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GABRIELLA DAIER OLIVEIRA PESSOA CARNEIRO

**SOIL RETENTION PROCESSES OF DIURON, HEXAZINONE AND
SULFOMETURON-METHYL HERBICIDES APPLIED ISOLATED AND IN
MIXTURE**

MOSSORÓ

2020

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Tese apresentada ao Doutorado em Agronomia do Programa de Pós-Graduação em Fitotecnia da Universidade Federal Rural do Semi-Árido como requisito para obtenção do título de Doutor em Fitotecnia.

Linha de Pesquisa: Manejo de Plantas Daninhas

Orientador: Prof. Dr. Daniel Valadão Silva

Co-orientador: Dr. Matheus de Freitas Souza

Co-orientador: Dr. Leilson Costa Grangeiro

MOSSORÓ

2020

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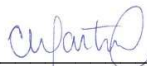
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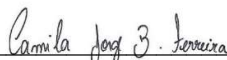
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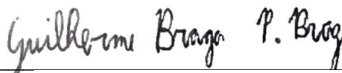
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“Something is only impossible until someone doubts and decides to prove it to the contrary. ”

Albert Einstein

ABSTRACT

The mixture of herbicides is an important tool used in the control of weeds in different cultures. However, interactions between herbicide molecules can alter their retention processes in the soil and, consequently, their effectiveness in controlling weeds and potential for environmental impact. In this research, the effects of the mixture on the kinetics and intensity of sorption and desorption in the soil of diuron, hexazinone and sulfometuron-methyl applied separately were evaluated. The sorption kinetics was estimated of isolated and mixed binary and triple herbicides using the pseudo-first order and pseudo-second order models. In the study of sorption and desorption, the Freundlich model was used because it presents a better fit in relation to the Langmuir and Linear models. Regardless of the herbicide, the mixture or the soil, adsorption occurred quickly during the first hour, followed by a much slower stage progressing towards an apparent equilibrium. The model, in general, that best fit the study was pseudo-second order, which consists of adsorption in the monolayer. The concentration absorbed at equilibrium was lower for the binary and ternary mixtures of the herbicides. The adsorption time and the sorption capacity of the herbicides showed the following order of diuron > hexazinone > sulfometuron-methyl in the dystrophic red Oxisol and diuron > sulfometuron-methyl > hexazinone in the red-yellow Oxisol. The binary and ternary combinations between diuron, hexazinone and sulfometuron-methyl reduced the sorption and desorption in the soils compared to the isolated tests of these herbicides. The sorption and desorption of hexazinone in soils is most affected by mixing with other herbicides. Sulfometuron-methyl promotes greater reduction in the sorption of diuron in relation to hexazinone. The mixture between diuron, hexazinone and sulfometuron-methyl increases the availability of these herbicides in the aqueous phase of the soil allowing the use of lower rates in the application compared to isolated applications. Higher availability also indicates a greater potential for environmental contamination via leaching or surface runoff.

Key words: Sorption. Desorption. Kinetics. Adsorption.

RESUMO

A mistura de herbicidas é uma importante ferramenta utilizada no controle de plantas daninhas em diversas culturas. Contudo, as interações entre as moléculas dos herbicidas podem alterar seus processos de retenção no solo e, conseqüentemente, sua eficácia no controle das plantas daninhas e potencial de impacto ambiental. Nesta pesquisa foram avaliados os efeitos da mistura na cinética e na intensidade da sorção e dessorção no solo do diuron, hexazinone e sulfometuron-methyl. A cinética de sorção dos herbicidas isolados e em mistura binárias e triplas foi estimada utilizando os modelos de pseudo-primeira ordem e pseudo-segunda ordem. No estudo de sorção e dessorção foi utilizado o modelo de Freundlich por apresentar melhor ajuste em relação aos modelos de Langmuir e Linear. Independente do herbicida, da mistura ou do solo, a adsorção ocorreu rapidamente durante a primeira hora, seguido de um estágio muito mais lento progredindo em direção a um aparente equilíbrio. O modelo, de maneira geral, que melhor se ajustou no estudo foi pseudo-segunda ordem, que consiste na adsorção na monocamada. A concentração sorvida no equilíbrio foi menor para as misturas binárias e ternárias dos herbicidas. O tempo de adsorção e a capacidade de sorção dos herbicidas mostraram a seguinte ordem de diuron > hexazinone > sulfometuron-methyl no Latossolo Vermelho Distrófico e diuron > sulfometuron-methyl > hexazinone no Latossolo Vermelho-Amarelo. As combinações binárias e ternárias entre diuron, hexazinone e sulfometuron-methyl reduziram a sorção e dessorção nos solos comparado aos ensaios isolados desses herbicidas. A sorção e dessorção do hexazinone nos solos é mais afetada pela mistura com outros herbicidas. O sulfometuron-methyl promove maior redução na sorção do diuron em relação ao hexazinone. A mistura entre diuron, hexazinone e sulfometuron-methyl eleva a disponibilidade desses herbicidas na fase aquosa do solo permitindo o uso de menores taxas na aplicação em comparação com aplicações isoladas. A maior disponibilidade também indica maior potencial de contaminação ambiental via lixiviação ou escoamento superficial.

Palavras-chave: Sorção. Dessorção. Cinética. Adsorção.

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LIST OF ABBREVIATIONS AND INITIALS

AICc	Akaike test
ALS	Aceto lactate synthase
AL	Alagoas
Labile C	Labile carbon
TOC	Total organic carbon
CEC	Cation exchange capacity
C18	Reverse phase column
E	Parameter values
K1	Pseudo-first order speed constant
K2	Pseudo-second order speed constant
Log	Logarithm
LVA	<i>Latossolo Vermelho-Amarelo</i> – Red-Yellow Oxisol
LVD	<i>Latossolo Vermelho Distrófico</i> – Red dystrophic Oxisol
P	Parameter
PFO	Pseudo-first order
pH	Hydrogenionic potential
PSO	Pseudo-second order
PSII	Photosystem II
Qe	Maximum sorption
RMSE	Root mean squared error
RN	Rio Grande do Norte
Std. Error	Standard error of the mean
UHPLC	Ultra high performance liquid chromatography

LIST OF SYMBOLS

1/n	Linearization factor
Al ⁺³	Aluminum cation
Ca	Calcium
CaCl ₂	Calcium chloride
Ca ⁺²	Calcium cation
Cs	Concentration of herbicide sorbed in soil
°C	Degrees Celsius
Ce	Herbicide equilibrium concentration in the solution
Cm	Centimeter
D1	Plastoquinone protein
G	Grams
G	Gravity
g. ha ⁻¹	Grams per hectare
g L ⁻¹	Grams per liter
g kg ⁻¹	Grams per kilogram
H	Hydrogen
H+Al	Potential acidity
K	Potassium
Kfs	Sorption constant
Kfd	Desorption constant
Kow	Octanol-water partition coefficient
Koc	Standardized sorption constant
M	Aluminum saturation
Mg ⁺²	Magnesium cation
mg L ⁻¹	Milligram per liter
mL	Milliliter
Mm	Millimeter
ml.min ⁻¹	Millimeter per minute
mM	Milimolar
Mpa	MegaPascal
Na ⁺²	Sodium cation

Nm	Nanometer
P	Phosphor
pKa	Dissociation constant – weak acid
pKb	Dissociation constant – weak base
Mm	Micrometer
QB	Plastoquinone B
qe	Adsorption capacity (mg.kg^{-1}) at equilibrium time
R ²	Determination coefficient
®	Trademark
V	Base saturation
%	Percentage

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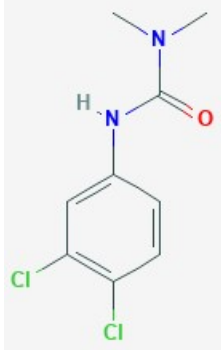
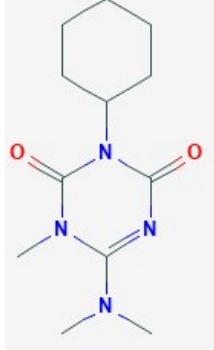
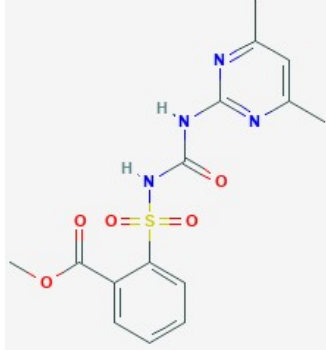
INTRODUCTION

Weed management has been one of the most important activities in sugar cane cultivation carried out in Brazil, since when improperly controlled they can cause reductions in productivity that vary between 30 to 70% (MILHOLLON et al., 1995; LEON et al., 2018). This reduction is the result of direct and indirect weed inferences, mainly in the initial stage of crop development, when sugar cane is more sensitive to the interference of the weed community (KUYA et al., 2003; PAULA et al., 2018). Thus, it is necessary to use control measures to minimize the negative effects of weeds in this crop (BASINGER et al., 2019).

In this sense, the chemical method has been the most used in the control of weeds in sugar cane crops, as it presents greater efficiency, ease of application and is of lower cost when compared to the others (RIAZ et al., 2015). Among the application modalities, pre-emergence, initial post-emergence and late post-emergence are mentioned, in addition to localized applications using non-selective herbicides. The effectiveness of the herbicide will depend on the environmental conditions, the position and growth stage of the weeds to be controlled (MEROTTO JUNIOR et al., 1997; MEHDIZADEH et al., 2017).

The formulated mixture of herbicides has been used to increase the spectrum of action in the control of weeds, reducing the number of applications. In sugar cane, the mixture between diuron and hexazinone (Velpar K[®]) was one of the most used formulations for the control in pre and post-emergence of weeds. In recent years, the herbicide sulfometuron-methyl has been included in the mixture, forming the commercial formulation Front[®] (603 g diuron kg⁻¹ + 170 g hexazinone kg⁻¹ + 14.5 g sulfometuron kg⁻¹) (BRASIL, 2020). In order to characterize each of the aforementioned herbicide molecules, Table 1 describes the main physicochemical properties of these active ingredients.

