Metsulfuron-methyl and glyphosate transport in a mollisol soil in the Pampean region of Argentina

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Abstract

The agricultural activity poses the potential risk of contaminating groundwater resources because of the leaching capacity of the agrochemicals used. Glyphosate and metsulfuron-methyl are two herbicides widely used in the Pampean region of Argentina. The objective of this study was to evaluate the vertical transport of both herbicides in the soil profile of a typic Argiudoll, under laboratory conditions. Bromide (equivalent to 1500 kg ha^{-1}) was used as a non-reactive solute, and metsulfuron-methyl (equivalent to 10 g ha^{-1} of the active ingredient, a.i.) and glyphosate (equivalent to 5 kg ha^{-1} of a.i.) were used as reactive solutes. Six replicates per horizon were used. The transport parameters were estimated using the convection-dispersion equation (CDE) and analysed using mixed models. A preferential flow by macropores was the mechanism dominating the transport of the substances in the horizons under study. The following recovery percentages were found in effluents: bromide 72.4, 83.75 and 90.49%, metsulfuron-methyl 51.7, 56.5 and 67.0%, and glyphosate 0.75, 1.76 and 0% in horizons A, B and C, respectively. Metsulfuron-methyl presented higher leaching capacity in the horizons studied than glyphosate, which was retained in the first centimetres of each column. Thus, metsulfuron-methyl poses a high potential risk of contaminating groundwater, as opposed to glyphosate, which involves a low to negligible risk.

Keywords: Soil columns, solute transport, groundwater, leaching, preferential flow, herbicides

Introduction

The General Assembly of the United Nations recognises the human right to sanitation and safe, healthy, and clean water. Nations have incorporated this right into several regulations (FAO, 2015). However, three out of ten people in the world (2.1 billion people) lack access to safe and available water, and six out of ten people (4.5 billion) lack safe sanitation (WHO, 2017).

In Argentina, seven million people do not have a drinking-water service. In rural areas, the potable water service is non-existent and the supply comes from surface and groundwater. The residents in these rural areas use domestic wells as a source of drinking-water (Costa *et al.*, 2002). Groundwater is the most important source of water for human consumption in the Argentine Pampean region. Despite its importance, this resource has limitations, in terms of quality, resulting from human activities (FAO, 2015).

Agricultural activities are considered a source of nonpoint pollution of groundwater due to the vertical transport of the compounds used (Rodriguez *et al.*, 2019). In this sense, the fate and movement of dissolved substances is a topic of interest to the scientific community (Toride *et al.,* 1995). Understanding the transport mechanisms that can occur in the soil is fundamental to determining the potential for contamination of a pesticide (Zhou *et al.*, 2010). The properties of the pesticides partly determine their leaching. Some databases can be used for this determination (e.g., PPDB, 2020), but caution should be exercised in their use. When possible, it is preferable to carry out measurements directly on the studied soils to obtain more precise values of their properties. In one study, the measured K_d were more in agreement with the pesticide lag in undisturbed soil column experiments than with the PPDB (2020) values, which were less reliable in view of the leaching results obtained (Cueff *et al.*, 2020). These authors concluded that the type of soil strongly influences the leaching of pesticides by conditioning the transport mechanisms. On the other hand, agricultural

practices can improve the connectivity of the pore network and the water flow becomes predominantly vertical. In such a situation, the main risk is that preferential flows occur in the macroporosity and generate pesticide transfers. Laboratory experiments with undisturbed soil columns are a starting point for estimating the leaching behaviour of pesticides. These experiments allow evaluating the mobility of the compound and estimating transport parameters through the use of models (Katagi, 2013). One of the most widespread models is the convection-dispersion equation (CDE) proposed by Parker and van Genuchten (1984).

Two million tons of pesticides are used annually in the world. China is the main contributor, followed by the United States and Argentina (Sharma *et al.*, 2019). In Argentina, it was estimated that pesticide consumption in 2017 was 196008.03 tons, 93.7% of which corresponded to herbicides, with glyphosate being the most widely used (FAO, 2018; Sharma *et al.*, 2019).

Glyphosate (N-(phosphonomethyl) glycine) is a systemic post-emergent, non-selective, broad-spectrum organophosphate herbicide (Calderón *et al.*, 2005). It is used in chemical fallows and in the production of genetically modified crops (Benbrook, 2016). Its main metabolite is AMPA (aminomethylphosphonic acid). Glyphosate is usually applied alone or in combination with other pesticides, and it is widely used throughout Argentina and the world. One of the herbicides with which glyphosate is used is metsulfuron-methyl (Methyl 2-(4-methoxy-6-methyl1, 3, 5-triazin-2-ylcarbamoylsulfamoyl) benzoate), a systemic herbicide, used because of its high activity at low rates of application and its residual power (Pons and Barriuso, 1998). In the Pampean region of Argentina, metsulfuron-methyl is used with glyphosate in fallow land of soybean, wheat and oats and with other agrochemicals during the growth stage of wheat and barley, in doses that reach 10 g active ingredient (a.i.) ha^{-1} per year. Glyphosate is also used in the chemical fallowing of sunflower, maize, barley, potato and rape, as well as in the growth of soybean and maize, in doses that reach 5 kg a.i. ha^{-1} per year (Pérez *et al.*, 2017). During the 2019/20 crop year, 40019861 ha were sown in Argentina, 42.2% of which were used for soybean production, 23.7% maize, 17.4% wheat, 3.9% sunflower, 3.7% oats, 3.2% barley, and the remaining 5.9% for other crops (Ministerio de Agricultura, Ganadería y Pesca, 2021), implying an intensive use of both herbicides, especially glyphosate. These herbicides have different physical-chemical characteristics, which result in different behaviours in the soil. Glyphosate is strongly sorbed to the soil matrix (Ozbay *et al.*, 2018), with limited leaching. Studies carried out on undisturbed soil columns in the

laboratory reported recovery rates of 0.24% (Okada *et al.*, 2016) and 0.01% (Dousset *et al.*, 2004) of the initial amount, while in an experiment with disturbed columns, the recovery rate was 4% (Calderón *et al.*, 2005). These recovery rates must be transformed in each environment to determine the total amount of herbicides leached. In the Rio Sali basin, it was estimated that the amount of atrazine leached should not exceed 1% and 0.5%, according to the standards of Australia and the United States for this molecule (Portocarrero *et al.*, 2019).

