



# Effect of the phosphate and mineralogical composition on the movement and mineralization of glyphosate in clay soils

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## Abstract

Glyphosate is one of the most used herbicides worldwide. In rice paddy fields, it is usually applied for weed control during the pre-planting stage. Phosphate fertilizers may enhance herbicide displacement in the soil matrix. The objective of this study was to assess the effect of monoammonium phosphate and the mineralogical composition on the movement and mineralization of glyphosate in clay soils (CS1; CS2 and CS3) in Colombia. Glyphosate miscible displacement experiments were performed in disturbed soil columns, with and without the addition of phosphate after the application of a pulse of N-(phosphonomethyl-<sup>14</sup>C) glycine. Simultaneously, <sup>14</sup>C-glyphosate mineralization was measured indirectly by quantifying the amount <sup>14</sup>C-CO<sub>2</sub> released daily. At the end of the experiment, the columns were divided into six horizontal sections and glyphosate-bound residues were determined in the soil. The addition of phosphate decreased glyphosate retention time (in CS1 and CS2) and increased the total leached amount only in CS1 soil. Overall, more than 95% of the applied glyphosate was retained in the soil columns. Glyphosate mineralization half-life adjusted to a bi-exponential model, implying that one fraction degrades rapidly due to being more bioavailable, and the other fraction presents a slow rate of degradation and, that although high contents of kaolinite clays are important in the adsorption and translocation of the herbicide, the presence of calcites and divalent cations modify this process, favoring the persistence of the molecule in the soil. Glyphosate partitions into an easily degradable fraction and a more recalcitrant fraction adsorbed to kaolinite clays, calcites, and divalent cations. This fraction is less available for biodegradation thus favoring glyphosate persistence in soil.

**Keywords** Herbicides · Leaching · Phosphate fertilizers · Soil · Columns transport · Cations adsorption · Miscible displacement experiments · Half lifetime

## Introduction

Glyphosate (GLY) is one of the most used herbicides worldwide, it is used as a broad-spectrum systemic herbicide for weed control and as a crop desiccant (Andert et al. 2019). Although GLY usage is limited to foliar applications, a

fraction of the herbicide solution may reach the soil and undergo physical, chemical, or biological transformations (Kanissery et al. 2019) that will determine, among other environmental factors, its distribution in the environment (Holland 2004). It is currently considered a potential pollutant of surface water and groundwater (Okada et al. 2018).

Several studies indicate that GLY is a mobile molecule that can be transported through the soil profile and contaminate groundwater reservoirs; for example, in Argentina, GLY has been detected in groundwater at concentrations from 0.1 to 8.5 µg L<sup>-1</sup> (Okada et al. 2018). In Denmark, it was found in groundwater at concentrations of 1.1 µg L<sup>-1</sup> (Strange-Hansen et al. 2004), in Austria 0.1 µg L<sup>-1</sup> was reported (Vereecken 2005) and in Mexico, amounts ranging between 0.097 and 12 µg L<sup>-1</sup> were registered (Ruíz et al. 2014).

GLY movement through the soil profile is usually studied in disturbed (Barret and McBride, 2007) or undisturbed (De Jonge et al. 2001) soil columns. Herbicide mobility

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is affected by several factors such as soil type, clay contents, physicochemical contents, tillage system, sowing history, and climatic conditions (Lipiec et al. 2006). Previous studies of GLY elution in soil columns indicate a low leaching rate due to its high adsorption capacity and affinity for soil particles (Strange Hansen et al. 2004; Zhao et al. 2009; Padilla and Selim 2019). Padilla and Selim (2019) report leached amounts equivalent to 3 and 2% of the total applied GLY, using packed columns of silty loam soil and clay soil respectively from the agricultural zone of Louisiana (USA). Calderon et al. (2005) report leached amounts of this herbicide close to 4% of a dose equivalent to 2.24 kg ha<sup>-1</sup> in packed columns of two types of soils from Extremadura (Spain) with zero tillage (with an 8-year-old cover) and conventional tillage. A study of undisturbed columns using a sandy clay loam soil and two sandy loam soils, reports leached amounts of the herbicide less than 0.24% of the initial dose applied (Okada et al. 2016). Studies carried out by authors such as Dollinger et al. 2015 point out that the cation exchange capacity affects the sorption processes of the herbicide, Caetano et al. (2012) indicate how the herbicide can generate stable complexes with Zn<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup>. Other authors such as Ghavamifar et al. (2023) indicate that some minerals such as calcite modify the adsorption processes of the herbicide.

Although GLY mobility in soils is generally low, the addition of phosphorus fertilizers enhances GLY desorption from soils (Dotor-Robayo et al. 2022). The phosphate (P) strongly competes for the same sorption sites as the herbicide, causing its displacement (Wang et al. 2005; Rashmi et al. 2018) and favoring the mobility and diffusion of the molecule (Al Rajab et al. 2008; Zhao et al. 2009; Kanissery et al. 2019). The persistence of GLY in the environment depends not only on its mobility but also on its degradation rates because GLY is mainly mineralized by microbial activity via aminomethylphosphonic acid (AMPA) or sarcosine pathways (Franz et al. 1997; Cuervo and Fuentes 2014).

In Colombia, GLY is the most used herbicide in a wide range of crops (ICA, 2017). Particularly, GLY has been intensively applied to control weed before sowing in paddy production. Earlier research has indicated that GLY has a higher persistence in rice field soils as compared to that of forest or grasslands from Colombian soils (Cuervo and Fuentes 2014). However, there is a gap of knowledge regarding GLY leaching potential and mineralization in tropical soils with similar clay contents and diverse proportions of cations and minerals and the effect of P fertilizers on these two phenomena. The objective of this study was to assess the effect of P on GLY transport and mineralization in tropical paddy soils with the same taxonomic classification but with different mineralogical compositions.