Table 1 – Structural formulas and physicochemical properties of the herbicides diuron, hexazinone and sulfometuron-methyl.

Herbicide properties	Diuron	Hexazinone	Sulfometuron-methyl
Chemical structure			
Solubility in water at 25 °C (mg L ⁻¹)	37.4	3.3 x 10 ⁴	244
Octanol-water partition coefficient (Log Kow)	2.68	1.85	1.20
Dissociation constant (pKa/pKb) at 25 °C	13.6	2.2	5.2
Vapor pressure (mPa)	1.15 x 10 ⁻³	3.0 x 10 ⁻²	7.3 X 10 ⁻¹¹
Molecular mass (g mol ⁻¹)	233.09	252.31	364.40
Polar surface area (Å ²)	32.3	56.2	136
Hydrogen bond donors/acceptors	2	4	9

Fonte: Adaptado de PPDB (2019).

Diuron is an herbicide applied in pre-emergence, from the group of urea replaced with the destruction mechanism of photosystem II (PSII) by its binding to protein D1, at

the site where the plastoquinone "Qb" is coupled, interrupting the flow of electrons between photosystems (DE LIMA et al., 2017). Hexazinone is a selective herbicide with systemic action in the pre and post-emergence of the chemical group of triazinones, besides being a PSII inhibitor (GUIMARÃES et al., 2018). Sulfometuron-methyl is a regulator of the chemical group of sulfonylureas recommended as a maturation agent for sugarcane by inhibiting the enzyme acetolactate synthase (ALS) that catalyzes the first step in the biosynthesis of branched chain amino acids valine, leucine and isoleucine (HRAC, 2019). Because these are herbicides with residual potential in the soil, they can control weeds for a longer period, reducing production costs. However, greater persistence can also contribute to the negative environmental impact.

The environmental conditions and the physicochemical characteristics of the herbicides determine the degradation by physical, chemical and biological agents, volatilization, sorption and leaching (SANTOS et al., 2018) for regulating their mechanisms of interaction with the organic and inorganic phases of the soil (BLASIOLI et al., 2011). In this sense, studies on the behavior of herbicides formulated in mixtures are essential to improve the understanding of the final destination of herbicides in the environment and to make the use of herbicide more efficient and environmentally sustainable (MENDES et al., 2017).

The environmental behavior of isolated herbicides diuron, hexazinone and sulfometuron-methyl are reported in scientific studies (AZCARATE et al. 2015; CHAUMET et al., 2019). However, the two-by-two mixture [(diuron + hexazinone), (diuron + sulfometuron-methyl), (sulfometuron-methyl + hexazinone) and the triple mixture (diuron + hexazinone and sulfometuron-methyl) has not been widely studied. Given the above, the hypothesis of this study is that application of diuron, hexazinone and sulfometuron-methyl in mixture (binary or tertiary) interferes with the environmental fate of these molecules and the efficiency of weed control in sugar cane culture when compared to the application of these isolated molecules. Therefore, the objective of the work was to evaluate the sorption and desorption processes of these herbicides isolated and mixed in classes of soils suitable for the cultivation of sugar cane.

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THE MIXTURE OF HERBICIDES AFFECT THE SORPTION KINETICS OF DIURON, HEXAZINONE AND SULFOMETURON-METHYL IN SOILS

Abstract: Kinetic studies are of great importance for understanding the processes and parameters involved in pollutant sorption in soils, mainly herbicides. In this study, the effects of the application of diuron, hexazinone, and sulfometuron-methyl alone or as a mixture on the sorption kinetics in sugarcane cultivation soils were investigated. Pseudo-first order and pseudo-second order models were used. Regardless of the herbicide, the mixture, or the soil, adsorption occurred quickly during the first hour, followed by a much slower stage progressing towards an apparent equilibrium. The model, in general, that best fit the study was pseudo-second order, which consisted of adsorption in a monolayer. The concentration adsorbed at equilibrium was lower for the binary and ternary mixtures of the herbicides. The adsorption was affected by the physical and chemical attributes of the soil, mainly the organic matter and the clay composition. The adsorption time and the sorption capacity of the herbicides had the following order of diuron > hexazinone > sulfometuron-methyl in the dystrophic red Oxisol and diuron > sulfometuron-methyl > hexazinone in the red-yellow Oxisol. The mixture of the herbicides reduced the amount adsorbed; however, it did little to change the speed of adsorption reactions.

Keywords: herbicide, pseudo-first order, pseudo-second order, soil retention.

1. INTRODUCTION

The herbicides diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H) dione] and sulfometuron-methyl {methyl 2-[(4,6-dimethylpyrimidin-2-yl) carbamoyl sulfamoyl] benzoate} are widely used to control annual broadleaf and grassy weeds, especially in sugar cane, and also in the cultivation of cereals, vegetables, and fruits as well as in

forestry (PPDB, 2019). Formulations of binary and ternary mixtures of these herbicides are widely used in the cultivation of sugar cane in Brazil (REIS et al., 2019), and the recommended dose for application depends on the soil texture of the cultivation area.

The three herbicides have different physical and chemical properties and, therefore, it is expected that the behavior of each in the soil would vary. For example, while diuron is considered a nonionic herbicide, hexazinone is a weak base ($pK_b = 2.2$) and sulfometuron-methyl is a weak acid ($pK_a = 5.2$) (SHANER et al., 2014; PPDB, 2019). Therefore, soil properties such as pH tend to directly influence the processes of retention, transport, and transformation of herbicidal molecules and, consequently, their efficiency in the control of weeds and the potential for environmental impact (MENDES et al., 2016).

The retention process of herbicides in colloids directly influences the transport and transformation processes of pesticide molecules in the soil. Sorption represents the ability of the herbicide to become adsorbed, absorbed, or precipitated in the soil and has been the most used parameter to represent the process of herbicide retention in the soil (SILVA et al., 2019; TAKESHITA et al., 2019).

The kinetics of sorption reactions of the herbicide in the soil influences its availability for weed control, as well as the potential for surface and groundwater contamination. In this sense, kinetic studies of herbicides in the soil are of great importance to determine the parameters and processes involved in their sorption, both from an agricultural point of view and of environmental relevance (PALMA et al., 2015). Little is known about the effects of herbicide mixtures on the soil, especially in tropical regions such as Brazil (MENDES et al., 2016).

Kinetic studies of the sorption of herbicides in the soil are generally performed considering single molecules (CÁCERES et al., 2010; CÁCERES-JENSEN et al., 2013; SPULER et al., 2019). Therefore, studies are needed to evaluate the effect of mixtures on the adsorption of herbicides in the soil and to understand the behavior and fate of these molecules in the environment. Knowledge of the influence of interactions between herbicidal molecules on sorption reactions is important for understanding the transport and availability of these chemicals in soils (TELI et al., 2017). In this context, this study evaluated the sorption kinetics of diuron, hexazinone, and sulfometuron-methyl isolated and in binary and ternary mixtures in Brazilian soils and the best kinetic model to describe the process.

2. MATERIAL AND METHODS

The experiments were carried out at the Weed Management Laboratory in the semiarid region of Brazil, belonging to the Federal Rural University of the Semiarid Region. The sorption and desorption tests of the herbicides diuron, hexazinone, and sulfometuron-methyl, isolated and in binary (diuron + hexazinone; diuron + sulfometuron-methyl; hexazinone + sulfometuron-methyl) and ternary mixtures (diuron + hexazinone + Sulfometuron-methyl), were performed using the ultra-high performance liquid chromatography (UHPLC) technique, in triplicate.

2.1. Characterization of soil

The soils were collected at a depth of 0 to 0,2 m. Two samples of Oxisols of the areas with sugarcane cultivation (no history of herbicide application) in the Northeast of Brazil with different physical and chemical attributes were used: *Latossolo Vermelho Amarelo* (SiBCS, 2018) (Red-Yellow Oxisol (LVA)) from Maceió-AL with geographic coordinates 9 ° 39 '21 "S and 35 ° 44' 38" O and *Latossolo Vermelho distrófico* (SiBCS, 2018) (dystrophic Red Oxisol (LVd)) of Mossoró-RN, with coordinates 5 ° 3 '37.7 "S and 37 ° 24' 14.4"W.

The soils were air-dried, sieved in a 2 mm mesh and chemically, and physically characterized (Teixeira et al., 2017). The collections were carried out in areas close to sugarcane cultivation but with no history of herbicide application. The chemical and physical characteristics are described in Table 1.

Table 1. Chemical and physical characteristics of the soils of the layer 0 – 0,2 m of *Latossolo Vermelho Amarelo* - Red Yellow Oxisol (LVA) from Maceió-AL and *Latossolo Vermelho distrófico* - Red Dystrophic Oxisol from Mossoró-RN (LVd).

Soils	Texture (g kg ⁻¹)			pH (water)	TOC (g kg ⁻¹)	Labile C (g kg ⁻¹)	P (mg dm ⁻³)	K (mg dm ⁻³)	Ca ⁺² (cmol _c dm ⁻³)	Mg ⁺² (cmol _c dm ⁻³)	Al ⁺³ (cmol _c dm ⁻³)	H+Al (cmol _c dm ⁻³)	CEC (cmol _c dm ⁻³)	V (%)	M (%)
	Sand	Silt	Clay												
LVA	640	120	240	5.84	9.46	2.0	0.91	108.13	1.37	1.77	0.00	5.45	8.90	38.2	0.00
LVd	770	24	200	4.58	4.71	1.3	0.25	28.00	0.86	0.85	3.30	5.45	7.20	25.0	64.7

Total organic carbon (TOC), labile carbon (labile C), potential acidity (H+Al), hydrogenionic potential (pH), cation exchange capacity (CEC), base saturation (V), aluminum saturation (M). *The labile carbon analyses were done according to Shang; Tiessen (1997). The other analyses were performed according to a methodology proposed by Silva, (2009). LASAPSA—Laboratory of Soil, Water, and Semiarid Plant Analysis, UFERSA.

