

## SORPTION, DESORPTION, HALF-LIFE AND LEACHING OF SULFOMETURON-METHYL IN DIFFERENT SOIL CLASSES<sup>1</sup>

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**ABSTRACT** – Understanding the behaviour of herbicides in the soil can contribute to adapting the correct dose for efficient weed control with less environmental impact. In this study, we sought to evaluate the factors involved in the sorption, desorption, half-life and leaching processes of sulfometuron-methyl in three soil classes: *Cambissolo Háplico* (CX) (Inceptisol), *Latossolo Vermelho* (LV) (Oxisol) and *Neossolo Quartzarênico* (RQ) (Entisol). The sorption and desorption tests were performed using the “*batch equilibrium*” method. The studies of degradation and formation of metabolites were estimated from the half-life at the end of 180 days. Leaching potential was estimated by testing PVC columns filled with soil. Analyses were performed by ultra-performance liquid chromatography coupled to a mass spectrometer for herbicide quantification. The higher sorption of sulfometuron-methyl in LV (2.81) is related to the low pH (4.7) and mineralogical composition, mainly due to the higher concentration of Fe and Al oxides in this soil, influencing the lower desorption of the herbicide in LV (0.59). This result contributed to more remarkable herbicide persistence in this soil, reducing the molecules available in the solution for degradation. These results contributed to the longer half-life (19 days) in LV compared to the other soils. Among the studied soils, RQ had the highest risk of transport of sulfometuron-methyl based on the GUS Index (2.2) due to its greater desorption (0.34). The results showed that the studied processes are dependent on the physical, chemical and mineralogical attributes of the different classes of soils.

**Keywords:** Retention. Transport. Transformation. Environmental contamination.

## SORÇÃO, DESSORÇÃO, MEIA-VIDA E LIXIVIAÇÃO DO SULFOMETURON-METHYL EM DIFERENTES CLASSES DE SOLOS

**RESUMO** – Entender o comportamento dos herbicidas no solo pode contribuir para adequação da dose correta para o controle das plantas daninhas eficiente com menor impacto ambiental. Nesta pesquisa, buscou-se avaliar os fatores envolvidos nos processos de sorção, dessorção, meia-vida e lixiviação do sulfometuron-methyl em três classes de solo: *Cambissolo Háplico* (CX), *Latossolo Vermelho* (LV) e *Neossolo Quartzarênico* (RQ). Os ensaios de sorção e dessorção foram realizados pelo método “*batch equilibrium*”. Os estudos de degradação e formação de metabólitos foi estimado pelo tempo de meia-vida ao final de 180 dias. O potencial de lixiviação foi estimado por meio do ensaio em colunas de PVC preenchidas com solo. As análises foram realizadas por cromatografia líquida de ultra performance acoplada ao espectrômetro de massas para quantificação do herbicida. A maior sorção do sulfometuron-methyl no LV (2,81) está relacionada ao baixo pH (4,7) e à composição mineralógica, principalmente pela maior concentração de óxidos de Fe e Al, deste solo, influenciando na menor dessorção do herbicida em LV (0,59). Tal resultado contribuiu para maior persistência do herbicida nesse solo reduzindo as moléculas disponíveis na solução para a degradação. Estes resultados contribuíram para o maior tempo de meia-vida (19 dias) no LV comparado aos demais solos. Entre os solos estudados, o RQ indicou o maior risco de transporte do sulfometuron-methyl pelo Índice de GUS (2,2), em decorrência da sua maior dessorção (0,34). Os resultados demonstraram que, os processos estudados são dependentes dos atributos físicos, químicos e mineralógicos das diferentes classes de solos.

**Palavras-chave:** Retenção. Transporte. Transformação. Contaminação ambiental.

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<sup>1</sup>Received for publication in 11/09/2021; accepted in 12/09/2021.

Paper extracted from the master's dissertation of the first author.

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## INTRODUCTION

Sulfometuron-methyl is an herbicide used in Brazil as a growth regulator in sugarcane when applied alone and to control weeds when applied in association with other herbicides, such as diuron and hexazinone. Its mechanism of action is based on the inhibition of the enzyme acetolactate synthase (ALS), blocking the synthesis of amino acids and cell division (PAVÃO et al., 2021). It is an herbicide classified as a weak acid (pKa 5.2), which has moderate solubility in water (300 mg L<sup>-1</sup> at pH 7; 25 °C) and a K<sub>ow</sub> of 1.04 (SHANER, 2014).