Despite its low mobility, groundwater monitoring has detected the presence of the herbicide and its metabolite, indicating some form of transport. Van Stempvoort *et al.* (2014) identified average glyphosate and AMPA concentrations of up to 0.663 µg L^{-1} and 0.698 µg L^{-1}, respectively, in Canada, while Okada *et al.* (2018) found average concentrations of 0.4 µg L^{-1} of glyphosate in south-eastern Buenos Aires. These data suggest that the herbicide can transport itself through the soil profile and reach the groundwater despite its great affinity for the soil matrix, implying a potential risk of contamination of the resource. The data also reveal a possible contradiction between laboratory studies and field monitoring, which may be due to the fact that the vertical transport studies carried out in laboratories so far have been mainly performed on the surface horizon of the soil. Gjettermann *et al.* (2009) studied the vertical transport of glyphosate in undisturbed soil columns obtained at a depth of 0–50 cm; Zhao *et al.* (2009), Zhou *et al.* (2009) and Okada *et al.* (2016) studied this process at a depth of 0–15 cm; de Jonge *et al.* (2000) used undisturbed soil columns obtained at a depth of 2–22 cm; and Dousset *et al.* (2004) used undisturbed soil columns extracted at 0–20 cm. Candela *et al.* (2007) and Calderón *et al.* (2005) worked with disturbed soil columns obtained in the first case at 0–20 cm and 70–100 cm in depth, and 0–30 cm in the second case. Although the former study mentioned includes deeper horizons, it was performed with samples of disturbed soil, which alters the structure of the soil and makes it difficult to understand the dominant transport mechanism. All the laboratory studies mentioned above focused on the superficial soil horizon but ignored the behaviour of this pesticide at greater depths, which may explain why a molecule that is strongly adsorbed to the soil and has such low mobility can be found in groundwater, as shown by the field monitoring.

By contrast, metsulfuron-methyl has been described as a compound with low soil adsorption (Oliveira *et al.,* 2001; Hall *et al.*, 2015) and high leaching capacity. The laboratory studies on soil columns reported so far are limited; Sondhia (2009) used disturbed soil columns and indicated that the

herbicide moved almost at the same rate as water in the soil, but the herbicide transport mechanism was not analysed. In a field experiment, Black *et al.* (1999) observed that metsulfuron-methyl leached between 40 and 80% of the initial amount, while Sarmah *et al.* (2000) detected the mobility of the compound down to a depth of 1.20 m. Broadly speaking, it is a less studied pesticide with a high leaching capacity and a considerable risk of groundwater contamination. Although several studies have estimated its leaching potential, the mechanisms dominating the vertical transport of this herbicide in the soil profile are unknown. As mentioned above, few studies have focused on the transport behaviour of this herbicide, and this line of research has mainly explored the superficial horizon. Therefore, the pesticide behaviour at greater depths of the soil profile is not known.

In an area where agriculture is the main economic activity, the importance of knowing the vertical transport of the pesticides applied in the soil profile is crucial to protecting such a vital resource for society as groundwater. Thus, the objective of this research was to study the vertical transport of glyphosate and metsulfuron-methyl in each of the three main horizons of a Mollisol (typic Argiudoll) soil profile, in undisturbed columns. Since there is still little or no information on the vertical transport behaviour of glyphosate and metsulfuron-methyl in deep soil horizons, this article contributes to the knowledge of this process, by focusing on the soil profile, and is the first report to consider deeper horizons.

Materials and Methods

Site description and sampling

This research was conducted using soil samples from a typic Argiudoll from EEA INTA Balcarce (37° 52' 49.64" S, 58° 17' 41.27" W), composed of the Mar del Plata (typic Argiudoll, fine silt, mixed, very deep, thermal) and Balcarce series (petrocalcic Argiudoll, silt fine, mixed, moderately deep, thermal) (INTA, 1970; USDA, 2014). This soil is designed for agricultural use, and it corresponds to a long-term experiment conducted by the National Institute of Agricultural Technology (INTA). The average annual rainfall in this area is 916 mm, and the average annual temperature is 14.3 °C. The frost-free period is 271 days (Caviglia *et al.*, 2019). This experiment consists of the subdivision of the lot into 10x40m plots where a treatment involving a reduction in the use of agrochemicals would be tested after our sampling and compared with the usual management carried out by producers in the area. This treatment was not relevant to our vertical transport study because we used the plots of the experimental lot only to collect soil samples, take them to the laboratory and study the vertical transport of the molecules in question. The soil samples were collected from the central point of each plot. Six undisturbed samples were taken from each main horizon in the soil under study to perform the vertical transport experiment (horizons A, B and C). Additional samples were taken from the same points to verify previous concentrations of glyphosate, AMPA and metsulfuron-methyl in each horizon. These samples were obtained using a soil sampler with a stainless steel cylinder (8.5 cm in inner diameter, 15 cm in length). The columns were covered and stored at 4 °C until use. The sampling depth for each horizon was 0–15 cm for horizon A, 30–45 cm for horizon B, and 75–90 cm for horizon C. At sampling time, the samples were taken and the soil was covered with pasture (start of the field experiment).

From the same points and depth, disturbed soil samples were taken (composite sampling), dried at 30 °C and sieved through 2 mm. For each horizon, six repetitions were used in each of the following determinations: texture (Robinson pipette method, Soil Conservation Service, 1972); organic carbon (OC, chromic acid method, Walkley and Black, 1934); cation exchange capacity (CEC, determined by displacement with ammonium acetate at pH 7, Chapman, 1965); pH (measured in soil-water solution [1:2.5] with Orion Expandable Ion Analyzer EA 940); and electrical conductivity (EC, measured in Orion Thermo Conductivity Meter, model 150+). Saturated hydraulic conductivity, bulk density (cylinder method, Blake and Hartge, 1986), porosity and macroporosity (Stakman *et al.*, 1969) were also determined for each sampling point.

Transport experiments

The study was conducted under controlled laboratory conditions, at constant temperature (23 °C under isothermal conditions). The temperature was kept constant by maintaining the laboratory as hermetically sealed as possible and using hot-cold equipment. Records were taken daily approximately every 6 hours to corroborate this value. At the beginning of the experiment, six repetitions were set for each horizon. Since two soil samples from horizon B failed to leach, four replicates were performed for this horizon, while six replicates were performed for horizons A and C (n=16).