Mineralogical characterization was carried out in the clay fraction, by chemical dispersion with sodium hexametaphosphate 0.025 mol L⁻¹ and mechanics with a “Wagner” type agitator for 16 h, according to Teixeira et al. (2017). Minerals were identified by X-ray diffraction (XRD) at the Integrated Center for Technological Innovation in the Semiarid Region (CITED) - UFERSA.

A Shimadzu diffractometer model XRD 6000 was used, in Japan, with Cu-K α 1 radiation. The source potential was 40 kV, and the current was 30 mA. A scanning speed with a step of 0.02° was applied every second. The scanning range (2 θ) was from 5 to 65°. The identification of mineral peaks was performed with the aid of the X-Ray program v. 1.0.0.37, and the phases were identified according to Chen (1977) (Figure 1).

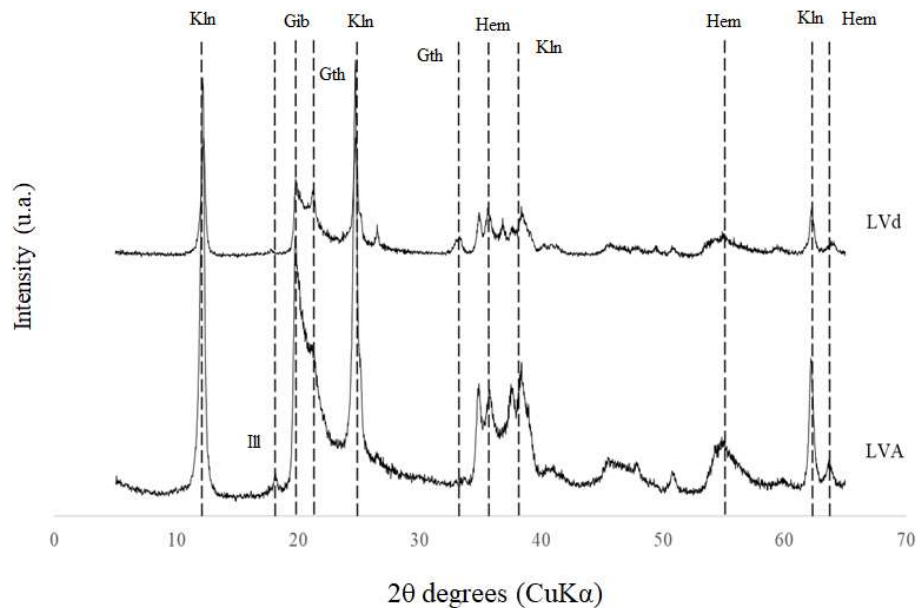


Figure 1. X-ray diffractometry of the clay fraction of horizons A of the *Latosolo vermeho-amarelo* (Red-Yellow Oxisol (LVA)) and of the *Latosolo vermeho distrófico* (Dystrophic Red Oxisol (LVd)). Kln = kaolinite, Illite = Ill, Gth = goethite, Hem = hematite, Gib = Gibbsite.

LVA: Kln, Ill, Gib, Gth, Hem. LVd: Kln, Gib, Gth, Hem.

2.2. Reagents

Analytical grade reagents and HPLC were used in the studies. The diuron, hexazinone standards were purchased from Sigma-Aldrich® (Saint Louis, MO, USA), with a purity of 99.6 and 99.5%, respectively. Sulfometuron-methyl was obtained from the company Supelco (Bellefonte, PA, USA), with a purity of 99.5%. A stock solution of each standard was prepared at a concentration of 1,000 mg L⁻¹ in acetonitrile. The working solutions were prepared by diluting with 10 mM aqueous CaCl₂ solution from the stock solutions.

2.3. Analytical method

The quantification of diuron, hexazinone, and sulfometuron-methyl was carried out using the Ultra-High Performance Liquid Chromatography system (UHPLC), the Shimadzu® DAD detector (model Nexera X2 SPD-M30A, Tokyo, Japan), equipped with a Restek Pinnacle column DB AQ C18, size 50 x 2.1 mm, with 1.9 µm particles, including two LC-30AD pumps, a DGU-20A5R degasser, a Sil-30AC autosampler, a CTO-30AC column oven, and a CBM-20A controller.

The chromatographic conditions used to quantify the herbicides were as follows: an elution mode involving isocratic conditions in a binary mobile phase composed of 0.1% formic acid in water (mobile phase A) and acetonitrile (mobile phase B), in the ratio of 33:67. The flow rate was 0.3 ml min⁻¹, with an injection volume of 5 µL. The temperature of the sample manager was 15°C. The wavelengths used were 254, 247, and 233 nm for diuron, hexazinone, and sulfometuron methyl, respectively.

2.4. Determination of sorption kinetics

The equilibrium time for sorption and desorption of the herbicides in the soils was carried out at 25±2°C by the batch equilibrium method (OECD, 2000). For the diuron and hexazinone herbicides, isolated and in binary and ternary mixtures, a volume of 10 ml of the solution of the herbicides in the concentration of 1 mg L⁻¹, prepared in 10 mM CaCl₂, was added in Falcon tubes containing 2 g of soil. For sulfometuron-methyl, isolated and in mixtures, samples with 4 g of soil were added to Falcon tubes, with a 16.0 mL aliquot of an aqueous solution containing the 1.0 mg L⁻¹ herbicides, prepared in 10 mM CaCl₂.

The analyses were performed separately for each herbicide, isolated and in binary and ternary mixtures. All evaluations were performed in triplicate.

The tubes were shaken vertically at different time intervals (0.0; 10.0; 20.0; 30.0; 60.0; 120.0; 240.0; 480.0; 720.0; 960 and 1,440.0 minutes). After stirring, the samples were centrifuged at 2,640 g for seven minutes. Then the supernatant was removed and filtered through a 0.22 µm PVDF membrane into 1.5 mL vials. Subsequently, the samples contained in the vials were quantified by UHPLC to estimate the concentration of the herbicides in the aqueous and solid phases in equilibrium.

2.5. Kinetic models

The models used to study the adsorption kinetics of the herbicides diuron, hexazinone and sulfometuron-methyl isolated and mixed in the evaluated soils were as follows:

a) Pseudo-first order equation

The pseudo-first order model can be expressed as shown in Equation (1).

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (1)$$

where q_e is the adsorption capacity (mg.kg⁻¹) at equilibrium time, q_t is the adsorption capacity (mg.kg⁻¹) at time t (min), and k_1 is the pseudo-first order velocity constant.

b) Pseudo-second order equation

The pseudo-second order model can be expressed as shown in Equation (2).

$$q_t = (k_2 q_e^2 t) / (1 + k_2 q_e t) \quad (2)$$

where q_e is the adsorption capacity (mg kg⁻¹) at equilibrium time, q_t is the adsorption capacity (mg kg⁻¹) at time t (min), and k_2 is the pseudo-second order velocity constant.

The comparison of the kinetic models in terms of quality of fit for each run and between them was based on the statistical parameters root mean squared error (RMSE) and the Akaike Information Criterion (AIC), obtained through Equations (3) and (4), respectively.

$$RMSE = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (q_{e,exp} - q_{e,calc})^2} \quad (3)$$

where n is the number of observations, $q_{e,exp}$ (mg.g⁻¹) are the experimental data of the equilibrium capacity, and $q_{e,calc}$ (mg.g⁻¹) the equilibrium capacity obtained from model

calculations. A lower value of *RMSE* indicates a better fit of the model (NARAYANAN et al., 2017).

$$AIC = n \ln \left(\frac{SSE}{n} \right) + 2k \quad (4)$$

where *SSE* is the sum of the squares of the residuals, *n* is the number of data points (sample size), and *k* is the number of model parameters. For small values of *n*, it is preferable to use a corrected AIC (AICc) obtained according to Equation (5). The best model is considered the one with the lowest AICc value (QUESADA-PEÑATE et al., 2009).

$$AICc = AIC + \frac{2k(k+1)}{n-k-1} \quad (5)$$

2.6. Statistical analysis

The kinetic models were compared in terms of the quality of the fit for each run and between them, which were based on the statistical parameters root mean squared error (RMSE), and the Akaike Information Criterion (AIC). Analysis of variance (ANOVA) was used to detect differences between q_e (maximum concentration absorbed mg g^{-1}) and time to maximum sorption (minutes) for the herbicides diuron, hexazinone, and sulfometuron-methyl alone and in mixtures. When significant, the means were compared using the Tukey test at 5% probability.

3. RESULTS AND DISCUSSION

3.1. Diuron sorption kinetics

The kinetic models of pseudo-first order (PFO) and pseudo-second order (PSO) were applied to the experimental data in order to determine the kinetic parameters and obtain information on the sorption mechanisms of the herbicide diuron isolated and in binary mixtures (diuron + hexazinone and diuron + sulfometuron-methyl) and in the ternary mixture (diuron + hexazinone + sulfometuron-methyl) in the Red-Yellow Oxisol (LVA) and Dystrophic Red Oxisol (LVd) (Figure 2 and Table 2).