The efficiency of weed control and the environmental fate of herbicides depends on the interactions of these molecules with the physicochemical and mineralogical attributes of the soil (PAVÃO et al., 2021). These interactions directly influence the magnitude of the retention, transport and transformation of herbicides in the soil, altering their bioavailability (FARIA, 2016). Weak acid herbicides, such as sulfometuron-methyl, tend to become more available in the soil solution when the pH of the medium is more significant than its pKa (KRAEMER et al., 2009). This can positively influence weed control, but on the other hand, it can also increase the risk of transport via leaching (SILVA et al., 2019).

In the contact of the herbicide with the soil, the retention of its molecule begins with the organic and inorganic colloids in the soil. This relationship is called sorption, which is dependent on the physical and chemical characteristics of the phytosanitary product and on the edaphoclimatic attributes (FARIA et al., 2018). Therefore, sorption directly influences the transport and transformation processes and is considered the primary process that affects the ecotoxicological impact, environmental mobility,

and degradation rate of phytosanitary products (PAVÃO et al., 2021).

Leaching is an essential process of transporting herbicides in the soil, the control of weed propagules, but when it occurs in excess, it can cause groundwater contamination (SILVA et al., 2019). Herbicides used in sugarcane cultivation are often found in groundwater (ISMAEL; ROCHA, 2019). This fact can be aggravated when the herbicide has high persistence in the environment (SOUZA et al., 2020). Furthermore, the excessive persistence of an herbicide in any soil can result in the intoxication of successive crops (SOUZA et al., 2020).

Thus, it is believed that knowledge of the dynamics of herbicides in cultivated soils can improve the efficiency of weed control and reduce the environmental impact caused by the application of these products. Thus, the objective of this study was to evaluate the sorption, desorption, leaching and half-life of sulfometuron-methyl in soils in North-eastern Brazil as a way to improve the understanding of the behaviour of the herbicide and its environmental risk.

## MATERIAL AND METHODS

### Soil collection and characterization

Soils were collected at a depth of 0 – 0.20 m in sugarcane producing regions with no history of applying the herbicide sulfometuron-methyl. After collecting the soils, the samples were air-dried and sieved through a 2 mm mesh and, subsequently, chemically and physically characterized (Table 1) according to Teixeira et al. (2017).

**Table 1.** Chemical and physical attributes of soils.

Attributes	Units	CX	LV	RQ
pH (water)	-	7.6	4.7	4.9
EC	dS m <sup>-1</sup>	0.1	0.14	0.1
N	g kg <sup>-1</sup>	1.8	0.7	1.1
SOM	g kg <sup>-1</sup>	14.1	9.2	12.1
P	mg dm <sup>-3</sup>	4.5	5.1	4.3
Na <sup>+</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	0.1	0.1	0.2
K <sup>+</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	1.5	0.1	0.2
Ca <sup>+2</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	11.7	1.1	1.4

*Cambissolo Háplico* (CX) (Inceptisol), *Latossolo Vermelho* (LV) (Oxisol), *Neossolo Quartzarênico* (RQ) (Entisol). Hydrogen potential (pH), electrical conductivity (EC), nitrogen (N), soil organic matter (SOM), phosphorus (P), sodium (Na<sup>+</sup>), potassium (K), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), aluminium (Al<sup>3+</sup>), potential acidity (H+Al), cation exchange capacity (CEC), base saturation (V), aluminium saturation (m), total organic carbon (TOC).

**Table 1.** Continuation.

Attributes	Units	CX	LV	RQ
Mg <sup>+2</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	1.0	0.2	0.5
Al <sup>+3</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	0.0	0.1	0.2
H+Al	cmol <sub>c</sub> dm <sup>-3</sup>	0.0	1.7	1.7
CEC	cmol <sub>c</sub> dm <sup>-3</sup>	14.3	1.6	2.5
V	%	100.0	48.0	59.0
M	%	0.0	6.0	6.0
TOC	g kg <sup>-1</sup>	8.2	5.3	7.0
Sand	g kg <sup>-1</sup>	500.0	810.0	840.0
Silt	g kg <sup>-1</sup>	150.0	50.0	100.0
Clay	g kg <sup>-1</sup>	350.0	140.0	60.0
Textural Class	-	Sandy Clay	Sandy Loam	Loamy Sand

*Cambissolo Háplico* (CX) (Inceptisol), *Latossolo Vermelho* (LV) (Oxisol), *Neossolo Quartzarênico* (RQ) (Entisol). Hydrogen potential (pH), electrical conductivity (EC), nitrogen (N), soil organic matter (SOM), phosphorus (P), sodium (Na<sup>+</sup>), potassium (K), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), aluminium (Al<sup>3+</sup>), potential acidity (H+Al), cation exchange capacity (CEC), base saturation (V), aluminium saturation (m), total organic carbon (TOC).