A porous membrane, a porous stainless steel plate and a cover with an inlet hole were placed at both ends of the columns. The columns were pre-saturated by capillarity with $CaCl_2$ (0.01 M). $CaCl_2$ was used as a leachate solution to prevent the columns from collapsing. The upper hole was connected to a syringe pump, and the lower hole to a vacuum chamber with constant pressure (-4.5Kpa), inside

which a fraction collector was installed (Retriever II, Isco Inc., Lincoln, NE, USA). $CaCl_2$ (0.01 M) with a flow rate of 4.43 mm h^{-1} was injected through the upper hole for 24 hours to reach equilibrium.

During the experiment, the columns received a constant flow of $CaCl_2$ (0.01 M), which was interrupted at two points. First, a pulse of KBr, used as an inert tracer, was injected and dissolved in $CaCl_2$ (0.01 M) for 15 minutes (equivalent to a dose of 1500 kg ha^{-1}). Once the tracer was leached, a pulse of glyphosate (CONTROL MAX, 72% a.i.) and metsulfuron-methyl (Nufarm, 60% a.i.), dissolved in $CaCl_2$ (0.01 M), was applied for 15 minutes, with an equivalent dose of 5 kg a.i. ha^{-1} and 10 g a.i. ha^{-1}, respectively. The samples were collected every 30 mL and leached by 4.5 pore volumes (PV) for bromide and 10.5 PV for the herbicides.

The bromide concentration in the leachate was determined with an ion-selective electrode (EA940 Orion, detection limit 0.0005 mmol L^{-1}). Glyphosate and AMPA concentrations were determined following the methodology described by De Gerónimo *et al.* (2018a) on a UHPLC-MS/MS (Waters®) (LD: 0.05µg L^{-1}; LQ: 0.1µg L^{-1}). The quantification of metsulfuron-methyl was performed by direct injection into the UHPLC-MS/MS (Waters®), after filtering through a 0.22 µm nylon membrane (LD: 0.002 µg L^{-1}; LQ: 0.006 µg L^{-1}). The relative concentration of each compound (C/C_0) was determined by dividing the concentration in the effluent (C) by the applied concentration (C_0). The obtained AMPA values were multiplied by the stoichiometric conversion factor (glyphosate molecular weight/AMPA molecular weight = 1.5), as defined by Coupe *et al.* (2011), and added to the glyphosate values (total glyphosate).

At the end of the experiment, the columns were weighed and cut into four segments: 0-2; 2-5; 5-10; 10-15 cm. Each segment was dried at 30 °C and sieved for 2 mm to determine the concentration of the herbicides. A subsample of each segment was extracted and dried at 105 °C to determine gravimetric moisture and pore volume. The quantification of glyphosate and AMPA in the soil samples was done following the methodology described by Okada *et al.* (2018) on a UHPLC-MS/MS (Waters®) (LD: 0.3 µg kg^{-1}; LQ: 0.8 µg kg^{-1}), while the determination of metsulfuron-methyl was done according to De Gerónimo *et al.* (2015) on a UHPLC-MS/MS (Waters®) (LD: 0.1 µg kg^{-1}; LQ: 0.3 µg kg^{-1}). The concentrations of the herbicides presented in this work were made in dry weight of the samples, corrected by the apparent density of each one.

The determination of herbicides was also performed on undisturbed samples taken from each horizon at the same sampling points where the soil samples used in the transport experiment were collected, in order to know the previous concentration of each compound. The concentrations determined in these samples were subtracted from the concentrations measured in the soil columns of the transport experiment to eliminate the previous concentration of glyphosate and AMPA from the field. Metsulfuron-methyl was not detected in any of the soil samples tested, so the concentration of this herbicide in the soil is not shown.

Model fitting

From the experimental data, a breakthrough curve (BTC) was plotted for each column, and the hydraulic transport parameters were calculated using the Convection-Dispersion Equation (CDE) proposed by Parker and van Genuchten (1984). The adjustment of CDE was performed in the software STANMOD (version 2.08.1130) developed by Simunek *et al.* (1999), using the inverse solution of the CXTFIT package (Toride *et al.*, 1995).

The CDE can be expressed in terms of equilibrium (CDE_{Eq}) and non-equilibrium (CDE_{Non-Eq}). The CDE_{Eq} model considers that the soil is homogeneous and produces a one-dimensional "ideal transport" of reactive solutes, which are subject to sorption, first-order degradation and first-order production processes (Toride *et al.*, 1995). The CDE_{Eq} equation (equation 1) proposed by Parker and van Genuchten (1984) shows the movement of solutes in x-direction:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (1)$$

where C is the flux-averaged concentration (µg L^{-1}), D is the hydrodynamic dispersion coefficient of the solute (mm^2 h^{-1}), v is the mean water velocity between pores (mm h^{-1}), x is the distance (mm), t is the time (h) and R is the retardation factor (dimensionless).

In contrast, the CDE_{Non-Eq} model considers that the transport of solutes in the soil is affected by a variety of processes. It distinguishes between physical (physical CDE_{Non-Eq}) and chemical (chemical CDE_{Non-Eq}) non-equilibrium transport (Toride *et al.,* 1995). The former assumes that the liquid phase can be partitioned into two regions: one mobile, where the water flows and the region is dominated by macropores, and another immobile, where the water is stagnant and micropores prevail. The latter considers that sorption processes occur with different intensity between the solute and the porous medium, and in some sites, the sorption is assumed to be instantaneous and in equilibrium (type 1 sites), while in others it is time-

dependent, governed by first-order kinetics, and not in

the partition coefficient between the equilibrium and non-

Table 1: Physical chemical properties of the soil studied

Horizon	A (0-15 cm)	B (30-45 cm)	C (75-90 cm)
pH	5.6[c]	6.5[b]	7.0[a]
EC (dS m^{-1})	0.10[a]	0.08[a]	0.07[a]
OC (%)	3.2[a]	1.0[b]	0.20[c]
CEC (cmol$^+$ kg^{-1})	24.3[a]	28.2[a]	19.1[b]
Clay (%)	24.7[b]	40.1[a]	23.9[b]
Silt (%)	27.6[a]	18.6[b]	20.1[b]
Sand (%)	47.7[b]	41.3[c]	56.0[b]
δb (g cm^{-3})	1.4[a]	1.3[a]	1.4[a]
P	0.49[a]	0.51[a]	0.49[a]
Ks (mm h^{-1})	97.4[a]	2.9[b]	9.8[b]