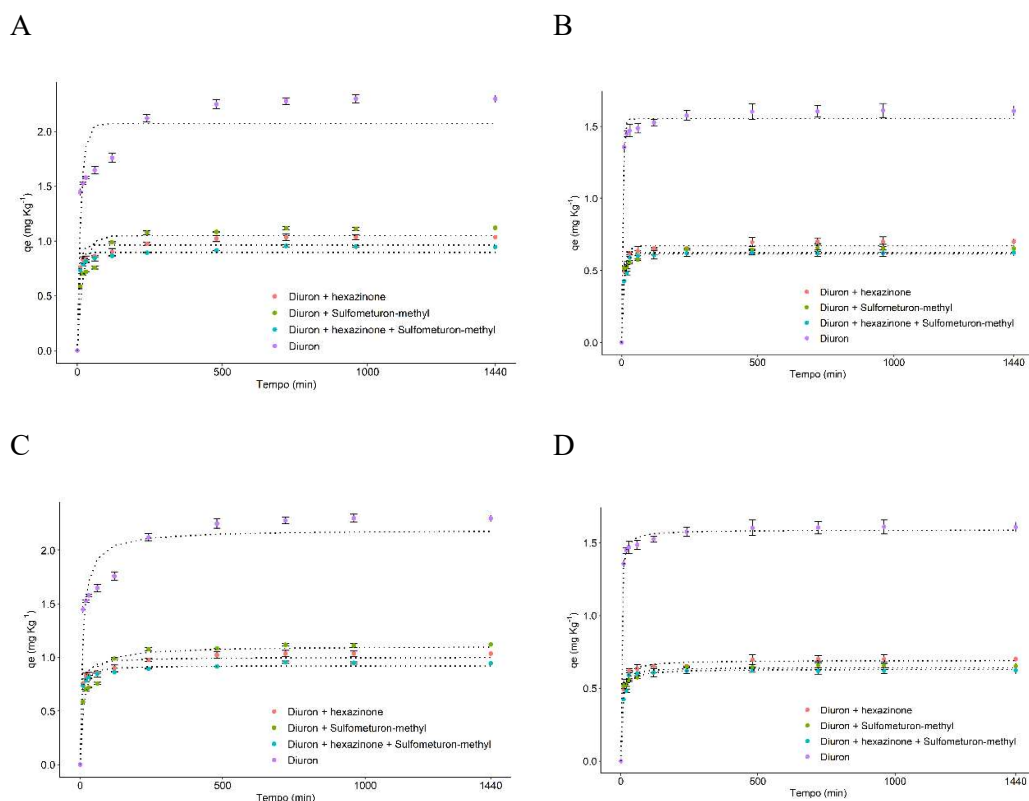


Figure 2. Sorption kinetics of diuron alone and in binary and ternary mixtures with hexazinone and sulfometuron-methyl in Red-Yellow Oxisol (LVA) (right) and Dystrophic Red Oxisol (LVd) (left) using the pseudo-first order models (PFO) (a, c) and pseudo-second order (PSO) (b, d). q_e : adsorption capacity (mg.kg⁻¹) at equilibrium time.

Sorption of the diuron alone and in mixtures increased rapidly during the first hour, followed by a much slower stage, progressing towards an apparent balance (Figure 2). Considering the solubility and hydrophobicity of the diuron, we assumed that the empty places in the soil particles were filled in the first hours. The herbicides then migrated and spread slowly over the colloids. With increasing time, the adsorption sites on the soil surface were gradually saturated, causing the adsorption rate to decrease until reaching equilibrium (DAS CHAGAS et al., 2018; DOS SANTOS et al., 2018). The concentration adsorbed at equilibrium was lower for the binary and ternary mixtures of the herbicides (Figure 2 and Table 2), which may be due to the competition of the herbicide molecules for the soil adsorption sites.

Table 2. Values of the parameters used to elaborate the pseudo-first order (PFO), and pseudo-second order (PSO) models to describe the sorption kinetics of diuron and binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Dystrophic Red Oxisol (LVd).

Soil	Treatment	Pseudo-first order			Pseudo-second order		
		P	E	Std. Error	P	E	Std. Error
LVA	Diuron	q_e	2.07	0.05	q_e	2.19	0.04
		k_1	0.07	0.01	k_2	0.05	0.01
	diuron + hexazinone	q_e	0.96	0.02	q_e	1.00	0.01
		k_1	0.13	0.02	k_2	0.24	0.03
	diuron + sulfometuron-methyl	q_e	1.05	0.02	q_e	1.10	0.02
		k_1	0.05	0.01	k_2	0.07	0.01
	diuron + hexazinone + sulfometuron-methyl	q_e	0.90	0.01	q_e	0.92	0.01
		k_1	0.15	0.01	k_2	0.35	0.03
LVd	Diuron	q_e	1.55	0.01	q_e	1.59	0.01
		k_1	0.19	0.02	k_2	0.33	0.04
	diuron + hexazinone	q_e	0.67	0.01	q_e	0.69	0.01
		k_1	0.11	0.01	k_2	0.31	0.03
	diuron + sulfometuron-methyl	q_e	0.62	0.01	q_e	0.64	0.01
		k_1	0.15	0.02	k_2	0.46	0.06
	diuron + hexazinone + sulfometuron-methyl	q_e	0.62	0.01	q_e	0.63	0.01
		k_1	0.10	0.01	k_2	0.34	0.04

Parameter (P); Parameter values (E); Standard error of the mean (Std. Error); Adsorption capacity ($\text{mg}\cdot\text{kg}^{-1}$) at equilibrium time (q_e); Pseudo-first order speed constant (k_1); Pseudo-second order speed constant (k_2).

The lowest values of AICc and RSME for each parameter and the precision to predict (q_e) were used as criteria to define the most appropriate models to describe the sorption kinetics of the isolated diuron and the binary and ternary mixtures (Table 3). The PSO model was not adequate to describe the interaction between diuron alone and in mixtures in the two soils studied (higher values of AICc and RMSE) (Table 3). The PSO model showed the best fit for sorption of diuron alone and in all mixtures in LVA and LVd (Table 3). This fact constitutes a preliminary point to establish that in Oxisols there is a high initial contribution of mass transport through the high number of vacant places accessible in the MO, MO-Al, and Fe complexes, resulting in an increase in the concentration gradient between the diuron in the solution and the diuron on the soil surface (WU et al., 2018).

Table 3. Akaike test to compare the models of pseudo-first order (PFO) and pseudo-second order (PSO) to describe the sorption kinetics of diuron and binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Red Oxisol Dystrophic (LVd).

Soil	Treatment	Modnames	AICc		RMSE
LVA	Diuron	PFO	-7.18		0.0437
		PSO	-18.29	*	0.0297
	diuron + hexazinone	PFO	-73.65		0.0128
		PSO	-101.86	*	0.0084
	diuron + sulfometuron-methyl	PFO	-49.31		0.0186
		PSO	-83.74	*	0.0110
	diuron + hexazinone + sulfometuron-methyl	PFO	-101.27		0.0084
		PSO	-137.79	*	0.0049
LVd	Diuron	PFO	-86.326		0.0106
		PSO	-114.85	*	0.0069
	diuron + hexazinone	PFO	-115.66		0.0068
		PSO	-144.95	*	0.0044
	diuron + sulfometuron-methyl	PFO	-109.97		0.0074
		PSO	-139.11	*	0.0048
	diuron + hexazinone + sulfometuron-methyl	PFO	-137.75		0.0049
		PSO	-141.79	*	0.0046

* Best model chosen according to the Akaike test; Akaike test (AICc); root mean squared error

The isolated diuron showed higher maximum sorption (q_e) for both soils. The q_e of the mixture of diuron + hexazinone was 53.0 and 56.3%, the mixture of diuron + sulfometuron-methyl was 47.6 and 62.5%, and the mixture of diuron + hexazinone + sulfometuron-methyl was 57.1 and 62.5% less, for LVA and LVd, respectively, when compared to isolated diuron (Table 4). The maximum sorption time of the diuron alone and in mixtures did not differ in the LVA. However, the time was 87% shorter for diuron + hexazinone mixtures and 37.7% shorter for diuron + sulfometuron-methyl mixtures in the LVd. In addition, there was a difference between the sorption speeds of the diuron + hexazinone mixture between the soils, with a 91% longer time in the LVA (Table 4).

There was an increase in competition for diuron binding sites when it was applied in a mixture with hexazinone and sulfometuron-methyl. This may have occurred due to a steric impediment caused by the progressive occupation of the diuron molecule in the adsorbent sites, which results in greater competition for the remaining assorted sites between the diuron and the sulfometuron-methyl in the monolayer, making it difficult for the molecules of these herbicides to bind with the soil colloids. (BORDÓN et al., 2017; YUE et al., 2017).

Table 4. Maximum sorption (q_e) and time (minutes) for maximum sorption of diuron alone and in binary and ternary mixtures.

Treatment	q_e (mg.kg ⁻¹)		Time (min)	
	LVA	LVd	LVA	LVd
Diuron	2.10 Aa	1.6 Ba	315.32 Aa	226.54 Aa
diuron + hexazinone	1.00 Ac	0.7 Bb	326.44 Aa	29.30 Bc
diuron + sulfometuron-methyl	1.10 Ab	0.6 Bc	224.34 Aa	141.11 Ab
diuron + hexazinone + sulfometuron-methyl	0.90 Ad	0.6 Bc	301.97 Aa	288.41 Aa
C.V. (%)	2.73		22.96	

Lower case letters in the columns differentiate the maximum adsorbed concentration and time between the herbicides and upper case letters differentiate the maximum adsorbed concentration and time between the LVA and LVd by the Tukey test $p \leq 0.05$. C.V.: coefficient of variation.

The Oxisols used in this study, LVA and LVd, are soils that contain a type of clay with low activity and few negative sites (MARÍN-SPIOTTA and SHARMA, 2013). Thus, organic matter is an important attribute that gives these more weathered soils a greater for cation exchange capacity (CEC) and consequently greater capacity for sorption of herbicides from the phenylureas group (WANG et al., 2015).

LVA has a higher amount of total organic carbon (TOC) (9.46 g kg⁻¹), labile carbon (labile C) (2.0 g kg⁻¹) and a higher CEC (8.9 cmol_c dm⁻³) when compared to the LVd (TOC: 4.71 g kg⁻¹; labile C: 1.3 g kg⁻¹ and CEC: 7.2 cmol_c dm⁻³). These chemical characteristics gave the LVA greater sorption capacity, as observed in this study.

There is a positive relationship between the organic carbon content and the sorption of the herbicide diuron (ROCHA et al., 2013; SPULER et al., 2019). Diuron is a molecule that has greater affinity with the nonpolar phase of the soil/water system, being preferably retained by the organic or mineral part of the soil (CEDERLUND et al., 2017). The interaction between diuron and organic matter favors hydrogen bonds between these compounds, which therefore increases the sorption of this herbicidal molecule (UMILJENDIC et al., 2013; ROCHA et al., 2013; TAKESHITA et al., 2019). In addition, soil organic matter increases sorption due to its high reactivity, which is related to its high specific surface area and the presence of various functions of the functional groups, such as carboxyls, hydroxyls, amines and aliphatic and aromatic structures (LI et al., 2017).