The minerals were identified by X-ray diffraction (XRD) using a Shimadzu diffractometer (model XRD - 6000, Tokyo, Japan) employing the copper  $\alpha_1$  emission with a source potential of 40 kV and a current of 30 mA. A scanning speed with a step of 0.02° was applied every second. The scanning range ( $2\theta$ ) was from 5 to 65°. The peaks of the minerals were identified with the help of the program *Raio X v. 1.0.0.37* and the phases were identified according to Chen (1977).

## Conducting the experiments

### Sorption kinetics study

The determination of herbicide sorption kinetics in soils was carried out at a temperature of 25 °C ± 2 °C using the "batch equilibrium" method (OECD, 2000). In Falcon tubes, 4 g of soil samples were mixed with a 16-mL aliquot of an aqueous herbicide solution at 1 mg L<sup>-1</sup>, prepared in 10 mM CaCl<sub>2</sub>. Sample evaluations were performed in triplicate. Tubes were shaken at time intervals of 0, 10, 20, 30, 60, 120, 240, 480, 720, 960 and 1440 minutes. Afterwards, they were centrifuged at 2,260 g for seven minutes, and the supernatant was collected, filtered on 0.22 µm Nylon membranes for vials and submitted to analysis by chromatography. The equilibration time established was 12 hours (data not shown) for the sorption and desorption tests.

### Determination of sorption (Kfs) and desorption (Kfd) coefficients

The working solution concentrations were prepared from the stock solution, according to the recommendations of the OECD (2000). Concentrations of 0.1, 0.2, 0.4, 0.8, 1.0, 1.5 and 3.0 mg L<sup>-1</sup> were prepared in 10 mM CaCl<sub>2</sub> and defined based on the highest commercial dose recommended for the commercial product based on sulfometuron-methyl (0.1 mg L<sup>-1</sup>). In the herbicide sorption tests carried out in triplicate, a 16-mL aliquot of each concentration was added to each Falcon tube containing 4 g of soil. The tubes were shaken at 25 °C ± 2 °C for 12 hours (hours established for the equilibrium time). Samples were centrifuged at 2,260 g for seven minutes. The supernatant was collected and filtered for chromatographic analysis for herbicide quantification (LC-MS/MS). The herbicide concentrations sorbed to the soils (Cs), in mg kg<sup>-1</sup>, were calculated by the difference between the concentration in the solution initially added to the soil and the concentration found in the equilibrium solution (Ce). For the interpretation of sorption, the values of Ce and Cs were fitted by Freundlich's Equation (1):

$$C_s = K_{fs} C_e^{N_s} \quad (1)$$

Where Cs = Amount of herbicide sorbed to the soil (mg kg<sup>-1</sup>); Ce = Amount of herbicide in the equilibrium solution (mg L<sup>-1</sup>); Kf = Sorption capacity and Ns = Linearity.

In the desorption tests, the analyses were carried out by removing all the supernatant from the Falcon tubes in the sorption test and adding 16 mL of herbicide-free 10 mM CaCl<sub>2</sub> solution. The tubes

were vortexed for 10 seconds and shaken vertically ( $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ ) for the time established in the kinetic study (12 hours). Subsequently, the supernatant from the Falcon tubes was collected and filtered directly into 1.5 mL vials. The sample contained in the vials was analysed by chromatography to quantify the herbicide. Desorption was quantified from the difference between the herbicide concentration in the soil before the desorption steps and the concentration in the equilibrium solution, fitted by Freundlich's Equation (2):

$$C_s = K_{fd} C_e^{N_s} \quad (2)$$

### Half-life

The experiment was carried out in 300 cm<sup>3</sup> pots, lined with plastic bags and filled with 300 g of each soil. Subsequently, a single application of sulfometuron-methyl was carried out on the soil surface, according to the maximum dose recommended in the package insert for the commercial product (33.35 g a.i. ha<sup>-1</sup>). Soil moisture was kept close to field capacity. The evaluation times were 1, 3, 7, 15, 30, 45, 60, 120 and 180 days after herbicide application, and the soil samples for each time were homogenized and stored at -20 °C.

