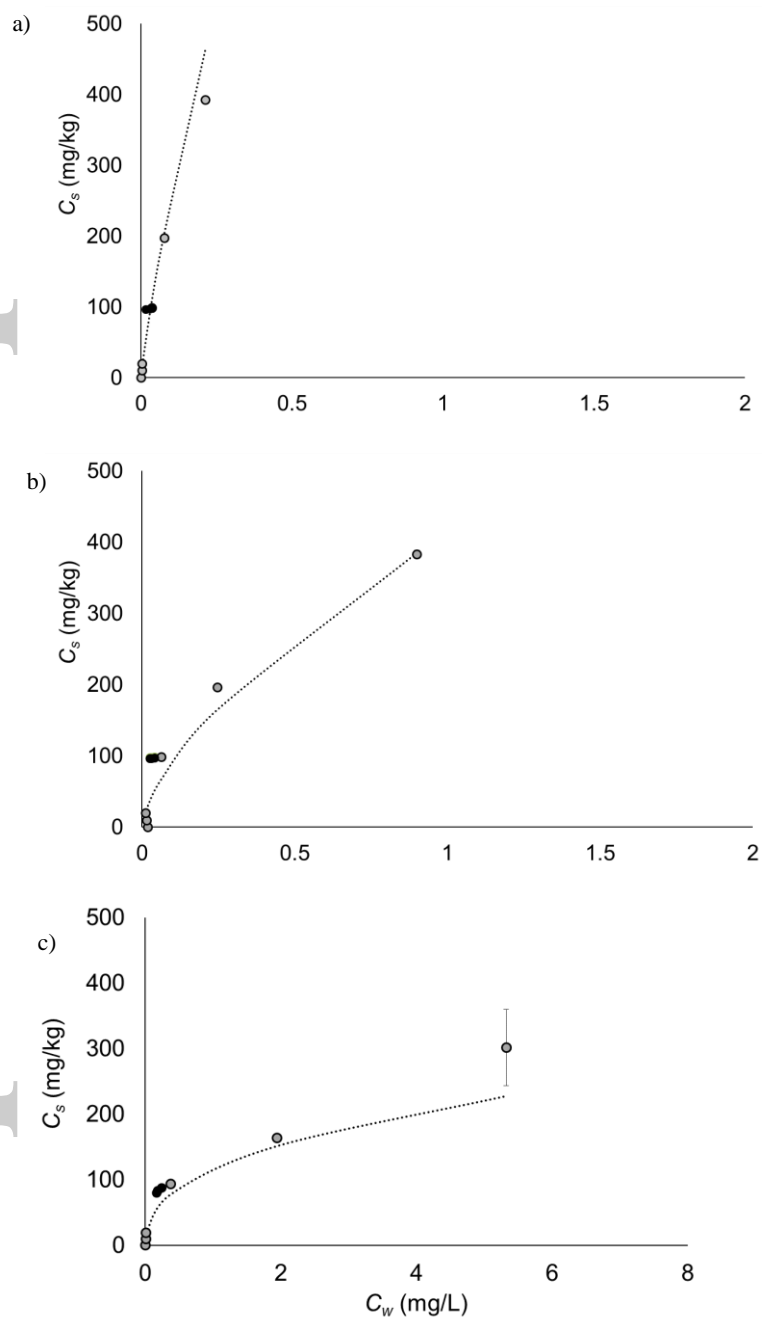
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Figure 1. Location of sampling sites in the provinces of Buenos Aires, La Pampa and Misiones, Argentina.

Figure 2. Adsorption (grey dots) and desorption (black dots) isotherms for a) Cerro Azul, b) Tandil and c) Anguil soils. Error bars represent standard deviation. Black dotted line represents the Freundlich model fit. Note different x-axis scale for Anguil soil.



Figure 1



**Figure 2**

**Table 1.** Main characteristics of the sampled locations and soil physico-chemical properties.

	Soil		
	Anguil	Cerro Azul	Tandil
Altitude (masl)	157	280	256
Annual average temperature (°C)	15.3	20.5	13.7
Mean annual precipitation (mm)	760	1844	993
Latitude	36°35'54"S	27°39'42"S	37°36'0.1"S
Longitude	63°58'31"W	55°26'25"W	59°04'29"W
Soil type	Mollisol	Ultisol	Mollisol
Main textural class	Loam	Clay	Loam
pH	6.3 a <sup>a</sup>	4.9 c	5.4 b
Clay (%)	14.7 c	78.5 a	23.0 b
Silt (%)	45.6 a	15.4 c	40.9 b
Sand (%)	39.6 a	6.1 c	36.0 b
OC (%)	1.3 c	2.4 b	3.4 a
P-Bray (mg/kg)	29.6 a	7.6 c	17.1b
CEC (meq/100 g)	17.4 c	20.6 b	25.2 a
Ca <sup>2+</sup> (meq/100 g)	8.1 b	5.6 b	14.7 a
Mg <sup>2+</sup> (meq/100 g)	2.9 b	3.2 b	5.1 a
K <sup>+</sup> (meq/100 g)	3.2 a	1.2 a	2.8 a
Na <sup>+</sup> (meq/100 g)	0.3 a	0.2 a	0.5 a
Al <sup>3+</sup> (meq/100 g) <sup>b</sup>	0.15 b	0.69 a	0.11 b



Total Fe (%) <sup>b</sup>	1.08 b	8.40 a	0.81 b
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OC= organic carbon; P-Bray= available phosphorous; CEC= cation exchange capacity

<sup>a</sup> Different letters indicate differences among soils (p<0.05)

<sup>b</sup>Gianelli et al. [8]

Table 2. Glyphosate Freundlich sorption and desorption parameters for Anguil, Cerro Azul and Tandil soils.

Soil	Sorption			Desorption <sup>a</sup>							
	$K_f^c$	$1/n$	$r^2$	$K_{fd}^c$	$1/n_d$	$r^2$	% <sup>d</sup>				$H^f$
							1°	2°	3°	Total <sup>e</sup>	
Cerro Azul	1612.0 (859.8)a	0.8 (0.5) <sup>a</sup>	0.97-0.99	101.2 (2.9) c	0.01 (0.0)c	0.99-0.99	0.7 (0.1)	0.6 (0.0)	0.5 (0.1)	1.6 (0.8)	0.01 (0.0)b
Tandil	412.6 (50.9)b	0.5 (0.07)ab	0.98-0.99	105.4 (1.7)b	0.02 (0.0)b	0.99-0.99	0.8 (0.1)	0.6 (0.0)	0.3 (0.0)	1.9 (0.5)	0.04 (0.0)b
Anguil	115.6 (12.9)b	0.4 (0.2)b	0.90-0.99	117.5 (0.6)a	0.20 (0.0)a	0.99-0.99	4.5 (0.3)	3.6 (0.1)	3.3 (0.3)	12.3 (4.1)	0.4 (0.2)a

Mean values of 4 replicates. Standard deviation in parenthesis.

<sup>a</sup> Desorption from initial glyphosate aqueous concentration  $C_0 = 5$  mg/L.

<sup>b</sup> Different letters indicate significant differences among soils ( $p < 0.05$ ).

<sup>c</sup> Units are  $\text{mg}^{-1/1/n} \text{L}^{1/n} / \text{Kg}$ .

<sup>d</sup> Percentage of desorbed glyphosate in the 1°, 2° and 3° desorption cycle.

<sup>e</sup> Total desorbed glyphosate after three successive desorption cycles.

<sup>f</sup> Hysteresis coefficient ( $H = 1/n_d / 1/n$ )