Although diuron is classified as a non-ionic herbicide, its behavior in the soil solution can be influenced by the pH of the medium through the chemical bonds formed between the molecule and the organic matter in the soil (PETTER et al., 2016). The LVA has a higher pH (5.84) than the LVd (4.58) (Table 1), which may also have favored the higher concentration adsorbed by the LVA. Higher pH soils tend to adsorb more diuron,

limiting its availability for absorption by plants or decomposition by the microbial population, thus favoring its persistence (ROCHA et al., 2013).

The onset of diuron sorption in the soil, mainly isolated, is rapid due to the greater presence of sites in the soil capable of interacting with the herbicide (MIRZAEI et al., 2013). However, the time required for maximum sorption of this herbicide is dependent on the physical and chemical attributes of the soil (type and amount of clay, organic matter, CEC and pH), that is, those which give a greater number of different sites. As the herbicide occupies the soil binding sites, sorption becomes slower due to the saturation of these sites, resulting in the balance between adsorbed concentration and the solution (YUE et al., 2017).

The maximum sorption time of the diuron did not change in the LVA with the mixtures. Whereas, in LVd the sorption time was shorter and consequently the maximum sorption was also shorter with the mixtures (Table 4). Because LVd has fewer sites available for adsorption of diuron, saturation was reached more quickly. Conversely, LVA has greater availability of sites on the surface of organic colloids and minerals in the soil that allowed greater adsorption of diuron even when it was applied with hexazinone and sulfometuron-methyl. Thus, a greater amount of the herbicide is necessary for saturation to be achieved, and this fact increases the time for soil and solution concentrations to reach equilibrium (MIRZAEI et al., 2013).

3.2. Hexazinone sorption kinetics

The sorption processes of hexazinone alone, in binary mixtures (hexazinone + diuron and hexazinone + sulfometuron-methyl), and the ternary mixture (hexazinone + diuron + sulfometuron-methyl) were similar between the two soils. Estimates on the sorption kinetics of hexazinone alone and in mixtures also showed a fast initial phase, followed by a slow phase (Figure 3). The presence of diuron and sulfometuron-methyl in the mixtures altered the sorption kinetics of hexazinone (Figure 3). The concentration absorbed at equilibrium was lower for the binary and ternary mixtures of the herbicides (Figure 3 and Table 5). The kinetic parameters are shown in Table 5.

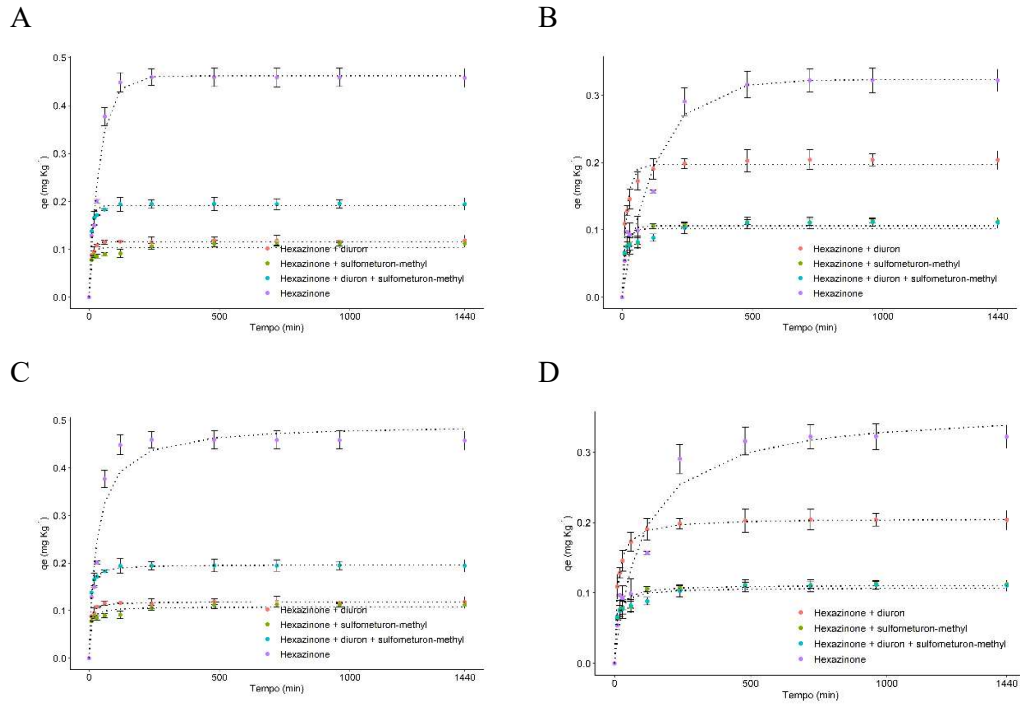


Figure 3. Sorption kinetics of hexazinone isolated and in binary and ternary mixtures with diuron and sulfometuron-methyl in Red-Yellow Oxisol (LVA) (right) and Dystrophic Red Oxisol (LVd) (left) using the pseudo-first order (PFO) (a, c) and pseudo-second order (PSO) (b, d) models. q_e : adsorption capacity (mg.kg^{-1}) at equilibrium time.

Table 5. Parameters used to elaborate the pseudo-first order (PFO) and pseudo-second order (PSO) models to describe the sorption kinetics of hexazinone and the binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Dystrophic Red Oxisol (LVd).

Soil	Treatment	Pseudo-first order			Pseudo-second order		
		P	E	Std. Error	P	E	Std. Error
LVA	Hexazinone	q_e	0.46	0.01	q_e	0.49	0.01
		k_1	0.02	0.00	k_2	0.07	0.01
	hexazinone + diuron	q_e	0.12	0.00	q_e	0.12	0.00
		k_1	0.12	0.01	k_2	2.27	0.35
	hexazinone + sulfometuron-methyl	q_e	0.10	0.00	q_e	0.11	0.00
		k_1	0.11	0.02	k_2	1.78	0.31
	hexazinone + diuron + sulfometuron-methyl	q_e	0.19	0.00	q_e	0.20	0.00
		k_1	0.11	0.01	k_2	1.23	0.14
LVd	Hexazinone	q_e	0.32	0.01	q_e	0.36	0.01
		k_1	0.01	0.00	k_2	0.03	0.00
	hexazinone + diuron	q_e	0.20	0.00	q_e	0.21	0.00
		k_1	0.06	0.00	k_2	0.45	0.05
	hexazinone + sulfometuron-methyl	q_e	0.11	0.00	q_e	0.11	0.00
		k_1	0.06	0.01	k_2	0.92	0.13
	hexazinone + diuron + sulfometuron-methyl	q_e	0.10	0.00	q_e	0.11	0.00
		k_1	0.07	0.01	k_2	1.01	0.17

Parameter (P); Parameter values (E); Standard error of the mean (Std. Error); Adsorption capacity (mg.kg^{-1}) at equilibrium time (q_e); Pseudo-first order speed constant (k_1); Pseudo-second order speed constant (k_2).

The PFO model showed a better fit for the sorption of hexazinone isolated in LVA and LVd, with lower values of AICc and RMSE (Table 6). The sorption of the binary mixtures (hexazinone + diuron and hexazinone + sulfometuron-methyl) and the ternary mixture (hexazinone + diuron + sulfometuron-methyl) was best represented by the PSO model in both studied soils (Table 6).

Table 6. Akaike test to compare the models of pseudo-first order (PFO) and pseudo-second order (PSO) to describe the sorption kinetics of hexazinone and binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Red Oxisol Dystrophic (LVd).

Soil	Treatment	Modnames	AICc		RMSE
LVA	Hexazinone	PPO	-151.16	*	0.0040
		PSO	-122.03		0.0062
	Hexazinone + diuron	PPO	-224.60		0.0013
		PSO	-234.39	*	0.0011
	Hexazinone + sulfometuron-methyl	PPO	-201.96		0.0018
		PSO	-221.40	*	0.0014
	Hexazinone + diuron + sulfometuron-methyl	PPO	-202.45		0.0018
		PSO	-216.09	*	0.0015
LVd	Hexazinone	PPO	-137.91	*	0.0048
		PSO	-136.72		0.0049
	Hexazinone + diuron	PPO	-175.62		0.0027
		PSO	-196.12	*	0.0020
	Hexazinone + sulfometuron-methyl	PPO	-196.86		0.0020
		PSO	-220.27	*	0.0014
	Hexazinone + diuron + sulfometuron-methyl	PPO	-190.05		0.0022
		PSO	-209.33	*	0.0016

* Best model chosen according to the Akaike test; Akaike test (AICc); root mean squared error (RMSE).

The isolated hexazinone showed higher maximum sorption (q_e) for both soils. The q_e had a reduction of 70 and 30% for the mixture hexazinone + diuron, 80 and 70% for hexazinone + sulfometuron-methyl, and 60 and 70% for hexazinone + diuron + sulfometuron-methyl in LVA and LVd, respectively (Table 7). The q_e was higher in LVA for hexazinone alone and for hexazinone + diuron + sulfometuron-methyl. On the other hand, the q_e of the hexazinone + diuron mixture was higher in LVd (Table 7). The maximum sorption time of hexazinone was reduced with the mixtures in both soils. The isolated hexazinone and the hexazinone + diuron mixture showed the longest time for maximum sorption at LVd (Table 7).

The decrease in the maximum amount adsorbed by hexazinone when mixed with diuron and sulfometuron-methyl may have occurred due to the increased competitiveness by the binding sites. The steric impediment caused by the progressive occupation of the adsorbent sites can result in greater competition for the remaining assorted sites and less

sorbed amount of these molecules, as previously shown for diuron (BORDÓN et al., 2017; YUE et al., 2017).