## Materials and methods

### Reagents

Two sources of GLY were used in this study: 1) Roundup® with a formulation of N-(phosphonomethyl) glycine potassium salt at a concentration of 480 g L<sup>-1</sup> equivalent to 363 g L<sup>-1</sup> of N-(phosphonomethyl) glycine (F-GLY) and 2) N-(phosphonomethyl-<sup>14</sup>C) glycine (<sup>14</sup>C-GLY) with an activity of 1.8 mCi mmol from Sigma-Aldrich®. Monoammonium phosphate (MAP, 93%), KBr (99.5%), NaOH, (99.7%), NaHCO<sub>3</sub> (99.5%), Na<sub>2</sub>CO<sub>3</sub> (99.5%) were supplied by J.T. Baker. Other reagents used in the different analytical phases were Carbosorb® and liquid scintillation cocktail Ultima Gold® (Perkin Elmer).

### Soils

Soil samples were taken from paddy fields located in Espinal (soil CS1) and Saldaña (soil CS2) (department of Tolima) and Villavicencio (soil CS3) (department of Meta). Twenty subsamples of each soil were collected (0–20 cm depth) and subsequently homogenized to obtain a representative final sample. The main physicochemical and mineralogical properties of the studied soils are shown in Table 1. The soil–water herbicide distribution coefficient ( $K_d = L \text{ Kg}^{-1}$ ) was determined using the *batch equilibrium* method. For this, in triplicate for each soil, 2 g of soil were placed in 50 mL Nalgene® centrifuge tubes to which 10 mL of GLY solution in Roundup® formulation and radiolabeled glyphosate were added. The final concentration in soil was 0.609 g of GLY kg<sup>-1</sup> and 167 Bq kg<sup>-1</sup> (dose equivalent to 4 L ha<sup>-1</sup> of Roundup®, considering a soil depth of 20 cm and the apparent density values). In the case of  $K_d$  P-gly, P adsorption was previously induced by adding 18.3 mg MAP L<sup>-1</sup> equivalent to 60 kg ha<sup>-1</sup> (Table 1).

### Solute transport

Soil samples were repacked manually into 30 cm long Polyvinyl chloride cylinder columns (Jodeh et al. 2014, Aslam et al. 2015, Gairhe et al. 2021), with an internal diameter of 9 cm. In total, six columns per soil were packed. Then, columns were wetted by capillary action by using water and placed on stands that allowed free drainage and the collection of leachates. Before the pulse, the leachate from the column was analyzed to confirm the presence or absence of GLY.

A pulse of 10 mL solution containing 0.0007954 g a.i. of commercial GLY and 0.2252 μCi of <sup>14</sup>C-GLY was manually applied to each column, homogeneously distributed over the



**Table 1** Soils physicochemical and mineralogical properties

	CS1	CS2	CS3
Soil classification <sup>1</sup>	Typic ustorthents	Typic ustorthents	Umbric tropepts
Coordinates	4° 11' 29.28'' N; 74° 57' 36.30'' W	3° 55' 36.88'' N; 74° 1' 3.49'' W	4° 3' 28.4'' N; 73° 28' 1.52'' W
$\rho_d^2$ (g cm <sup>-3</sup> )	1.2	1.4	1.2
pH	5.9 <sup>a</sup>	5.7 <sup>a</sup>	4.6 <sup>b</sup>
CEC <sup>3</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	12.1 <sup>a</sup>	12.2 <sup>a</sup>	13.2 <sup>a</sup>
OC <sup>4</sup> (%)	1.1 <sup>a</sup>	1.1 <sup>a</sup>	0.08 <sup>b</sup>
Sand (%)	30.5 <sup>a</sup>	31.6 <sup>a</sup>	20 <sup>b</sup>
Silt (%)	19.6 <sup>b</sup>	19.5 <sup>b</sup>	31.9 <sup>a</sup>
Clay (%)	49.9 <sup>a</sup>	48.9 <sup>a</sup>	48.1 <sup>a</sup>
Chlorite (%)	14.5 <sup>c</sup>	23.1 <sup>a</sup>	19.2 <sup>b</sup>
Mica (%)	9.6 <sup>b</sup>	28.0 <sup>a</sup>	–
Amphibol (%)	10.2	–	–
Kaolinite (%)	43.2 <sup>b</sup>	30.6 <sup>c</sup>	54.3 <sup>a</sup>
Lepidocrite (%)	< 1	–	–
Cristobalite (%)	2.2 <sup>b</sup>	2.2 <sup>b</sup>	9.2 <sup>a</sup>
Quartz (%)	11.6 <sup>a</sup>	10.8 <sup>b</sup>	6.0 <sup>b</sup>
Feldespars (%)	2.1 <sup>b</sup>	4.5 <sup>a</sup>	4.3 <sup>a</sup>
Halita (%)	5.2	–	–
Hematite (%)	< 1	–	–
Dolomite (%)	–	< 1	–
Pirofilite (%)	–	–	4.4
Calcite (%)	–	–	2.6
Al <sup>3+</sup> (exchange)	0.2 <sup>b</sup>	0.2 <sup>b</sup>	1.15 <sup>a</sup>
Ca <sup>2+</sup> (meq 100 g <sup>-1</sup> )	3.6 <sup>a</sup>	2.58 <sup>b</sup>	1.96 <sup>b</sup>
Mg <sup>2+</sup> (meq 100 g <sup>-1</sup> )	0.63 <sup>a</sup>	0.68 <sup>a</sup>	0.16 <sup>b</sup>
Mn <sup>2+</sup> (mg Kg <sup>-1</sup> )	17.5 <sup>a</sup>	18.7 <sup>a</sup>	2.40 <sup>b</sup>
P (mg Kg <sup>-1</sup> )	24.07 <sup>a</sup>	5.35 <sup>c</sup>	18.64 <sup>b</sup>
Fe (mg Kg <sup>-1</sup> )	71.7 <sup>c</sup>	144 <sup>a</sup>	61.5 <sup>b</sup>
<i>Kd</i> (gly L Kg <sup>-1</sup> ) <sup>5</sup>	52.96 ± 4.23 <sup>c</sup>	64.09 ± 1.00 <sup>b</sup>	118.41 ± 5.77 <sup>a</sup>
<i>Kd</i> (P-gly L Kg <sup>-1</sup> ) <sup>6</sup>	12.05 ± 1.09 <sup>c</sup>	45.60 ± 2.53 <sup>b</sup>	242.42 ± 6.76 <sup>a</sup>