Different letters indicate differences between horizons (Tukey, $p < 0.05$). EC: electrical conductivity. OC: organic carbon. CEC: cation exchange capacity. δb: bulk density. ρ: soil porosity. Ks: saturated hydraulic conductivity.
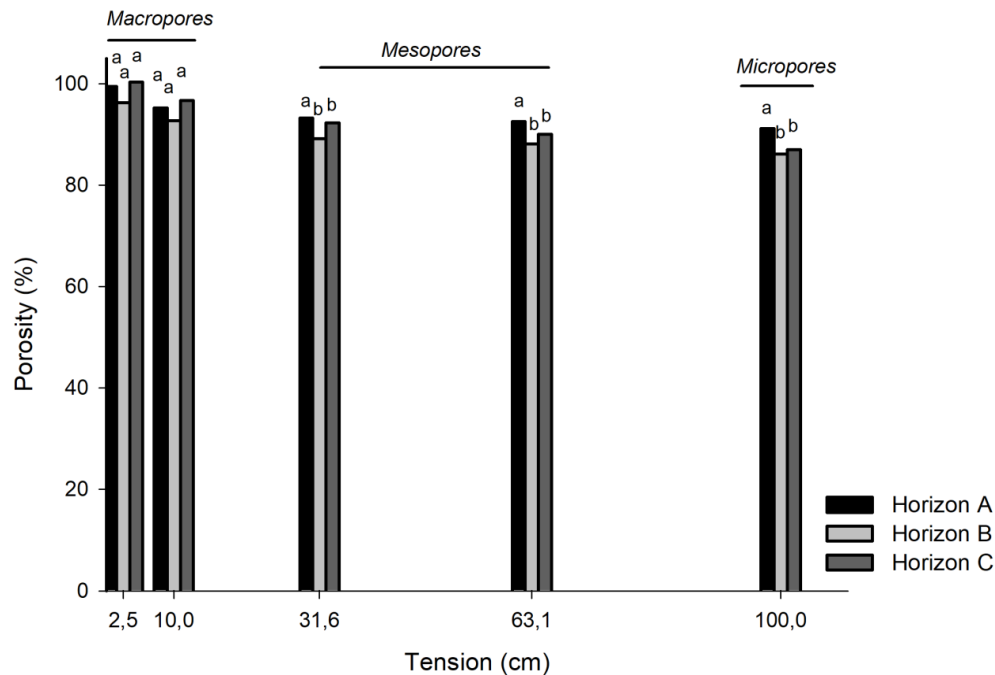
Figure 1: Pore size distribution
Different letters indicate significant differences between the horizons, according to Tukey's test ($\alpha=0.05$)

equilibrium (type-2 sites) (Toride *et al.,* 1995). If non-dimensional parameters are used, both models are reduced to the following equation:

$$\beta R \frac{\partial c_1}{\partial t} = \frac{1}{Pe} \frac{\partial c_1}{\partial Z} - \frac{\partial c_1}{z} - \omega(C_1 - C_2) - \mu_1 C_1 \quad (2)$$

where T=vt/L, Z=x/L and Pe=vL/D is the Peclet number. L is the length of the column (mm), and C_1 and C_2 are the relative concentrations in the regions or sites according to the model. The dimensionless parameter β is

equilibrium sites or regions, while ω is the dimensionless mass transfer coefficient (Toride *et al.*, 1995).

Bromide BTCs were first adjusted by the CDE$_{Eq}$ model, to obtain the velocity (v) and dispersion (D) parameters. For this purpose, the water velocity for each column was calculated from the experimental data, and this value was used for the adjustment. Then, an adjustment was made using the physical CDE$_{Non-Eq}$ model, adjusting the parameters D, β and ω. The retardation factor R was

Table 2: Bromide and metsulfuron-methyl parameters

	Parameter	Horizon A	Horizon B	Horizon C
Bromide	v (mm h⁻)*	8.6[a]	7.8[a]	8.3[a]
	D (mm² h⁻)*	325[a]	351[a]	75.3[b]
	β(dimensionless)*	0.78[a]	0.61[a]	0.65[a]
	ω(dimensionless)*	0.42[a]	0.51[a]	2.89[a]
	λ (mm²)*	38.8[a]	46.3[a]	9.2[b]
	r²	0.97 – 0.99	0.93 – 0.99	0.81 – 0.97
	C/C0 max (PV)	0.44	0.28	0.70
Metsulfuron-methyl	R (dimensionless)*	8.5[a]	5.1[ab]	1.5[b]
	β(dimensionless)*	0.18[b]	0.42[ab]	0.64[a]
	ω(dimensionless)**	5.4[a]	1.5[ab]	0.05[b]
	μ₁ (h⁻)**	3.6[a]	0.33[a]	0.90[a]
	α(h⁻)**	0.05[a]	0.07[a]	1.8[a]
	Kd (mm³mg⁻¹)*	2.6[a]	1.4[ab]	0.14[b]
	r²	0.78 – 0.91	0.79 – 0.96	0.66 – 0.97
	C/C0 max (PV)	1.05	0.37	0.59
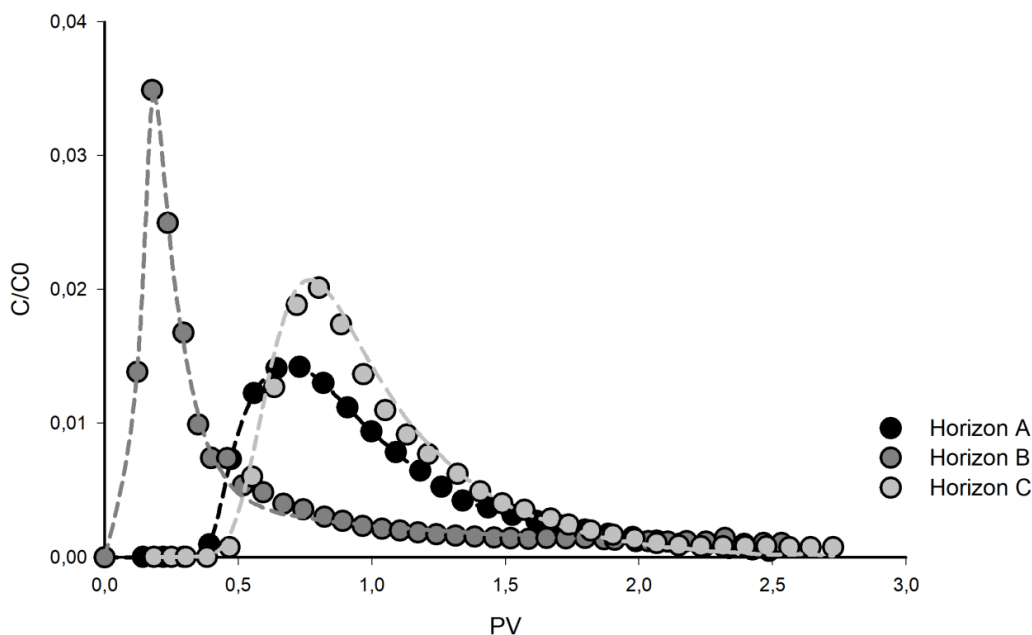
Figure 2: Bromide breakthrough curves
Experimental data (points) and estimates (dashed line) of BTCs using the physical CDE$_{Non-eq}$ model