The extraction of sulfometuron-methyl from soil samples was carried out by the QuEChERS method, with modifications, according to Pang, Wang and Hu (2016), whose extraction process followed the same procedure described in the leaching topic. After extraction, the samples were analysed by LC-MS/MS to quantify the herbicide. To estimate the half-life of sulfometuron-methyl in the three soils studied, pseudo-first-order (PFO) (Equation 3) and pseudo-second-order (PSO) (Equation 4) kinetic models were tested using the Akaike test (Akaike Information Criterion - AIC). AIC prioritizes models with few variables, preferably lower values in their results, reducing the error percentage, so this parameter was used to define the best model of herbicide degradation kinetics.

$$\frac{dCt}{dt} = k (C_e - Ct) \quad (3)$$

For the linear fit, equation (3) was reorganized as  $\ln(C_e - Ct) = -kt + \ln C_e$ :  $k$  is the pseudo-first-order rate constant and can be estimated from the slope after plotting  $\ln(C_e - Ct)$  versus  $t$ , and  $C_e$  is the equilibrium concentration of sulfometuron-methyl.

$$\frac{dCt}{dt} = k (C_e - Ct)^2 \quad (4)$$

Equation (4) was reorganized as  $\frac{t}{Ct} = \frac{t}{C_e} + \frac{1}{kC_e^2}$  for linear fit:  $k$  is the pseudo-second-order rate constant and can be estimated from the slope after plotting  $t/Ct$  versus  $1/C_e^2$ .  $C_e$  is the equilibrium concentration of sulfometuron-methyl. The estimated values of  $t_{1/2}$  were calculated from the linear equation obtained from the regression between  $\ln Ct$  (pseudo-first-order model),  $t/Ct$  (pseudo-second-order model) of the experimental data.

### Leaching

The study was carried out in PVC columns measuring 10 cm in diameter and 35 cm in length, internally lined with paraffin and filled with soil (CX, LV and RQ). A layer of fibreglass was inserted at the base of the column to prevent the passage of soil particles and allow only the passage of water, which was collected for analysis of the leached material.

The soil columns were saturated by capillarity for three hours, and after that time, the columns were arranged to drain excess water for 24 hours. After drainage, the soil columns received 10 mL of herbicide solution with 0.0262 mg L<sup>-1</sup> of the herbicide in each soil type according to the recommended technical dose. After applying sulfometuron-methyl, the upper end of the column was protected with aluminium foil to avoid product degradation by light. After 24 hours of herbicide application, uniform precipitation of 60 mm on the soil surface divided into four hours of application was simulated. After 24 hours of the last precipitation, the soil columns were sectioned longitudinally every 5 cm, totalling seven depths (0-0.05; 0.05-0.10; 0.10-0.15; 0.15-0.20; 0.20-0.25; 0.25-0.30; 0.30-0.35 m). The samples were dried and crushed, sieved through a 2 mm mesh, stored at -20 °C and analysed by LC-MS/MS.

The extraction was performed using the QuEChERS method with modifications (PANG; WANG; HU, 2016). 5 g of soil were weighed in Falcon tubes, followed by the addition of 10 mL of acetonitrile, 100 µL of acetic acid and 2 mL of distilled water. The mixture was subjected to an ultrasonic bath for 15 minutes. 1 g of NaCl and 2 g of MgSO<sub>4</sub> were added to each tube after the ultrasound bath, and these were shaken to homogenize the solution. 1 mL of the supernatant was collected and put into 1.5 mL microtubes containing 0.2 g of MgSO<sub>4</sub>, and these were centrifuged at 2,260 g for five minutes to decant the solid phase. The supernatant was collected, filtered with 0.22 µm Nylon filters into vials and analysed by liquid chromatography.

The GUS Index (Groundwater Vulnerability Index) was used to assess the potential risk of contamination by the plant protection product. This parameter is based on the partition coefficient

between organic carbon and water, mL g<sup>-1</sup> (Koc), and the half-life (t<sub>1/2</sub>), in days, or persistence of the herbicide in the soil, calculated according to equation (5), proposed by Gustafson (1989):

$$GUS = \log\left(\frac{t_1}{2}\right) \times [4 - \log(Koc)] \quad (5)$$

Where: Koc is the normalized sorption constant; t<sub>1/2</sub> represents the half-life of the herbicide in soil (days).

### Chromatographic conditions

The LC-MS/MS is an ultra-high-performance liquid chromatography (UHPLC) system (Shimadzu) coupled to a Shimadzu triple quadrupole mass spectrometer (LCMS-8040). The UHPLC is equipped with a Restek column (Pinnacle DB AQ C18, size 50 x 2.1 mm, with 1.9 μm particles), including two LC - 30AD pumps, a DGU degasser - 20A<sub>5R</sub>, an autosampler Sil - 30AC, one CTO - 30AC column oven, and one CBM - 20A controller.