<sup>1</sup>Soil survey staff (2014), <sup>2</sup>density, <sup>3</sup>CEC Cation exchange capacity, <sup>4</sup>OC Organic carbon, <sup>5</sup>value obtained for 4L ha<sup>-1</sup> using the batch equilibrium method, <sup>6</sup>value obtained by previously inducing the adsorption of MAP in a dose equivalent to 60kg ha<sup>-1</sup>, <sup>7</sup>Different lower-case letters indicate statistically significant differences between soils

entire surface using a 10 mL pipette, while ensuring no contact with the column edges. The applied dose was equivalent to the recommended Roundup® field dose (4 L ha<sup>-1</sup>). To estimate non-reactive solute transport parameters, bromide (0.58 g KBr) was also included in the pulse solution. Immediately after the pulse application, 90 mL of deionized water was added to the columns to complete a total volume of 100 mL applied to each column. Then a water addition of 100 mL day<sup>-1</sup> was established. Twenty-four hours after the application of the initial pulse, 60 kg ha<sup>-1</sup> of MAP was added to three of the columns of each soil. The leachate was collected and weighed every 24 h. The experimental design consisted of a factorial arrangement, with the following factors: type of soil and treatment with (P) or without MAP

(PO), with three replicates for each treatment resulting in a total of 18 columns.

### Bromide (Br<sup>-</sup>) quantification

The quantification of Br<sup>-</sup> in the leachate was carried out by High Performance Liquid Chromatography (HPLC) (Agilent Technologies 1100 series, Palo Alto, CA, USA) equipped with a quaternary pump, a manual injector (20 µL loop), an Alltech Allsep analytical column (100 × 4.6 mm, 7 µm) and a diode array detector (DAD). The mobile phase consisted of an aqueous buffer solution (2.8/2.2 mM 100% NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>) in isocratic mode, with a flow of 1.3 mL min<sup>-1</sup>. Before the chromatographic injection, an aliquot of 1.5 mL of each leachate

sample was filtered with 0.45-mm syringe filters and subsequently transferred to 2 mL vials. A calibration curve was prepared, using known Br<sup>-</sup> concentrations that contained 0; 6.71; 13.42; 26.86; 33.59; 3357.25; 6714.69; and 10,071.74 mg of Br L<sup>-1</sup> (R<sup>2</sup> = 0.98). The retention time for Br<sup>-</sup> was 4.3 min, and the wavelength used for the determination was 299 nm. The parameters of the quantification process were carried out according to the methodology implemented by Martínez-Cordón et al. (2015). The detection limit was determined at 0.046 mg L<sup>-1</sup> and the quantification limit at 0.15 mg L<sup>-1</sup>.

## GLY analysis

### Leachates

The daily collected leachates were analyzed to determine the concentration of <sup>14</sup>C-GLY using a Perkin Elmer 29010TR Tri-Carb Liquid Scintillation Counter (LSC). The quantification was carried out using 1 mL of each sample, which was mixed with 5 mL of Ultima Gold™ liquid scintillation cocktail in Picoglass® vials.

### Elution curves

Breakthrough curves (BTC) for Br<sup>-</sup> and GLY were obtained by plotting the C/C<sub>0</sub> ratio versus the number of pore volumes (V/V<sub>p</sub>) collected in the effluent; V<sub>p</sub>, the pore volume, was calculated as the difference between the weight of water saturated soil and the weight of dry soil in the columns, after 24 h of drainage.

### Quantification of mineralized GLY

CO<sub>2</sub> traps were used to quantify <sup>14</sup>C-GLY mineralization in the columns. The traps consisted of a 10 mL solution of 10% NaOH w/v placed at the top of the columns, which were sealed to prevent any gas leaks. The NaOH solution was collected daily and replaced with a new 10% NaOH solution. <sup>14</sup>CO<sub>2</sub> concentration (which corresponded to the degradation of labeled GLY) was measured in the collected sample by mixing 1 mL of the NaOH solution with 10 mL of Ultima Gold® liquid scintillation cocktail and quantified in the LSC.