assigned a value of 1 because bromide is a non-reactive solute. Dispersion (λ) (mm) was calculated as the ratio between D and v. The results presented for the inert tracer correspond to the adjustment made with the physical CDE$_{Non-Eq}$ model.

For the herbicides, the BTCs were adjusted for metsulfuron-methyl only by the chemical CDE$_{Non-Eq}$ model, using v and D values obtained from the bromide BTCs. As

the concentrations of glyphosate in the leachate were low and in some cases undetected, it was not possible to estimate the transport parameters.

Statistical analyses

The parameters obtained from each column and the concentrations of glyphosate, AMPA and total glyphosate in soil were analysed using mixed models (Pinheiro and Bates, 2000) in the statistical software R (R Core Team, 2018). An

ANOVA test was performed between horizons for each variable and a Tukey comparison ($\alpha=0.05$) was made. Bromide parameters D, ω, y, λ, and metsulfuron-methyl parameters R, β and K_d were transformed logarithmically to satisfy the necessary assumptions for the ANOVA. The variables ω, μ_1 and α of metsulfuron-methyl were analysed by the nonparametric test Kruskal-Wallis. The remaining variables showed a normal distribution. Correlations between the parameters obtained and soil properties were analysed, using Pearson's correlation coefficient for the variables with normal distribution and those transformed logarithmically, and Spearman's correlation coefficient for the variables to which the Kruskal-Wallis test was applied.

For these analyses, we used the packages nlme (Pinheiro *et al.*, 2018), emmeans (Lenth, 2018), multcomp (Hothorn *et al.*, 2009), multcompView (Graves *et al.,* 2012) and pgirmess (Giraudoux *et al.*, 2018) available for R.

Results and Discussion

Description of horizons

There were significant differences in the physical-chemical properties of the horizons under study (Table 1). An increase in pH and a decrease in OC content were observed with depth. These properties influence the retention capacity of some compounds in the soil, such as the positive effect of OC on the sorption of glyphosate (Ozbay *et al.*, 2018) and metsulfuron-methyl (Oliveira *et al.,* 2001), or the negative effect of pH on glyphosate sorption (Borggaard and Gimsing, 2008).

The percentage of clay in horizon B was significantly higher than in the other horizons ($p<0.05$). De Gerónimo *et al.* (2018b) indicated that glyphosate is strongly sorbed to soils with high clay content and stated that this property is one of the main factors controlling glyphosate adsorption in soil. In addition to reporting the relationship between sorption and glyphosate clay content, Borggaard and Gimsing (2008) indicated a moderate positive correlation between glyphosate sorption and CEC. Likewise, Oliveira *et al.* (2001) reported a high correlation between metsulfuron-methyl sorption and the CEC content of the soil but did not detect a significant correlation with clay content. In this study, CEC was significantly higher in horizons A and B than in C.

There were no significant differences between horizons in bulk density (δb) and porosity (ρ). For Ks, statistical differences were detected in favour of horizon A ($p<0.05$), which supports the interpretation of a better condition for

transport on this horizon. Figure 1 shows the pore size distribution for each horizon. No significant differences were observed for macropores, but there were significant differences for mesopores and micropores, with a higher percentage in the surface horizon. Although the proportion of macropores did not differ statistically between horizons, A horizon presented greater Ks, which could be explained by a difference in smaller pores. Although these smaller pores do not conduct the water as quickly as the macropores under conditions of saturation (as Ks is measured), they could be responsible for greater hydraulic conductivity. The evaluation of the edaphic properties of this soil confirms that it presents a good aptitude for agricultural development. Therefore, it is important to study the vertical transport mechanisms of frequently used herbicides.

Bromide vertical transport

Bromide BTCs were asymmetric and tailed (Figure 2), indicating rapid transport in soil (Comegna *et al.*, 2001). The maximum average concentration of the tracer (C/C$_{0\text{ max}}$) was given before the elution of 1 PV in the three horizons, validating the transport under non-equilibrium physical conditions (Ersahin *et al.,* 2002). The physical CDE$_{\text{Non-Eq}}$ model had an adjustment greater than 0.81 in all cases. The adjusted bromide transport parameters are summarised in Table 2, which presents the average values obtained for each horizon.

The high water velocity between pores (v) obtained in the three horizons validates the elution tails in the BTCs (Ersahin *et al.*, 2002), while the high values of D concerning v justify the asymmetry of the BTCs and the early advance of the tracer (Sugita and Gillham, 1995). A significant correlation was detected between v and Ks (r=0.48), and between D and the content of clay (r=0.49), sand (r=-0.58) and OC (r=0.64). Bromly et al. (2007) related high D values to soil texture, suggesting that clay favours the formation of structural pores, which benefits solute dispersion. This may explain why the BTC of horizon B is so different from that of the other horizons. Horizon B has a higher clay content than the others, which favours greater bromide dispersion and, therefore, a more asymmetric BTC. However, the statistical analysis showed significant differences for D between horizon C and the others ($p<0.05$), and since horizons A and C have similar clay contents, another soil property must intervene in the dispersion of the solute, such as the organic carbon content. Horizon A has a higher OC content, which favours soil structure and the development of pores of different sizes, thus influencing the dispersion of solutes (Bromly *et al.,* 2007).