### Extraction method validation

The validation of the method was carried out by evaluating the performance parameters selectivity, linearity, detection limit and quantification, precision, accuracy and matrix effect, to assess the reliability of the results provided by the method (ANVISA, 2017).

### Recovery Study

The recovery studies of the method in the three soils were evaluated at fortification levels of 1,

10 and 100 μg kg<sup>-1</sup> for sulfometuron-methyl, with addition of 5 g of soil into 50 mL Falcon tubes, followed by 1 mL of embedding solution. These samples were left to stand in the dark for complete solvent evaporation, and unfortified samples were subjected to the same conditions as a control. After extraction, fortified sample solutions and unfortified sample solutions were used to quantify recovery. Three repetitions were done for each concentration level.

### Statistical analysis

Statistical analyses were performed using RStudio software version 3.4.1. The Kfs and Kfd were estimated by Freundlich isotherms and compared through descriptive analysis of means and standard error. The leaching tests estimated data by the mean confidence interval (p ≤ 0.05). The t<sub>1/2</sub> was calculated using pseudo-first-order and pseudo-second-order kinetic models, which were compared for their root mean square error (RMSE), coefficient of determination (R<sup>2</sup>) and Akaike test (AIC) values.

## RESULTS AND DISCUSSION

### Sulfometuron-methyl sorption and desorption

Sorption and desorption of herbicides depend on their different attributes and interactions, which are complex and non-linear (SINGH; SINGH, 2012). In the present work, the herbicide's sorption coefficient (Kfs) values ranged from 1.91 to 2.81 for RQ and LV, respectively (Table 2). CX had moderate sorption compared to the other soils (2.43).

**Table 2.** Parameters of the Freundlich sorption (Kfs and Ns) and desorption (Kfd and Nd) models and hysteresis index (H) for sulfometuron-methyl in three soils (*Cambissolo*, *Latossolo* and *Neossolo*).

Soil	Sorption				Desorption				Hysteresis index (H)
	Kfs	Ns	R <sup>2</sup>	RMSE	Kfd	Nd	R <sup>2</sup>	RMSE	
<i>Cambissolo</i>	2.43 (0.06)	0.83 (0.04)	0.98	0.03	0.37 (0.03)	0.41 (0.06)	0.79	0.01	0.49
<i>Latossolo</i>	2.81 (0.09)	0.67 (0.04)	0.97	0.02	0.59 (0.02)	0.16 (0.02)	0.87	0.01	0.23
<i>Neossolo</i>	1.91 (0.04)	0.75 (0.03)	0.98	0.02	0.34 (0.03)	0.61 (0.07)	0.88	0.01	0.82

R<sup>2</sup>= coefficient of determination. RMSE= Root mean square error. Value within parentheses indicates the standard error of the mean.

LV had the lowest pH value (4.7), favouring the highest sorption of sulfometuron-methyl (2.81). This is due to the predominance of the herbicide in its molecular form. Weak acid herbicides, such as sulfometuron-methyl, at soil pH values lower than the pKa value, tend to remain in their molecular

state, reducing the repulsion between the herbicide and the negative charges in the soil and, consequently, favouring sorption of the active ingredient (MARINHO et al., 2018).

Another factor that may favour greater sorption of LV compared to other soils is the

presence of iron and aluminium oxides (ROUCHAUD et al., 2001). Anions can be adsorbed onto the surfaces of aluminium and iron oxides and hydroxides. These oxides present in the *Latossolo* exhibit pH-dependent surface charges, and the degree of positive charge depends on the pH of the system (MOTT, 1981). A pH value below the point of zero charge (PZC) results in more  $H^+$  ions accumulating on the surface of the colloid, thus generating a net positive charge, enabling the sorption of the herbicide (STEVENSON, 1994).

Mineralogy may have influenced the lower sorption of sulfometuron-methyl in RQ (1.91). The predominance of 1:1 silicate minerals, such as mica and quartz, reduces the soil sorption process, in addition to revealing a lower degree of soil weathering and, consequently, sediments (clays) from this process will be less present, reducing the plastic capacity of clays in RQ. In addition, a large amount of sand, as verified in this soil (RQ), promotes a slower exchange electrostatic surface, favouring lower herbicide adsorption (MARINHO et al., 2018).

Another factor contributing to the lower sorption of RQ (1.91) is that the silt contents form a structure composed of micro aggregates formed by small granules that somehow function as silt and sand. Therefore, in RQ, the silt contents ( $0.10 \text{ kg kg}^{-1}$ ), related to the number of microaggregates, maybe retain the herbicide, preventing it from returning to the soil solution.