With the quantified values of <sup>14</sup>CO<sub>2</sub>, mineralization kinetics were determined using the bi-phasic model (Eq. 1). This model assumes there are two different degradation rates of the compound, one for the strongly-bound residues to the soil matrix and another for the easily bio-degradable residues of the compound (Bohany et al. 2015).

$$C_t = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \quad (1)$$

where, C<sub>t</sub> = concentration at time t (day), C<sub>1</sub> and C<sub>2</sub> = initial concentration for compartments 1 and 2, k<sub>1</sub> and k<sub>2</sub> = first and

second order dissipation rate constant (day<sup>-1</sup>) and t = time (Bohany et al. 2015). Due to the analytical results, the DT<sub>50</sub> values could not be determined directly. Therefore, iterative methods based on Nafta (2011); Okada et al. (2019) were employed to estimate the DT<sub>50</sub> values.

### Soil-bound residues

At the end of the transport experiment, the columns were horizontally sectioned into six fractions (5 cm). Each fraction weighed approximately 215 ± 15 g. Then, samples were individually homogenized, and a portion of the soil was taken from each fraction and air-dried for 24 h. An aliquot of each sample (150–200 mg) was combusted in a Harvey Corporation 0X-600® Biological Oxidizer. The <sup>14</sup>CO<sub>2</sub> generated in the Biological Oxidizer was captured in vials containing 20 mL of Carbosorb®. Once the oxidation process of the sample was completed, 20 mL of Permafluor® was added to each trap and subsequently analyzed in the LCC to quantify the <sup>14</sup>C-GLY bound residues.

### Statistical analysis

The ANOVA and Tukey test were used to compare means between soils and treatments using the software package from SAS OnDemand for Academics. The relationship between variables was carried out by regression analysis and the significance level was set at a p < 0.05.

## Results and discussion

### Characterization of Br<sup>-</sup> leaching

Br<sup>-</sup> is used as a tracer in pesticide transport studies in soils. It is a rare and non-reactive element in soils, so describing its movement allows us to describe the movement of water in the columns (Dousset et al. 2007). Br<sup>-</sup> BTC are shown in SI Fig. 1. The average values of Br<sup>-</sup> total recovery, peak time arrival, and pore velocity for each soil are shown in SI Table 1. Br<sup>-</sup> recovery ranged from 87.78 ± 2.78 to 90.25 ± 0.68%. Normally, Br<sup>-</sup> recoveries above 85% are accepted in this type of assay (Dousset et al. 2007). The statistical analysis indicated that the addition of MAP did not affect Br<sup>-</sup> transport, therefore only the average values for each soil are presented. The Br<sup>-</sup> peak was recorded at approximately 0.9 V/V<sub>p</sub> in soils CS2 and CS3, while in soil CS1 the Br<sup>-</sup> peak occurred at 1.1 V/V<sub>p</sub> (S3). The retardation in peak arrival observed in CS1 could be explained by the higher clay content and density of this soil. These factors can