Moreover, according to Comegna *et al.* (2001), given   were small, which suggests that the transfer of mass

Table 3: **Glyphosate, AMPA and total glyphosate concentration per horizon**

	Glyphosate (μg kg^{-1})	AMPA (μg kg^{-1})	Total glyphosate (μg kg^{-1})
Horizon A	2510.91	1799.36	5250.47
Horizon B	3919.33	794.54	5129.04
Horizon C	3871.38	1900.92	6765.56
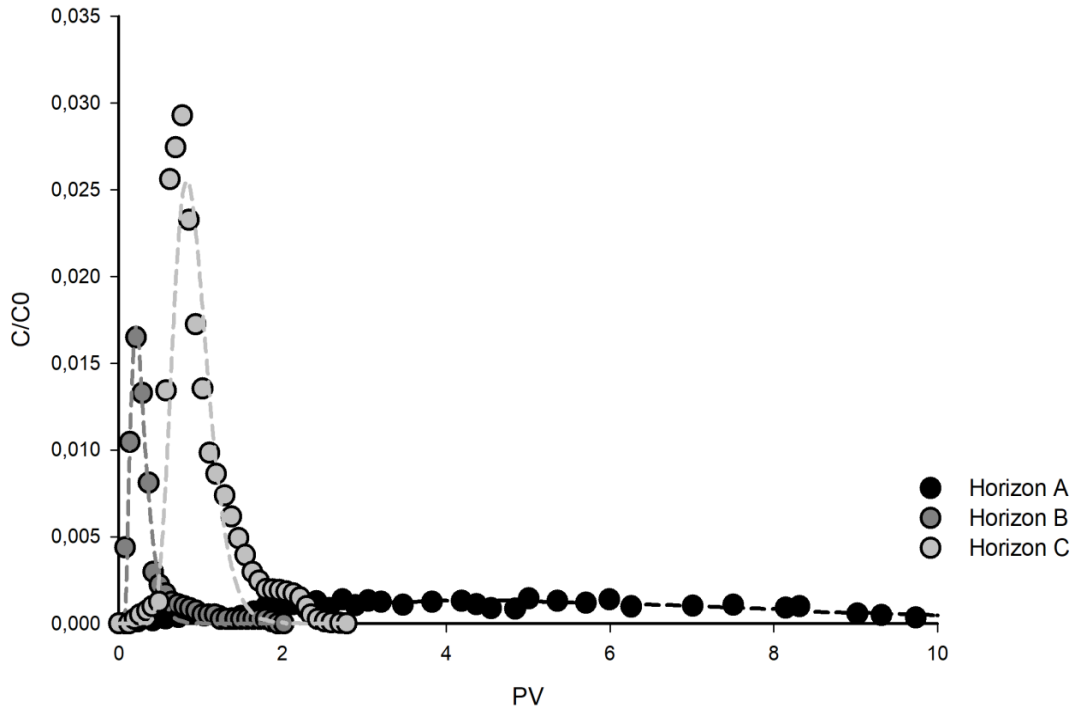
Figure 3: Metsulfuron-methyl breakthrough curves
Experimental data (points) and estimates (dashed line) of metsulfuron-methyl BTCs using the chemical CDE$_{Non-Eq}$ model

that the values λ obtained are greater than the unit, the porous medium of these horizons can be described as heterogeneous. The results obtained in this study suggest that horizons A and B are characterised by a more heterogeneous porous system than horizon C, which would have fewer flow paths and less influence of dispersive transport. This is confirmed by the somewhat symmetric BTC and a more uniform solute front. The statistical analysis showed significant differences between horizon C and horizons A and B ($p<0.05$). Significant correlations of this parameter were detected with clay (r=0.47), sand (r=-0.55), Ks (r=-0.46), OC (r=0.62) and CEC (r=0.50).

The β parameter refers to the fraction of mobile water, while ω refers to the mass transfer between regions. According to these results, the immobile water content was higher in horizon B (38.6%), followed by C (35%) and finally A (21.6%). On the other hand, the ω values obtained

between regions was limited. According to Rodríguez *et al.* (2006), low ω values indicate that non-equilibrium conditions predominate, and therefore, some molecules of the solute were transported faster than others, generating asymmetric BTCs.

In summary, water transport in this soil was explained under the physical CDE$_{Non-Eq}$ model, according to which transport is dispersive and dominated by preferential flow paths or macropores (Jarvis, 2007). Although in no case was there a direct correlation with the total soil porosity or pore size distribution found, the BTCs obtained and the parameters estimated confirm that in the three horizons the transport was dispersive and occurred through macropores, resulting in rapid water flow through the mobile region, with a low lateral mass exchange, as described by Jarvis (2007). Furthermore, Stone and Wilson (2006) argue that macropores can contribute very little to the total porosity of

the soil but could have a significant effect on the movement rate of water and solutes.

Metsulfuron-methyl vertical transport

Metsulfuron-methyl BTCs differed among horizons, as illustrated in Figure 3. This figure, like Figure 2, shows the BTCs for one of the repeats performed. For this reason, the values of $C/C_{0 \, max}$ do not coincide with those presented in Table 2. The BTCs shown in Figure 3 are asymmetric and tailed, with a more pronounced peak in horizons B and C. The maximum concentration of the herbicide was close to 1 PV in the three cases, with recovery rates of 51.7%, 56.6% and 67.0% in horizons A, B and C, respectively. As mentioned by Porfiri *et al.* (2015) in their work on imazapyr, the chemical CDE_{Non-Eq} model satisfactorily described the front and tail of the BTCs, but an adequate adjustment of most of the peaks was not achieved. Table 2 presents the transport parameters of metsulfuron-methyl in the horizons under study.

The obtained results prove that the transport of metsulfuron-methyl occurred under conditions of non-chemical equilibrium. Montoya *et al.* (2006) and Porfiri *et al.* (2015) agree that the tailing phenomenon in BTCs is a consequence of sorption during transport. The average retardation factor obtained in the three cases was higher than that of the inert tracer (assumed to be 1), indicating slower mobility of the herbicide concerning bromide. However, in the three horizons, the R-value obtained was low, following the tendency A>B>C, with significant differences between horizons A and C (*p*<0.05). According to Bedmar *et al.* (2004), low values of R, such as those obtained in this study, account for the mobility of the compound.

The β and α parameters under the chemical CDE_{Non-Eq} model refer to the sorption of the herbicide in the soil matrix (Toride *et al.,* 1995). The values obtained suggest that in horizon A, the transport was influenced by type-2 sites, in horizon C by type-1 sites, while in horizon B, an intermediate situation was observed, with the influence of type-1 and type-2 sites, confirmed by the statistical analysis carried out.