Despite the high pH (7.60), CX obtained greater sorption (2.43) compared to RQ (1.91) due to higher clay and total organic carbon (TOC) contents ( $8.2 \text{ g kg}^{-1}$ ). It is known that TOC allows high soil sorption power. However, in a study carried out by Sodr , Lenzi and Costa (2001), the authors did not identify a positive relationship between TOC and its sorption capacity due to other attributes that, together, played a more prominent role in adsorption. Thus, as noted in this study, TOC and clay did not have the most significant expected contribution to these processes since sorption in LV (2.81) was higher than that recorded in the other soils.

The Kfs value found in CX (2.43), which had a pH value of 7.6, favoured its lower sorption when compared to LV (2.81). However, according to the chemical analysis of the evaluated soils, CX was the one with the highest contents of TOC ( $8.2 \text{ g kg}^{-1}$ ) and CEC ( $14.29 \text{ cmolc dm}^{-3}$ ), justifying the second-highest sorption between soils (Table 2), which also allowed equal desorption capacity (0.37). The mineralogical composition present in RQ, which contributed to its low sorption (1.91), also allowed this soil to have the lowest desorption (0.34) among the studied soils.

The lowest value for Kfd in RQ (0.34) indicates greater desorption of the herbicide, demonstrating lower stability of the bonds between soil and herbicide, in addition to lower energy needed to break these interactions. The reduced TOC value of RQ ( $7.0 \text{ g kg}^{-1}$ ), compared to CX ( $8.2 \text{ g kg}^{-1}$ ), also reduces the interactions between soil and herbicide, so less energy is needed for the herbicide to return to the soil solution.

The desorption coefficient (Kfd) of LV (0.59) was 37 and 42% higher than those observed for CX (0.37) and RQ (0.34), respectively. Desorption is characterized by the return of the compound molecules sorbed to the soil particles to the solution. Desorption intensity reflects the degree of reversibility of the sorption process, with desorption being entirely or partially reversible; where only part of the sorbed herbicide returns to the soil solution, which gives rise to the phenomenon called hysteresis (ALLEONI; MELO, 2009).

The hysteresis coefficient (H) measures herbicide desorption (PINNA et al., 2014). Thus, it can be observed that the hysteresis index (H) of RQ was the highest one among the values of the studied soils (Table 2). Hysteresis index  $H < 1$  indicates that the desorption rate is lower than the sorption rate (PINNA et al., 2014), with positive hysteresis occurring. Based on the data, the sorption and desorption of herbicides were hysteretic in the three soils: CX (0.49), LV (0.23) and RQ (0.82).

### Half-life

Pseudo-first-order (PFO) and pseudo-second-order (PSO) models are most frequently used to determine the degradation of herbicides (ROCHA et al., 2012). Generally, the PSO model better describes the kinetics, possibly due to chemical adsorption. Valence forces are involved in sharing or exchanging electrons between the adsorbent and the adsorbate (MAYAKADUWA et al., 2016), unlike the PFO models, where the slower physical forces act. These models were tested for sulfometuron-methyl degradation kinetics.

The Akaike test indicated that both models were appropriate to describe the observed data of sulfometuron-methyl degradation in the studied soils, as the other parameters (RMSE and  $R^2$ ) could not be used as criteria, considering that lower RMSE values and high values of  $R^2$  indicate that the model shows better performance in predicting the results (REMINI et al., 2015), contrary to the values obtained by AIC. The PFO model fit the LV best, while the PSO model showed the best fit to the data for CX and RQ soils (Table 3).

**Table 3.** Parameters of the kinetic degradation models (pseudo-first-order – PFO and pseudo-second-order – PSO), Akaike test value (AIC), and half-life time ( $t_{1/2}$ ) for sulfometuron-methyl in three soils (*Cambissolo*, *Latossolo* and *Neossolo*).

Soil	Model	Parameters			Std. Error	R <sup>2</sup>	RMSE	AIC	$t_{1/2}$ (days)
		Co	Std. Error	K					
<i>Cambissolo</i>	PFO	95.32	2.65	3.80E-02	3.10E-03	0.96	1.4	212.4	17
	PSO	102.9	1.07	7.88E-04	2.54E-05	0.99	0.47	146.7*	13
<i>Latossolo</i>	PFO	92.43	2.64	3.30E-02	2.80E-03	0.95	1.43	176.5*	19
	PSO	100.5	1.74	7.45E-04	4.02E-05	0.99	0.77	213.4	13
<i>Neossolo</i>	PFO	96.42	1.96	3.37E-02	2.00E-03	0.98	1.06	195.4	19
	PSO	103.1	1.12	6.75E-04	2.31E-05	0.99	0.51	151.3*	15

\*Best model according to Akaike test for each soil. Std.Error = Standard error of the mean. R<sup>2</sup> = coefficient of determination. RMSE = root mean square error.