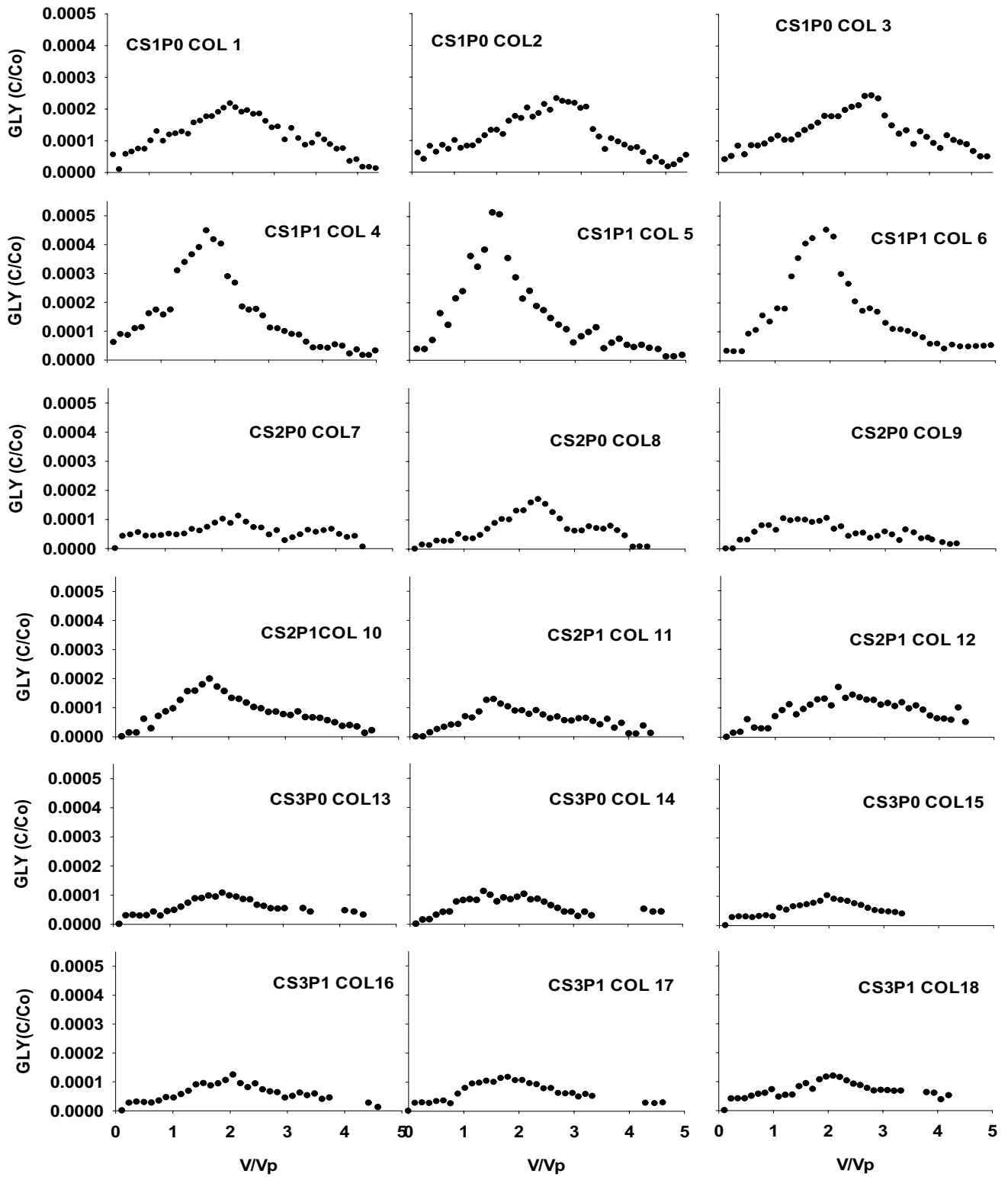


Fig. 1 Experimental BTC of GLY in the soil columns without P (P0) and with added phosphorous (P1)

cause a longer time in the movement of the solute through the column (Dousset et al. 2007; Bromly et al. 2007).

### Characterization of GLY leaching

GLY BTC are shown in Fig. 1. GLY was detected in the first fractions of the leachates indicating that a small fraction of the herbicide is not retained in the soil column and thus, is transported with the water flow (Okada et al. 2018). GLY peak arrival time ( $T_a$ ) ranged from 1.90 to 3.38  $V/V_p$  (Table 2). In all soils and treatments, GLY had a higher peak arrival time than  $\text{Br}^-$ , indicating that the sorption capacity of the soils causes a delay in the vertical transport of GLY. The  $T_a$  of GLY was significantly different in the interaction soils-treatment ( $p < 0.05$ ) (Table 2). In Soil CS1 the  $T_a$  was 1.5 times higher than the  $T_a$  in CS2 and CS3. However, when MAP was added to the columns, GLY  $T_a$  decreased significantly in soils CS1 and CS2, but it did not affect GLY displacement in CS3 (Table 2 and Fig. 1).

The maximum peak concentration ( $T_{max}$ ) ranged from  $1.04^{-4}$  to  $4.94^{-4}$ . There was a significant interaction between soils and treatments, in which soil CS1 had the highest GLY concentration at the peak of the leachate, both at P0 and P1 treatments when compared to the other soils (Table 2). When we compare treatments among the same soil, the addition of P increased by 200% the amount of GLY detected at the  $T_{max}$  concentration in soil CS1. In soils CS2 and CS3, the peak concentration did not differ when P was added to the columns.

$T_a$  positively correlated with kaolinite content ( $r = 0.974$ ). The  $T_{max}$  correlated negatively with  $\text{Mg}^{2+}$  ( $r = -0.93$ ),  $\text{Fe}^{3+}$  ( $r = -0.813$ ),  $\text{Mn}^{2+}$  ( $r = -0.967$ ) and calcite ( $r = -0.946$ ). The results in  $T_a$  and  $T_{max}$  are indicators that, although the soils have similar clay percentages, the movement of the herbicide is recorded at different speeds and concentrations,

and in this case, the presence of high contents of kaolinite clays is not the only factor that affects the movement of the herbicide. Furthermore, it is found that the presence of cations (in this case  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ) and other minerals, such as calcite, also affect the behavior of the molecule in each soil. Results associate the possibility that GLY forms complexes with divalent cations (Borggaard et al. 2005), such as manganese (Huber and Jones 2013), magnesium, and iron (Caetano et al. 2012). The correlation observed in the case of calcite would be in accordance with that reported by Ghavamifar et al. (2023) who point out this mineral as a potential GLY adsorbent.

The amount of GLY leached in all columns was less than 7% of the initially applied concentration (Table 2). The highest percentage of leached GLY occurred in soil CS1, compared to the amount leached in soils CS2 and CS3. This result can be associated to the higher pH and P concentration found in soil CS1, which increase GLY retention. Leached quantities correlated negatively with the parameters  $Kd$  ( $r = -0.864$ ), % adsorption ( $r = -0.871$ ),  $\text{Ca}^{2+}$  ( $r = -0.997$ ),  $\text{Mg}^{2+}$  ( $r = -0.715$ ),  $\text{Mn}^{2+}$  ( $r = -0.734$ ). These results are consistent with others reported in Borggaard et al. (2005), Caetano et al. (2012), Huber and Jones (2013), who point out that cations act as herbicide adsorbents. In relation to pH, Sidoli et al. (2016) reported that an increase in this parameter favors changes in the protonation of the substrate, which results in greater frequency in the repulsion of the soil molecule and bioavailability. In this study, CS1 and CS2 have a higher pH value, compared to CS3.

In soil CS1, the addition of P caused a significant increase in the amount of displaced GLY by 1.2%. Phosphorous fertilizers can increase GLY leaching depending on the retention capacity and the composition of the soils (Munira et al. 2016). Zhao et al. (2009), found that the addition of P increases the velocity of GLY movement in sandy loam soils, while in a sandy soil, the addition of P does not generate changes in GLY.

The  $Kd$ -the ratio between the herbicide concentration in soil and the concentration in the liquid phase-, is a parameter frequently used in fate and contaminant transport calculations, as it estimates the potential for the adsorption of dissolved contaminants in contact with soil (Fenn et al. 2023). When no MAP was applied (P0) the soils had different  $Kd$  values (Table 1). However, after the addition of MAP (Table 1), the  $Kd$  values in CS1 decreased significantly when compared to the P0 treatment (Table 1). The  $Kd$  values are consistent with what was observed in the displacement of the herbicide in the columns, the effect of P on the adsorption process was associated with the higher affinity of the soil for P, a process that results in the displacement of GLY previously adsorbed in the soil (Waiman et al. 2012).