Table 7. Maximum sorption (q_e) and time (minutes) for maximum sorption of hexazinone alone and in binary and ternary mixtures.

Treatment	q_e (mg.kg ⁻¹)		Time (min)	
	LVA	LVd	LVA	LVd
Hexazinone	0.46 Aa	0.32 Ba	161.18 Ba	344.88 Aa
Hexazinone + diuron	0.12 Bc	0.21 Ab	42.35 Bb	218.40 Ab
Hexazinone + sulfometuron-methyl	0.11 Ac	0.11 Ac	55.33 Ab	102.99 Ac
Hexazinone + diuron + sulfometuron-methyl	0.20 Ab	0.11 Bc	79.57 Ab	108.38 Ac
C.V. (%)	4.29		20.01	

Lower case letters in the columns differentiate the maximum adsorbed concentration and time between the herbicides and upper case letters differentiate the maximum adsorbed concentration and time between the LVA and LVd by the Tukey test $p \leq 0.05$. C.V.: coefficient of variation.

The lower sorption speed of isolated hexazinone and hexazinone + diuron in LVd can be attributed to the smaller number of different sites in this soil. The LVA has higher TOC content (Table 1) and higher amounts of 1:1 clay, such as kaolinite, hydroxides, iron oxides (hematite and goethite), and aluminum (gibbsite) (Figure 1). In addition, LVA has illite (II) in its constitution (Figure 1) and is a 2:1 clay that provides greater reactivity and a greater number of negative charges (MARCO-BROWN et al., 2019) that can favor the sorption of hexazinone (DOS SANTOS et al., 2019).

Inorganic minerals such as hematite, goethite, and gibbsite contribute to sorption through the dissociation of active surface groups (Fe-OH and Al-OH). Organic matter also contributes for the dissociation of its functional groups (mainly carboxylic and phenolic) and the humus-Al and Fe complexes with amphoteric characteristics (WU et al., 2018). In addition, kaolinite-free surfaces can interact with hexazinone by hydrophobic bonding and Van Der Waals forces (LAIRD and KOSKINEN 2008). On the other hand, the pH values above the pKa (2.2) of hexazinone in both soils indicate that the molecules of this herbicide are predominantly in the molecular (neutral) form.

This condition associated with high water solubility (33 g L⁻¹ at 20°C) can favor the permanence of its molecules in the soil solution. The efficiency of hexazinone in weed control in the pre-emergence is directly related to the availability of the herbicide in the soil solution. However, in the soil solution, the herbicide may be subject to leaching and, thus, contaminate water resources, especially in regions with high precipitation rates (MENDES et al., 2016). The lower sorption of hexazinone and the longer time to reach

equilibrium observed in LVd shows that this soil presents a higher potential risk for leaching of this herbicide. The LVA had greater sorption in less time, which reduces the movement of this herbicide along the soil profile, reducing the potential for groundwater contamination.

3.3. Sulfometuron-methyl sorption kinetics

The sorption of sulfometuron-methyl alone and in mixtures in both soils increased rapidly in the initial stage, while the slower sorption rate was obtained because of the decrease in the active sorption sites (Figure 4). This phenomenon is frequently observed during sorption of herbicides in soils such as diuron, 2,4-D and metsulfuron-methyl (INOUE et al., 2004; FERNANDEZ-BAYO et al., 2008; CÁCERES et al., 2010; CÁCERES et al., 2013; SPULER et al., 2019). Another important fact is that the maximum concentration adsorbed at equilibrium was lower for sulfometuron-methyl in binary and ternary mixtures (Figure 4). The parameters of the kinetic models are shown in Table 8.

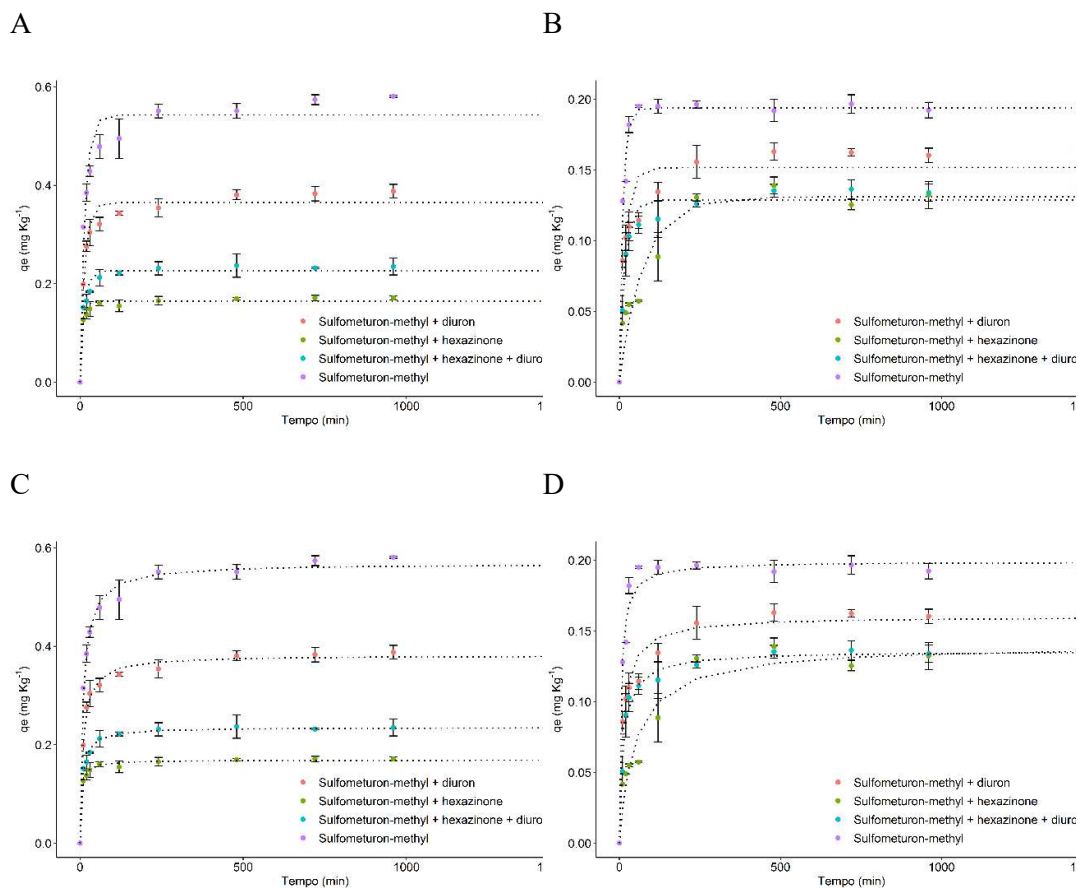


Figure 4. Sorption kinetics of Sulfometuron-methyl isolated and in binary and ternary mixtures with diuron and sulfometuron-methyl in Red-Yellow Oxisol (LVA) (right) and Dystrophic Red Oxisol (LVd) (left) using the pseudo-first order models (PFO) (a, c) and pseudo-second order (PSO) (b, d). q_e : adsorption capacity (mg.kg^{-1}) at equilibrium time.

Table 8. Parameters used to elaborate the pseudo-first order (PFO) and pseudo-second order (PSO) models to describe the sorption kinetics of sulfometuron-methyl and the binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Dystrophic Red Oxisol (LVd).

Soil	Treatment	Pseudo-first order			Pseudo-second order		
		P	E	Std. Error	P	E	Std. Error
LVA	sulfometuron-methyl	q_e	0.54	0.01	q_e	0.57	0.01
		k_1	0.07	0.01	k_2	0.19	0.01
	sulfometuron-methyl + diuron	q_e	0.37	0.01	q_e	0.38	0.00
		k_1	0.07	0.01	k_2	0.30	0.02
	sulfometuron-methyl + hexazinone	q_e	0.16	0.00	q_e	0.17	0.00
		k_1	0.12	0.01	k_2	1.55	0.20
	sulfometuron-methyl + hexazinone + diuron	q_e	0.23	0.00	q_e	0.24	0.00
		k_1	0.08	0.01	k_2	0.63	0.07
LVd	sulfometuron-methyl	q_e	0.19	0.00	q_e	0.20	0.00
		k_1	0.09	0.00	k_2	0.93	0.10
	sulfometuron-methyl + diuron	q_e	0.15	0.00	q_e	0.16	0.00
		k_1	0.05	0.01	k_2	0.51	0.06
	sulfometuron-methyl + hexazinone	q_e	0.13	0.00	q_e	0.14	0.00
		k_1	0.01	0.00	k_2	0.15	0.02
	sulfometuron-methyl + hexazinone + diuron	q_e	0.13	0.00	q_e	0.14	0.00
		k_1	0.05	0.00	k_2	0.59	0.07

Parameter (P); Parameter values (E); Standard error of the mean (Std. Error); Adsorption capacity (mg.kg^{-1}) at equilibrium time (q_e); Pseudo-first order speed constant (k_1); Pseudo-second order speed constant (k_2).

The calculated AICc and RMSE values indicate that the best fit was obtained with the PSO model for sorption of sulfometuron-methyl in binary mixtures (sulfometuron-methyl + diuron and sulfometuron-methyl + hexazinone) and ternary (sulfometuron-methyl + diuron + hexazinone) mixtures in both soils (Table 9). For the sorption of sulfometuron-methyl isolated in the LVA, the best fit was obtained by the PSO model (AICc = -157.24 and RMSE = 0.0036), however, for the LVd the PFO model described the data with greater precision. Experimental tests for sorption of isolated sulfometuron-methyl (AICc = -214.97 and RMSE = 0.0015) (Table 9).

The best adjustment of the sorption kinetics of sulfometuron-methyl in binary and ternary mixtures obtained by the PSO equation may be related to a high initial contribution of mass transport through the high number of vacant places accessible to organic matter and the minerals that compose the clays, resulting in a gradual increase in

concentration between the herbicides in solution and on the soil surface (CÁCERES et al., 2010).