In LV, the model that best fitted was the PFO due to the lower AIC value (176.5) (slightest error assumed by the model) (Table 3). In addition, this soil had the highest  $t_{1/2}$  of 19 days. The more remarkable persistence of sulfometuron-methyl in LV is related to greater herbicide sorption in the soil, reducing the molecules available in the solution for the degradation process, probably due to the low pH and mineralogical composition present in this soil. Sulfonylureas are degraded in the soil due to microbiological and chemical processes (BURNET; HODGSON, 1991). Few studies have determined the persistence of sulfometuron-methyl isolated in the field, with typical values of  $t_{1/2}$  from 28 to 30 days (HARVEY JR; DULKA; ANDERSON, 1985).

CX (AIC = 146.7) and RQ (AIC = 151.3) showed  $t_{1/2}$  at 13 and 15 days after herbicide application, respectively, and, consequently, less persistence for the sulfometuron-methyl herbicide (Table 3). Considering the concern with water contamination, these results are important because the short half-life of the herbicide reduced the risks of contamination of natural resources to the detriment of products with greater longevity. The short  $t_{1/2}$  of herbicides also prevents the residues of the molecules from interfering with subsequent crops. On the other hand, regarding agronomic efficiency, it will reduce weed control.

The lower persistence of sulfometuron-methyl in CX (13 days) may be related to its higher content of TOC = 8.2 g kg<sup>-1</sup> when compared to those found in LV, which had TOC content = 5.3 g kg<sup>-1</sup>, and in RQ, which had TOC content = 7.0 g kg<sup>-1</sup>, indicating that microbiological degradation under the conditions studied was one of the factors for the degradation of sulfometuron-methyl. Furthermore, this herbicide is decomposed in the soil at a rate mainly dependent on soil pH and moisture content (ANDERSON; DULKA, 1985).

Trubey, Bethem and Peterson (1998),

evaluating the degradation and mobility of sulfometuron-methyl under natural field conditions in the United States, obtained  $t_{1/2}$  values ranging from 12 to 25 days. The herbicide showed rapid degradation in the four experimental sites. In another study, evaluating the  $t_{1/2}$  of herbicides, Smith (1995) concluded that the half-lives of the sulfonylureas chlorsulfuron, chlorimuron-ethyl, metsulfuron-methyl and sulfometuron-methyl in an aqueous medium at 45 °C and pH 5.0 were 1.7, 0.6, 2.1 and 0.4 days, whereas with pH 7.0 the half-life data were 51, 14, 33 and 6 days, respectively, under similar conditions, showing that the results obtained by the authors were different from those found in this study.

### Leaching

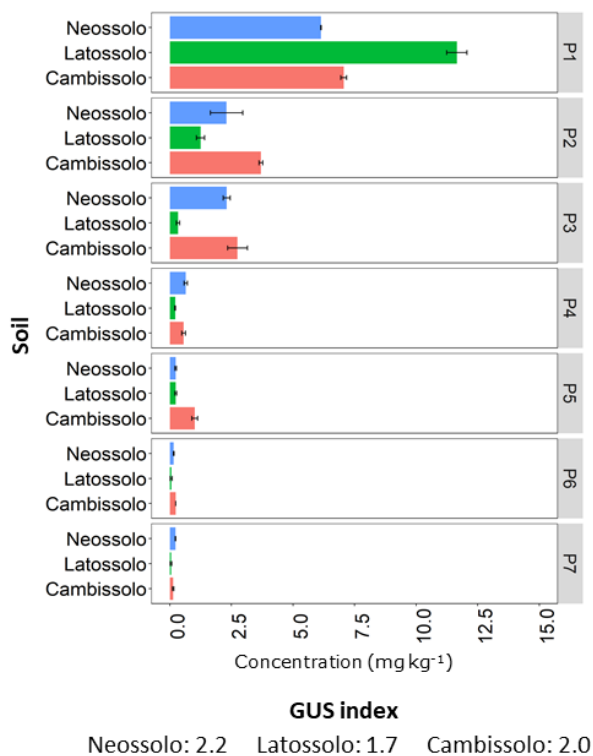
Herbicide leaching occurred differently in the studied soils. A higher concentration of sulfometuron-methyl was verified in the superficial layers of all soils (Figure 1), but LV had greater herbicide retention in the 0-0.05 m layer. The herbicide leached more steeply to the 0.10-0.15 m layer of LV, whereas for RQ and CX it was up to the 0.15-0.20 m and 0.20-0.25 m layers, respectively. The herbicide leached below its detection limit in the 0.25-0.30 m and 0.30-0.35 m layers.