Previous results in soil columns have shown that phosphorus fertilizers can increase the leaching of GLY

**Table 2** Experimental transport parameters for GLY BTC

Soil	treatment	$T_a$ ( $V/V_p$ )	$T_{max}$ ( $C/C_0$ )	TL Gly (%)
CS1	P0	$3.38^{a(1)A(2)} \pm 0.28$	$2.31^{-4b} \pm 1.29^{-5}$	$5.05^b A \pm 0.12$
	P1	$1.77^b A \pm 0.11$	$4.94^{-4a} \pm 4.02^{-5}$	$6.24^a A \pm 0.49$
CS2	P0	$2.28^a B \pm 0.07$	$1.29^{-4a} \pm 3.59^{-5}$	$4.40^a B \pm 0.23$
	P1	$1.62^b A \pm 0.19$	$1.50^{-4a} \pm 4.19^{-6}$	$4.89^a B \pm 0.43$
CS3	P0	$1.99^a B \pm 0.09$	$1.04^{-4aB} \pm 2.6^{-6}$	$4.00^a B \pm 0.12$
	P1	$1.90^a A \pm 0.09$	$1.20^{-4aB} \pm 3.7^{-6}$	$4.16^a B \pm 0.47$

$T_a$  Peak arrival time,  $T_{max}$  Maximum GLY concentration in peak, TL Total leached GLY <sup>(1)</sup>Different lower-case letters indicate statistically significant differences between treatments for each soil, <sup>(2)</sup>Different upper-case letters indicate statistically significant differences between soils under the same treatment



depending on the retention capacity due to the composition of the soils (Barret and Mc Bride, 2007; Zhao et al. 2009; Fenn et al. 2023). Zhao et al. (2009), in the case of a sandy loam soil (Alluvic Primosols) at a dose of 220 mg of herbicide in a column, recorded a maximum leaching peak at 5.44 Vp when P is not applied and 4.33 Vp when it is applied, while in a soil sandy Sandic Primosols, with the same dose of GLY, the addition of P does not generate changes in the peak values, being 3.39 Vp without the addition of P and 3.62 Vp with the addition of P. These authors highlight that the addition of P can increase the speed of herbicide movement, but it is not a generalizable result in soils. In this regard, Wang et al. (2005) indicate

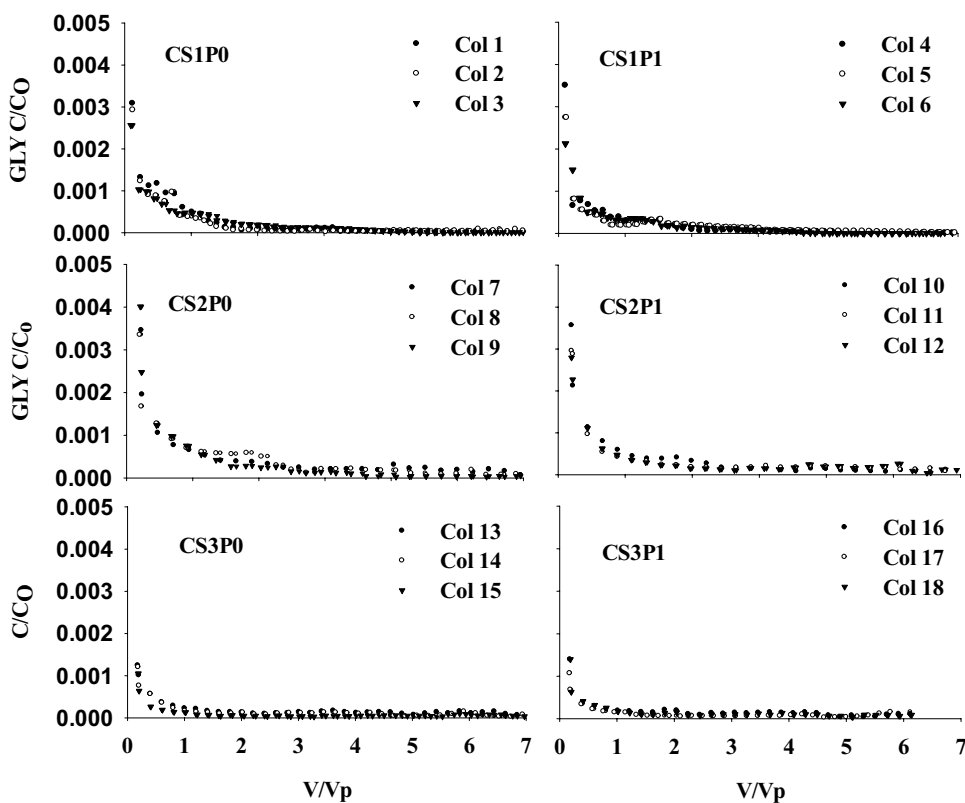
that, although P can alter the adsorption of GLY, the effect depends on the carrying capacity of the soil, among other factors.

### Mineralization

GLY mineralization was quantified by measuring the amount of <sup>14</sup>CO<sub>2</sub> released daily in the columns. In all soils and treatments, there was an initial fast dissipation of GLY during the first V/V<sub>p</sub> (V<sub>p</sub>= six days approximately) (Fig. 2).