Table 9. Akaike test to compare the models of pseudo-first order (PFO) and pseudo-second order (PSO) to describe the sorption kinetics of Sulfometuron-methyl and binary and ternary mixtures in Red-Yellow Oxisol (LVA) and Red Oxisol Dystrophic (LVd).

Soil	Treatment	Modnames	AICc		RMSE
LVA	sulfometuron-methyl	PPO	-116.74		0.0067
		PSO	-157.24	*	0.0036
	sulfometuron-methyl + diuron	PPO	-150.90		0.0040
		PSO	-178.97	*	0.0026
	sulfometuron-methyl + hexazinone	PPO	-202.33		0.0018
		PSO	-222.49	*	0.0013
	sulfometuron-methyl + diuron + hexazinone	PPO	-170.21		0.0030
		PSO	-193.73	*	0.0021
LVd	sulfometuron-methyl	PPO	-214.97	*	0.0015
		PSO	-212.04		0.0016
	sulfometuron-methyl + diuron	PPO	-173.27		0.0028
		PSO	-202.12	*	0.0018
	sulfometuron-methyl + hexazinone	PPO	-181.78		0.0025
		PSO	-189.04	*	0.0022
	sulfometuron-methyl + diuron + hexazinone	PPO	-203.72		0.0018
		PSO	-212.29	*	0.0016

* Best model chosen according to the Akaike test; Akaike test (AICc); root mean squared error (RMSE).

Sulfometuron-methyl isolated showed higher sorption ($q_e = 0.57$ and 0.19 mg.g^{-1}) for both soils when compared to binary and ternary mixtures. The q_e of the sulfometuron-methyl + diuron mixture was 30 and 20%, sulfometuron-methyl + hexazinone was 70 and 30%, and the sulfometuron-methyl + diuron + hexazinone mixture was 50 and 30% lower for LVA and LVd, respectively, when compared to sulfometuron-methyl alone (Table 10). The LVA showed greater sorption capacity than the LVd independent of herbicide mixtures. The shortest time to reach maximum sorption was observed for sulfometuron-methyl isolated in LVd (33.90 min) and for the mixture of sulfometuron-methyl + hexazinone in LVA (62.89 min) (Table 10). On the other hand, sulfometuron-methyl + hexazinone showed the longest time to reach maximum LVd sorption (404.27 min).

Table 10. Maximum sorption (q_e) and time (minutes) for maximum sorption of Sulfometuron-methyl alone and in binary and ternary mixtures.

Treatment	q_e (mg.kg ⁻¹)		Time (min)	
	LVA	LVd	LVA	LVd
Sulfometuron-methyl	0.57 Aa	0.19 Ba	281.65 Aa	33.90 Bb
Sulfometuron-methyl + diuron	0.38 Ab	0.16 Bb	238.34 Aa	122.34 Ab
Sulfometuron-methyl + hexazinone	0.17 Ad	0.14 Bc	62.89 Bb	404.27 Aa
Sulfometuron-methyl + diuron + hexazinone	0.24 Ac	0.14 Bc	102.10 Ab	104.48 Ab
C.V. (%)	2.55		52.56	

Lower case letters in the columns differentiate the maximum adsorbed concentration and time between the herbicides and upper case letters differentiate the maximum adsorbed concentration and time between the LVA and LVd by the Tukey test $p \leq 0.05$. C.V.: coefficient of variation.

The decrease in the maximum sorption capacity of sulfometuron-methyl mixed with diuron and hexazinone may be the result of greater competition for the different soil sites when two or three herbicides are in the system (TAKESHITA et al., 2019). In general, acidic herbicides are adsorbed on organic matter by hydrophobic interactions and hydrogen bonding, and by hydrophilic mechanisms on surface oxides through anion exchange. In addition, the Ca²⁺ bridge on the mineral surface and organic matter have been reported as relevant mechanisms in soils of variable load (MARCO-BROWN et al., 2019).

Sulfometuron-methyl is a weak acid (pKa = 5.2), and pH is one of the most important soil attributes that control its adsorption through ionization; at pH higher than the pKa value, the anionic form of this herbicide prevails, which is more soluble in water and less susceptible to hydrolysis (PPDB, 2019). Under these conditions, their leaching potential increases because of decreased soil adsorption. However, sulfometuron-methyl, according to the pH value of LVd (4.54), can reduce its anionic fraction in solution (SILVA et al., 2019) contributing to maximum sorption in less time.

4. FINAL CONSIDERATIONS

Sorption is lower for herbicides in mixtures. The sorption kinetics data for diuron and sulfometuron-methyl isolated and in binary and ternary mixtures and hexazinone in the mixtures are better modeled by pseudo-second order kinetic equations. The pseudo-first order model describe of the sorption kinetics with better precision only for isolated hexazinone. Diuron showed a greater maximum adsorption capacity than hexazinone and sulfometuron-methyl. The initial sorption was similar for the three herbicides studied,

with a fast sorption stage followed by a slow equilibrium stage. Soil attributes such as TOC content, mineral composition, and pH affect the sorption kinetics of diuron, hexazinone, and sulfometuron-methyl in different ways.

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MIXTURES OF HERBICIDES USED IN SUGAR CANE ALTER THE AVAILABILITY OF ITS MOLECULES IN THE SOIL: EFFECTS ON WEED CONTROL AND RISK OF ENVIRONMENTAL CONTAMINATION

Abstract: The use of herbicide mixtures has been a common practice in the control of weeds in sugarcane crops. The concern with the interactions between the molecules of different herbicides has been limited to compatibility before application. In this sense, little is known about the interactions between mixed herbicides and the soil. This study evaluated the sorption and desorption in the soil of three herbicides (diuron, hexazinone, and sulfometuron-methyl) widely used in isolated conditions and mixed in sugarcane, using two soils collected from production regions in Brazil. The Freundlich model showed a better fit for sorption and desorption of the isolated and mixed herbicides compared to the Langmuir and Linear models. The binary and ternary combinations between diuron, hexazinone, and sulfometuron-methyl reduced the sorption and desorption in the soils compared to the isolated tests of these herbicides. The sorption and desorption of hexazinone in soils is most affected by mixing with other herbicides. Sulfometuron-methyl promotes greater reduction in the sorption of diuron in relation to hexazinone. The mixture between diuron, hexazinone, and sulfometuron-methyl increases the availability of these herbicides in the aqueous phase of the soil allowing the use of lower rates in the application compared to isolated applications. Higher availability also indicates a greater potential for environmental contamination via leaching or surface runoff.

Key words: Adsorption, Front[®], soil retention, physicochemical properties.

1. INTRODUCTION

The need to control weeds in agricultural crops is due to the competitive capacity of these plants with the crop, promoting, in some cases, losses of up to 100% in productivity (GHARDE et al., 2018; SOLTANI et al., 2017; DASS et al., 2017). In sugarcane, it has been proven that the presence of weeds can reduce the accumulation of fresh matter and sugar by up to 80% (PROCÓPIO et al., 2015). The intense interference caused by weeds in sugarcane crops requires that integrated management via cultural, physical, mechanical, and chemical methods be adopted to ensure the maximum

productive potential of the crop. Although there are different methods for weed control, the chemical is the most method used in the sugarcane producing properties (REIS et al., 2019). Currently, several herbicides are registered for the control of weeds in sugarcane crops, ranging from 15 to 20 molecules frequently applied (REIS et al., 2019).

Among the main herbicides used for sugarcane, the inhibitors of photosystem II have greater prominence due to the high amount applied to crops. For example, a survey carried out by Reis et al. (2019) during 2010 to 2014 in the state of São Paulo, Brazil (the main sugar cane producing region in the country) revealed that almost 90% of the chemical control of weeds is carried out through the application of photosystem II inhibitors. In addition, these authors identified that most of the time these applications involve mixtures between different chemical groups of herbicides that inhibit of photosystem II. These photoinhibitors are, in the vast majority of cases, diuron and hexazinone, which are sold in different commercial brands such as Hexaron[®], Velpar K[®], and Hexaxinona-D[®] (AGROFIT, 2019). Another product formulated with diuron + hexazinone recently launched on the market is Front[®]; however, it differs from other mixtures due to the presence of a third molecule, sulfometuron-methyl.

Diuron belongs to the group of substituted urea, applied pre-emergence of weeds, while hexazinone belongs to the group of triazinones, applied pre- and post- emergence. Sulfometuron-methyl is a residual pre-emergent herbicide from the chemical group of sulfonylureas, and unlike diuron and hexazinone, it acts by inhibiting the action of the enzyme acetolactate synthase (ALS) (AGROFIT, 2019). When mixed, these herbicides demonstrate high efficiency in the pre-emergent control of weeds in sugarcane due to the increase in the spectrum of action and control of sowing in depth (PROCÓPIO et al., 2015; GALON et al., 2012; DOS SANTOS et al., 2011; FADAYOMI et al., 1988).

Diuron, hexazinone, and sulfometuron-methyl have a medium to high residual (90 to 180 days) in the soil (PUBCHEM, 2019), controlling weeds for a long time after application. However, there is an environmental risk associated with molecules with a long residual period (PASSOS et al., 2018; GUIMARÃES et al., 2018). When exposed to many rain events, herbicides can leach to deep soil layers, contaminating water sources. This action is even more worrying for herbicides with greater water solubility (NETO et al., 2017; PASSOS et al., 2019). Studies have already reported that the herbicides atrazine and tebuthiuron have been detected in groundwater in the state of São Paulo, Brazil (MACHADO et al., 2017). In another recent study, Portal et al. (2019) detected the presence of atrazine and hexazinone in shallow wells in the state of Rio de Janeiro, Brazil.

In other countries, studies have also reported the presence of herbicides in water sources (MASIOL et al., 2018; FENOLL et al., 2012).

The mobility and persistence of an herbicide depends on the sorption and desorption capacity of the soil. The greater or lesser sorption and desorption will depend on the physicochemical properties of the soil and herbicide, and the result of this interaction will define the final destination of the pesticide molecule (SILVA et al., 2019). An alternative to study the sorption and desorption of herbicides in the soil is through the construction of adsorption isotherms, using appropriate mathematical models such as Freundlich and Langmuir (CHUNG et al., 2015; FOO et al., 2010).