In a study carried out by Reis et al. (2017), the highest concentration of sulfometuron-methyl was found in the first layer of the soil (0-0.05 m), and herbicide leaching was higher in sandy soil and lower in clayey soil. Such results were similar to those obtained in the present study. According to the GUS Index, RQ had a higher risk of leaching, indicating that sulfometuron-methyl leaching is more significant in sandy soils than in clayey soils.

Sulfonylurea herbicides are weak acids, meaning that under neutral to alkaline conditions, the molecules are negatively charged, and as the soil pH rises, the herbicide mobility is also increased

(OLIVEIRA; BRIGHENTI, 2011), as noted in the movement of the herbicide in CX at depth 5 (Figure 1). This condition justifies that CX has shown more significant leaching (mobility) between the layers in

the soil profile. According to Sondhia (2009), the solubility of sulfometuron-methyl increases with increasing soil pH.



**Figure 1.** Sulfometuron-methyl leaching and GUS index calculated in three soils (*Cambissolo*, *Latossolo* and *Neossolo*) at seven depths (P1, P2, P3, P4, P5, P6 and P7) after simulating a 60 mm rainfall applied in 4 hours. Bars indicate the confidence interval of the mean ( $p \leq 0.05$ ).

Furthermore, because herbicides from the chemical group of sulfonylureas are weak acids, they usually have pKa within the range from 3 to 5 (HAY, 1990). Due to this, their solubility in water at pH 7 is approximately ten times greater than at pH 5 (SMITH, 1995), which may have contributed to the greater mobility of the herbicide in CX. The significant leaching of sulfometuron-methyl observed in CX (0.20-0.25 m) (Figure 1) is probably due to its pH value (7.6), which favours the occurrence of the herbicide in dissociated form and with lower sorption to the soil, being more available in the solution and, consequently, with a greater risk of leaching.

The leaching of sulfometuron-methyl in alkaline soils is more significant than in acidic soils, as it has low sorption and high solubility with increasing pH (SENSEMAN, 2007). In other works carried out with weak acid herbicides (picloram and imazethapyr), the soil pH increased the number of molecules in a dissociated state, promoting more significant leaching of these herbicides (CASTRO NETO et al., 2017).

Sulfometuron-methyl showed lower leaching in LV due to the high sorption and low desorption in

this soil class. This means that most of its sorbed molecules remained under this condition. In other words, the soil attributes that allowed its higher sorption also favoured low desorption, which is confirmed by the lower hysteresis index of LV (0.23), which means that the sorption rate was higher than the desorption rate.

Due to their high solubility and poor sorption in soils with neutral and alkaline pH values, sulfonylureas generally have great leaching potential, especially under high rainfall (HAY, 1990). Mathematical models predict the potential for contamination, highlighting the GUS Index for surface water (GAMA; OLIVEIRA; CAVALCANTE, 2013). According to Gustafson (1989), herbicides with GUS values <1.8 are classified as non-leachable, herbicides with GUS between 1.8 and 2.8 are transient, and herbicides with GUS > 2.8 are classified as leachable. RQ showed a moderate risk of percolation of sulfometuron-methyl according to the GUS Index, which assesses the potential risk of an herbicide leaching contaminating groundwater. This fact is justified by the herbicide's greater desorption in RQ.



## CONCLUSIONS

The sorption, desorption, half-life and leaching of sulfometuron-methyl are dependent on the soil class and its physical, chemical and mineralogical attributes. The greater herbicide sorption in the *Latossolo Vermelho* is related to the low pH and mineralogical composition, mainly due to iron and aluminium oxides. The more remarkable persistence of the herbicide in the *Latossolo* is related to its greater sorption and lower desorption, reducing the molecules available for degradation in the solution. The *Neossolo Quartzarênico* had a moderate risk of leaching, showing a potential risk of groundwater contamination.

## ACKNOWLEDGMENTS

This work was carried out with support from the Coordination for the Improvement of Higher Education Personnel - Brazil (CAPES) - Financing Code 001 and from the National Council for Scientific and Technological Development (CNPq).

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