The GLY mineralized data adjusted well to a bi-exponential model (Fig. 2, Table 3) and show how the partition of GLY in soil and water generates different degradation

**Fig. 2** Relative concentration of GLY mineralized in the soil columns without P (P0) and with the addition of P (P1)



**Table 3** GLY mineralization bi exponential model parameters. C<sub>1</sub> and C<sub>2</sub> represent the initial concentrations for compartments 1 and 2, respectively; mineralized total (%), first (k<sub>1</sub>) and second (k<sub>2</sub>) GLY mineralized day<sup>-1</sup>

Soil	Treatment	Total mineralized (%)	r <sup>2</sup>	C <sub>1</sub> (mg Kg <sup>-1</sup> )	K <sub>1</sub> (days <sup>-1</sup> )	C <sub>2</sub> (mg Kg <sup>-1</sup> )	K <sub>2</sub> (days <sup>-1</sup> )
CS1	P0	19.14 <sup>b(1)A(2)</sup> ± 0.88	0.99	0.008 <sup>a</sup> ± 0.001	-0.193 <sup>a</sup> ± 0.079	0.021 <sup>a</sup> ± 0.002	-0.001 <sup>a</sup> ± 0.001
	P1	16.76 <sup>bB</sup> ± 0.43	0.98	0.008 <sup>a</sup> ± 0.001	-0.147 <sup>a</sup> ± 0.069	0.024 <sup>a</sup> ± 0.001	-0.001 <sup>a</sup> ± 0.0002
CS2	P0	24.45 <sup>aA</sup> ± 1.47	0.99	0.009 <sup>a</sup> ± 0.001	-0.261 <sup>a</sup> ± 0.105	0.03 <sup>a</sup> 1 ± 0.001	-0.004 <sup>a</sup> ± 0.001
	P1	23.12 <sup>aA</sup> ± 0.63	0.99	0.008 <sup>a</sup> ± 0.000	-0.413 <sup>a</sup> ± 0.140	0.033 <sup>a</sup> ± 0.001	-0.004 <sup>a</sup> ± 0.001
CS3	P0	10.93 <sup>cA</sup> ± 2.54	0.99	0.008 <sup>a</sup> ± 0.009	-0.183 <sup>a</sup> ± 0.217	0.036 <sup>a</sup> ± 0.009	-0.002 <sup>a</sup> ± 0.0002
	P1	10.72 <sup>cA</sup> ± 1.11	0.99	0.007 <sup>a</sup> ± 0.010	-0.128 <sup>a</sup> ± 0.110	0.036 <sup>a</sup> ± 0.009	-0.002 <sup>a</sup> ± 0.0003

<sup>(1)</sup>Different lower-case letters indicate statistically significant differences between soil, <sup>(2)</sup>Different upper-case letters indicate statistically significant differences between treatments for each soil

rates ( $k_1 > k_2$ ) (Bohany et al. 2015) and is in accordance with Strange-Hansen et al. (2004) who show the fast mineralization during the first days after applying GLY to the soil columns. The average total mineralization in each soil was  $CS2^a$  (22.65%)  $< CS1^b$  (17.95%)  $< CS3^c$  (11.05%), the addition of MAP affects the mineralization only in CS1 (Table 3). A negative Pearson correlation ( $r = -0.61$ ) was observed between the bound residues in the soil and the mineralized quantities. These results indicate that the strength of herbicide adsorption affects negatively the mineralization rate due to the lower availability of the herbicide for degradation (Strange-Hansen et al. 2004; Kulikova et al. 2020), aspect that partly explains the lower  $^{14}CO_2$  production in CS3.

Considering other studies, the percentage of total GLY mineralization with respect to the initial applied concentration are low, probably due to the small percentages of organic carbon (OC) in soils (OC CS1 = 1.1%; OC CS2 = 1.1%; OC CS3 = 0.08%) which do not favor the development of the microbial populations that can metabolize the herbicide (Kanissery et al. 2015). Landry et al. (2005), evaluated the movement of the herbicide in columns in a bare Calcosol soil (3.6% OC) and with vegetal cover (3.5% OC) and they recorded, after 42 days of the test, mineralization values of 43.5 and 46.5% respectively. In Colombia, Cuervo and Fuentes (2014), found in forest soils (3.97% OC), grass (7.41% OC) and rice cultivation (1.3% OC), in biometers, under laboratory conditions, values of 53, 38 and 23%, respectively, 106 days after application, being the rice cultivation values closer to those observed in this study. In this case, the authors relate the results to high clay contents in soils and low contents of OC (Cuervo and Fuentes 2014).