As for the linear adsorption coefficient (K_d), significant differences were detected between A and C (*p*<0.05), with differences being higher at the surface horizon. This indicates that the highest sorption of the herbicide occurred in horizon A, which coincides with the highest value of R obtained in this horizon and the shape of the flatter BTC.

In addition, parameter μ_1 represents the first-order degradation constant (Toride *et al.*, 1995). The statistical analysis did not show significant differences between horizons. The values obtained were low, indicating that degradation during transport was negligible and occurred only in the liquid phase. Cordón *et al.* (2015) obtained smaller degradation constants in their study of oxadixyl transport. The authors suggest that since no degradation is evident, the recovery rate of the pesticide should be high, as was the case in this study.

The ω showed significant differences between A and C (*p*<0.05), with the surface horizon showing the longest hydrodynamic residence time. This could be related to increased herbicide retardation, an increased affinity for the solid phase and an extended BTC, as shown in Figure 3.

The analysis of correlations between transport parameters and soil properties indicates that particle size distribution, OC content and pH are the factors that strongly influence the transport of metsulfuron-methyl in the soil profile. Tahir *et al.* (2008) identified OC content as one of the edaphic properties that control the behaviour of this herbicide in the soil , while Ismail and Ooi (2012) indicated that the higher the OC content, the higher the sorption of metsulfuron-methyl. The OC content of the horizons was correlated with R (r=0.71), K_d (r=0.715), ω (r=0.78) and β (r=-0.72), indicating the influence of this component in the metsulfuron-methyl sorption, and therefore, in the retardation and increase in the hydrodynamic residence time.

Regarding the particle size distribution, significant correlations were found for the sand content with R (r=-0.72), β (r=0.80), *f* (r=0.78) and K_d (r=-0.57), the clay content with α (r=-0.74) and μ_1 (r=0.64) and the silt content with R (r=0.65), β (r=-0.68), ω (r=0.84) and K_d (r=0.63). This means that the texture of each horizon is another factor that directly influences the behaviour of metsulfuron-methyl. These data suggest that the higher the clay or silt content (and the lower the sand content), the higher the sorption of the compound, and therefore, the longer the retardation. In a field study, Black *et al.* (1999) reported that the herbicide mobility rate was higher in soils with higher sand content and lower OC and clay content.

In addition, soil pH was correlated with R (r=-0.65), β (r=0.70), ω (r=-0.78), and K_d (r=-0.69). Sarmah *et al.*, (1998) indicated that an increase in soil pH causes a decrease in the binding of the herbicide to the soil components, while Ismail and Ooi (2012) hypothesised that if the effective pH on the clay surface approaches the pKa of the herbicide, the number of neutrally charged metsulfuron-methyl molecules could be higher, resulting in increased adsorption.

As regards the presence of herbicide residues in the soil columns, metsulfuron-methyl was not detected in any of the

samples analysed. Given the percentages recovered in the column leachate, and due to the weak soil adsorption (explained by parameter K_d), it was expected that herbicide residues would be detected in the soil samples analysed. However, this could be due to the limit of detection and quantification of UHPLC-MS/MS (0.1 and 0.3 µg kg^{-1}, respectively).

There are several ways to reduce the risk of groundwater contamination. A viable alternative is the absence of use of these pesticides through a more diversified agronomic management in species (Aparicio *et al.*, 2018). If herbicide use is preferred, it is important to know the soil, the herbicide load before its application and the agrometeorological conditions, especially the prediction of rainfall, which could favour its rapid leaching. The adoption of these measures, together with the application of necessary but not excessive doses, can contribute to reducing the leaching of the compound and, therefore, the risk of groundwater contamination.

Glyphosate vertical transport

Glyphosate mobility in the three horizons was limited. The concentration of total glyphosate leached was very low: 0.75%, 1.76% and 0% in horizons A, B and C, respectively. AMPA was detected only in a replicate of horizon B. Numerous authors reported low herbicide leaching in undisturbed soil columns of the surface horizons. Okada *et al.* (2016) reported leaching of 0.24% of the applied mass. Gjettermann *et al.* (2009) indicated that the mass recovered in the leachate was between 0.007 and 0.32%. Dousset *et al.* (2004) obtained leaching rates of between 0.01 and 0.008% of glyphosate+AMPA. The highest leaching percentages were found by Zhou *et al.* (2010), with 16% of the amount injected, and by de Jonge *et al.* (2000), with 19.6% in sandy loam soil. In contrast, in studies conducted on disturbed soil columns, the recovery rates were higher. Candela *et al.* (2007) obtained recoveries of 90%, 30% and 15% of the applied glyphosate mass by varying the flow rates. Calderón *et al.* (2005) recovered 4% of the glyphosate applied concentration under non-continuous flow conditions.

It is, therefore, possible to state that the mobility of this herbicide in the soil is limited. The values obtained suggest that the transport of glyphosate in the soil under study is poor and that the low leached concentrations may have been transported through preferential flow paths. Given that this transport mechanism dominated the flow of bromide and metsulfuron-methyl in these horizons and that glyphosate is highly soluble in water (10,500 mg L^{-1} at 20°C), it is possible to hypothesize that such quantities were transported by preferential pathways dissolved in soil water. In his

review, Jarvis (2007), citing Focus (2001), mentions that pesticide losses due to macroporous flow are usually less than 1% of the amount applied but can reach up to 5%. However, he concludes that such amounts represent a concern for both the environment and human health.

Due to the low leaching of the herbicide in the horizons, its detection in the soil was high. Table 3 summarises the average soil concentrations for each horizon. These data show the low mobility of the herbicide and its strong adsorption to the soil, in addition to its possible degradation, which is consistent with the quantification of AMPA. If the three horizons are compared, the total glyphosate concentration follows the trend C>A>B, which is related to the concentrations of total glyphosate leached (B>A>C).

Total glyphosate concentration in soil was positively correlated with pH (r=0.59) and electrical conductivity (r=0.51), and negatively correlated with OC content (r=-0.54). Several authors, including Borggaard and Gimsing (2008), suggest that glyphosate sorption in soil is pH-dependent. Regarding the organic carbon content, Vereecken (2005) and the authors mentioned above indicate that the role of this soil property is quite controversial. They suggest that soil organic matter favours glyphosate sorption by H-bond formation, while soil OM may block sorption sites for glyphosate, although this behaviour is not thoroughly studied. Thus, the results obtained in this study indicate that soil OC seems to influence herbicide retention negatively, with a higher OC content seeming to block the sorption of this molecule, leaving it available in the soil solution. In addition, different authors relate the higher glyphosate sorption in the soil to the clay content (Borggaard and Gimsing, 2008). Nevertheless, in this work, no significant correlations were detected with the clay content of the soil.

Figure 4 shows the measured concentrations of average total glyphosate in each soil segment. In the three horizons, the largest sorption occurred in the first two centimetres of the soil, decreasing with depth. Horizon C had the lowest mobility of the compound in the column with respect to the other horizons, since most of the glyphosate was concentrated in the upper part of the column. These data show that there was strong sorption of the herbicide in all three horizons in the soil matrix.

Similar results were obtained by Okada *et al.* (2016) and Zhao *et al.* (2009), who indicated that the highest concentrations of glyphosate applied to the soil columns occurred in the first 5 cm. Both works were performed on surface soil samples (0-15 cm). The former study indicated

that the percentages of total glyphosate extracted from the soil ranged from 81.8 to 57.4% of the initially applied concentration, while the latter reported sorption of 61% in the same portion of the soil column. As a result, there may

On the other hand, the strong adsorption of glyphosate to the soil can lead to an accumulation of the herbicide and even AMPA, with recurrent use, which can have a negative impact on the soil biota and subsequent crops, or be subject
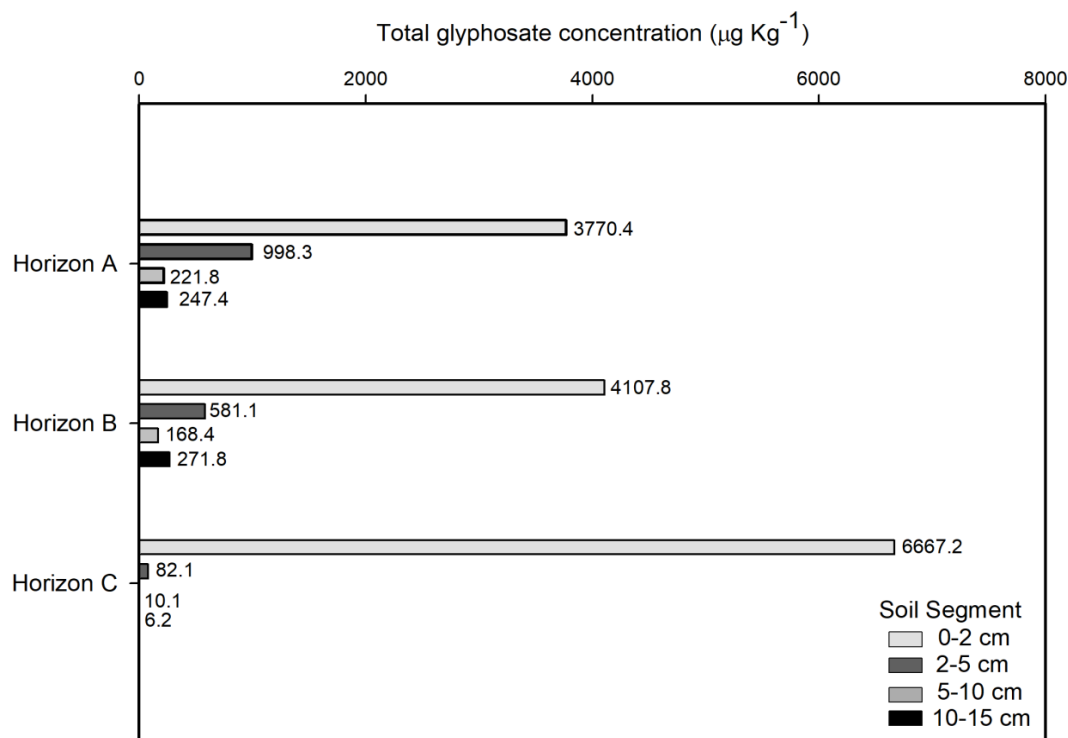
Figure 4: Average total glyphosate concentration per horizon and soil segment
The numbers on each bar indicate the average concentration of total glyphosate for a specific segment of the horizon.

have been a stratification of the herbicide in these horizons, with the amount of glyphosate sorbed to the soil decreasing in the order of 0-2cm>2-5cm>5-10cm>10-15cm.

The strong sorption of glyphosate to the soil components suggests that a mobilisation mechanism may be the transport facilitated by colloids, which depends on the size, geometry and connectivity of the pores (Kjaergaard *et al.*, 2004). However, in this work, this mechanism was not evaluated because $CaCl_2$ was used as a leachate solution. De Jonge *et al.* (2000), Borggaard and Gimsing (2008) and Bergström *et al.* (2011) agree that this mechanism can act in conjunction with the preferential flow and contribute to the leaching of strongly adsorbed compounds.

In this study, glyphosate leaching was shown to be null. However, as mentioned above, other studies have shown that this molecule is susceptible to transport through the soil profile. It is, therefore, necessary to carry out further studies of this type to analyse the transport facilitated by colloids and reduce the potential risk of groundwater contamination.

to water or wind erosion and reach areas far from the application sites. To avoid this situation, and as suggested for metsulfuron-methyl, the use of this herbicide should be reduced and, when applied, the soil and agrometeorological conditions of the environment should be known.

Conclusion

In this study, we have characterised the vertical transport of glyphosate and metsulfuron-methyl in the main horizons of a typic Argiudoll. The movement of the inert tracer was analysed using the physical CDE_{Non-Eq} model. In the three horizons, Br transport was dispersive and dominated by the presence of preferential flow pathways. The transport of metsulfuron-methyl was explained by the chemical CDE_{Non-Eq} model, with the preferential flow paths of each horizon governing the transport of this herbicide. The recovery rates of the herbicide in the leachate of the columns were higher than 51% of the initial concentration applied, with horizon C exhibiting the highest rate. The vertical transport of glyphosate could not be adjusted by the

proposed models due to the low recovery rates in the leachate. The low mobility was attributed to the strong retention in the soil.

This is the first study of the vertical transport of two herbicides used in grain production that considers three main horizons of a Mollisol soil profile.

Acknowledgements

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