### Glyphosate-bound residues (GBR) in soil columns

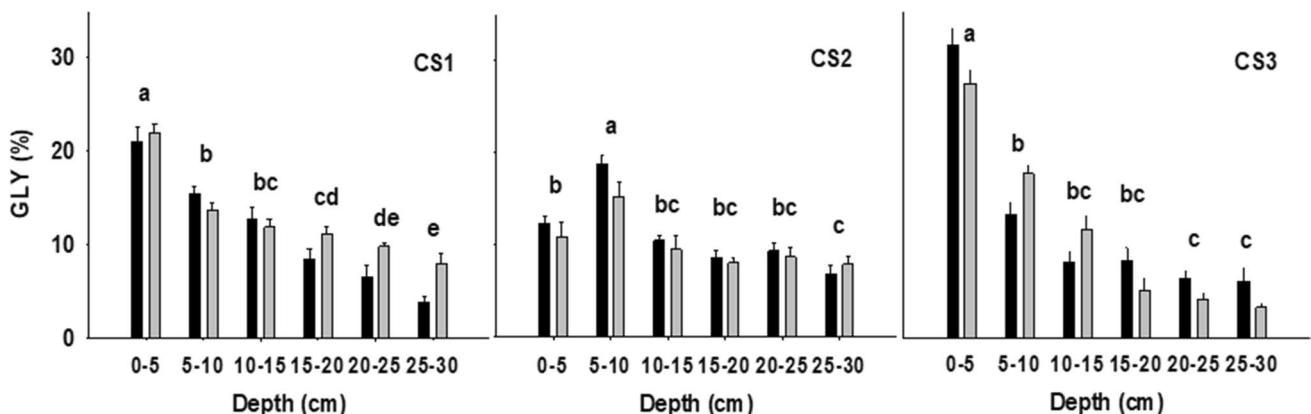
At the end of the leaching experiment, the soil columns were divided into six fractions and GLY concentration was measured in each segment. Overall, more than 60% of the

applied GLY was retained in the soil columns, indicating a high retention of the herbicide in the soil matrix. GLY was mostly retained in the upper 5 cm of the soil columns in CS1 and CS3, while in soil CS2 GLY maximum concentrations were detected in the 5–10 cm segment (Fig. 3).

There were no differences between treatments in GLY concentration in each segment, therefore the addition of P did not influence GLY vertical distribution in the soil column. The percentages of GLY-bound residues (GBR) in the soils were  $69.31 \pm 5.45\%$  for CS1,  $63.36 \pm 2.24\%$  for CS2 and  $71.04 \pm 2.00\%$  for CS3 (Table 4), no statistical difference was observed due to treatment. The percentage of GBR was positively correlated with kaolinite content in soils ( $r = 0.85$ ) and exchangeable Al ( $r = 0.59$ ) and was negatively correlated with the soil pH ( $r = -0.50$ ). The results indicate that GLY does not dissipate quickly, since a high percentage remains in the soils, forming bound residues. The GBR percentages are higher than those presented in other studies. Al Rajab et al. (2008) report herbicide residues between 15 and 46% in a  $^{14}C$ -GLY infiltration test in soil columns and Mamy et al. (2016) found non-extractable GLY values between 8 and 16%. Other studies have shown how the percentage of bound residues in the soil increases as the soil-herbicide contact time increases (Al Rajab et al. 2014). CS2 exhibits variations in the distribution of GBR within the first 10 cm

**Table 4** GLY half-life time ( $DT_{50}$  and  $DT_{90}$ ) and first and second order dissipation rate constant ( $k_1$  and  $k_2$ )

Soil	CS1	CS2	CS3
Total GLY in soils	$69.31 \pm 5.45$	$63.36 \pm 2.24$	$71.045 \pm 2.0$
$R^2$	0.99	0.99	0.99
$K_1$	$0.225 \pm 0.05$	$0.245 \pm 0.04$	$0.4 \pm 0.164$
$K_2$	$0.002 \pm 0.0001$	$0.0035 \pm 0.001$	$0.002 \pm 0.0004$
$DT_{50}$ (days)	$3.44 \pm 1.19$	$2.36 \pm 0.84$	$2.35 \pm 1.35$
$DT_{90}$ (days)	$1209.86 \pm 342$	$833.09 \pm 360$	$1212.45 \pm 488$



**Fig. 3** Soil GLY-bound residues at different depths of the soil columns





compared to CS1 and CS3 soils (Fig. 3). This result suggests that in this soil there is greater availability of the herbicide present in the upper layer for mineralization since the final percentage of leachates is not greater, and neither is the formation of bound residues (the least of the three soils).

## Persistence in soil

The half-life time ( $DT_{50}$ ) and  $DT_{90}$  was calculated to the GLY remanent in soils (excluding leached and mineralized GLY). The values show adjustment to the bi-exponential or biphasic model -Eq. 1- (Table 4) and there was no statistical difference between treatments (P0 and P1). The estimated values of  $DT_{50}$  for CS1 were  $3.44 \pm 1.19$ ; CS2  $2.36 \pm 0.84$  and CS3  $2.35 \pm 1.35$  days. The  $DT_{90}$  in CS1 were  $1209.86 \pm 342$ ; CS2  $833.09 \pm 360$  and CS3  $1212.45 \pm 488$  (Table 4).

The results suggest that the herbicide, once in the soil, undergoes interactions of varying energy levels and reversibility. This implies that a fraction of the herbicide degrades rapidly, likely due to higher bioavailability, while another fraction exhibits a slower degradation rate (Sun et al. 2019; Okada et al. 2019).

## Conclusion

Approximately, 95% of GLY was retained in the studied rice paddy soils, indicating that GLY has a low leaching potential under the studied conditions. The addition of P increased glyphosate displacement by 1.2% only in CS1 soil.

The results indicate that although high contents of kaolinic clays are important in the adsorption and translocation of the herbicide, the presence of calcites and divalent cations modify this process, favoring the persistence of the molecule in the soil.

In all the cases evaluated, the high percentages of GLY soil bound residues indicate the stability of the interaction between the herbicide and the soil. This finding implies a greater permanence of the herbicide in the environment, as shown by the high  $DT_{90}$  values (average 1084.84 days for all soils). Most GLY degradation occurs during the first days of soil-GLY contact indicating that the retention of the soil in the first moments is not stable enough, allowing the mineralization of the molecule. Subsequently, the biodegradation process progressively decreases as more stable bonds are formed and the herbicide descends in depth. There was no effect on the degradation rate after the addition of MAP in the studied soils.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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