Several studies have sought to evaluate the sorption and desorption capacity of different soils for diuron, hexazinone, and sulfometuron-methyl (DOS SANTOS et al., 2019; DAS CHAGAS et al., 2019; AZCARATE et al., 2015; MISHAEL et al., 2002; CELIS et al., 2002; HARVEY et al., 1985). In a more recent study, Silva et al. (2019) determined the sorption and desorption of these three herbicides in 16 soils collected from different sugarcane regions in Brazil. However, these studies evaluated the sorption and desorption process of diuron, hexazinone, and sulfometuron-methyl in isolation, disregarding possible interactions between these molecules in the soil. A higher risk of environmental contamination can occur if the combinations between these herbicides show different behavior regarding sorption and desorption in the soil.

Few studies have sought to understand the effect of interactions of mixed organic molecules on the sorption and desorption of pesticides. Some studies have already reported that the presence of adjuvants and surfactants alters the sorption and desorption of herbicides in soils (KOČÁREK et al., 2018; KHAN et al., 2017), raising an alert for other pesticide mixtures that directly reach the soil. In this sense, we raise the following hypotheses about the behavior in the soil of the herbicides diuron, hexazinone, and sulfometuron-methyl when combined in binary and ternary mixtures: i) Does the mixture of the herbicides diuron, hexazinone, and sulfometuron-methyl alter the sorption and desorption of its molecules in the soil compared to isolated conditions? ii) Is there a difference in the sorption and desorption capacity between binary and ternary mixtures? To answer these questions, our objective was to determine the sorption and desorption of diuron, hexazinone, and sulfometuron-methyl in isolated and mixed conditions, using two soils collected from sugarcane producing regions in Northeast of Brazil.

2. MATERIALS AND METHODS

The experiments were carried out at the Weed Management Laboratory in the semiarid region of Brazil, belonging to the Federal Rural University of the Semiarid Region. The sorption and desorption tests of the herbicides diuron, hexazinone, and sulfometuron-methyl, isolated and in binary and ternary mixtures, were performed using the *Ultra-High Performance Liquid Chromatography* (UHPLC) technique, in triplicate.

2.1. Characterization of soil

The soils were collected at a depth of 0 to 20 cm. Two samples of Oxisols with different physical and chemical attributes were used: *Latosolo Vermelho-Amarelo* (SiBCS, 2018) Red-Yellow Oxisol (LVA) from Maceió-AL with geographic coordinates 9 ° 39 '21 "S and 35 ° 44' 38" O and *Latosolo Vermelho distrófico* (SiBCS, 2018) dystrophic Red Oxisol (LVd) of Mossoró-RN, with coordinates 5 ° 3 '37.7 "S and 37 ° 24' 14.4". The chemical and physical characteristics are described in Table 1. The soils were air-dried, sieved in a 2 mm mesh and chemically, and physically characterized (TEIXEIRA et al., 2017). The collections were carried out in areas close to sugarcane cultivation but with no history of herbicide application.

Table 1. Chemical and physical characteristics of the soils Red Yellow Oxisol (LVA) from Maceió-AL and Red Dystrophic Oxisol from Mossoró-RN (LVd).

Soils	Texture (g kg ⁻¹)			pH (water)	TOC (g kg ⁻¹)	Labile C (g kg ⁻¹)	P (mg dm ⁻³)	K (mg dm ⁻³)	Ca ⁺² (cmol _c dm ⁻³)	Mg ⁺² (cmol _c dm ⁻³)	Al ⁺³ (cmol _c dm ⁻³)	H+Al (cmol _c dm ⁻³)	CEC (cmol _c dm ⁻³)	V (%)	M (%)
	Sand	Silt	Clay												
LVA	640	120	240	5.84	9.46	2.0	0.91	108.13	1.37	1.77	0.00	5.45	8.90	38.2	0.00
LVd	770	24	200	4.58	4.71	1.3	0.25	28.00	0.86	0.85	3.30	5.45	7.20	25.0	64.7

Total organic carbon (TOC), labile carbon (labile C), potential acidity (H+Al), hydrogenionic potential (pH), cation exchange capacity (CEC), base saturation (V), aluminum saturation (M). *The labile carbon analyses were done according to Shang; Tiessen (1997). The other analyses were performed according to a methodology proposed by Silva, (2009). LASAPSA—Laboratory of Soil, Water, and Semiarid Plant Analysis, UFERSA.

2.2. Mineralogical characterization

Mineralogical characterization was carried out in the clay fraction, by chemical dispersion with sodium hexametaphosphate 0.025 mol L^{-1} and mechanics with a “Wagner” type agitator for 16 h, according to Teixeira et al. (2017). Minerals were identified by X-ray diffraction (XRD) at the Integrated Center for Technological Innovation in the Semiarid Region (CITED)—UFERSA.

A Shimadzu diffractometer model XRD 6000 was used, in Japan, with $\text{Cu-K}\alpha 1$ radiation. The source potential was 40 kV, and the current was 30 mA. A scanning speed with a step of 0.02° was applied every second. The scanning range (2θ) was from 5 to 65° . The identification of mineral peaks was performed with the aid of the X-Ray program v. 1.0.0.37, and the phases were identified according to Chen (1977) (Figure 1).

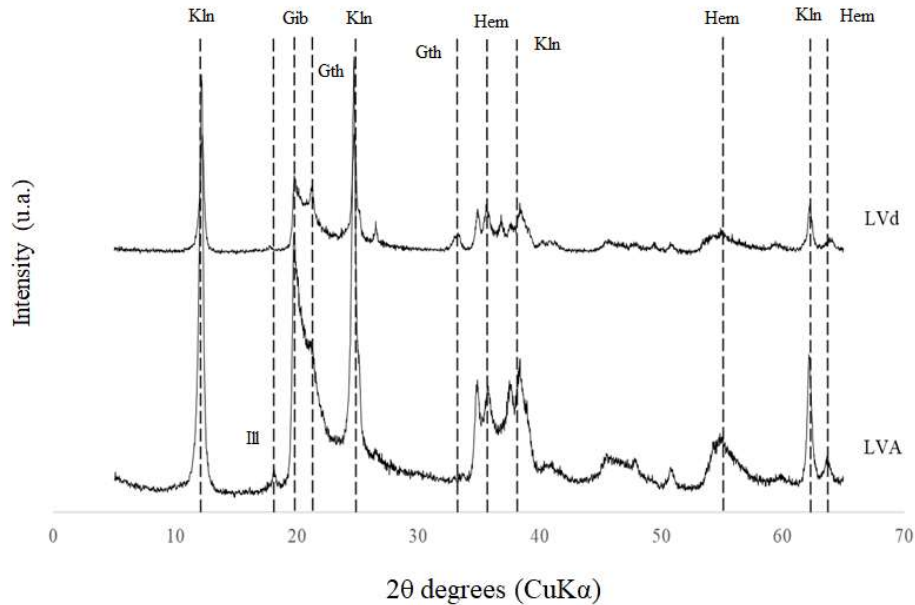


Figure 1. X-ray diffractometry of the clay fraction of horizons A of the X-ray diffractometry of the clay fraction of horizons A of the *Latossolo vermeho-amarelo* (Red-Yellow Oxisol (LVA)) and of the *Latossolo vermelho distrófico* (Dystrophic Red Oxisol (LVd)).

Kln = kaolinite, Illite = Ill, Gth = goethite, Hem = hematite, Gib = Gibbsite.

LVA: Kln, Ill, Gib, Gth, Hem. LVd: Kln, Gib, Gth, Hem.

2.3. Reagents

Analytical grade reagents and HPLC were used in the studies. The diuron, hexazinone standards were purchased from Sigma-Aldrich® (SAINT LOUIS, MO, USA), with a purity of 99.6 and 99.5%, respectively. Sulfometuron-methyl was obtained from the company Supelco (BELLEFONTE, PA, USA), with a purity of 99.5%. A stock solution of each standard was prepared at a concentration of 1,000 mg L⁻¹ in acetonitrile. The working solutions were prepared by diluting with 10 mM aqueous CaCl₂ solution from the stock solutions.

2.4. Analytical method

The quantification of diuron, hexazinone, and sulfometuron-methyl was carried out using the Ultra-High Performance Liquid Chromatography system (UHPLC), the Shimadzu® DAD detector (model Nexera X2 SPD-M30A, Tokyo, Japan), equipped with a Restek Pinnacle column DB AQ C18, size 50 x 2.1 mm, with 1.9 µm particles, including two LC-30AD pumps, a DGU-20A5R degasser, a Sil-30AC autosampler, a CTO-30AC column oven, and a CBM-20A controller.

The chromatographic conditions used to quantify the herbicides were as follows: an elution mode involving isocratic conditions in a binary mobile phase composed of 0.1% formic acid in water (mobile phase A) and acetonitrile (mobile phase B), in the ratio of 33:67. The flow rate was 0.3 ml min⁻¹, with an injection volume of 5 µL. The temperature of the sample manager was 15°C. The wavelengths used were 254, 247, and 233 nm for diuron, hexazinone, and sulfometuron methyl, respectively.

2.5. Determination of sorption kinetics

The equilibrium time for sorption and desorption of the herbicides in the soils was carried out at 25±2°C by the batch equilibrium method (OECD, 2000). For the diuron and hexazinone herbicides, isolated and in binary and ternary mixtures, a volume of 10 ml of the solution of the herbicides in the concentration of 1 mg L⁻¹, prepared in 10 mM CaCl₂, was added in Falcon tubes containing 2 g of soil. For sulfometuron-methyl, isolated and in mixtures, samples with 4 g of soil were added to Falcon tubes, with a 20.0 mL aliquot of an aqueous solution containing the 1.0 mg L⁻¹ herbicides, prepared in 10 mM CaCl₂. The analyses were performed separately for each herbicide, isolated and in binary and ternary mixtures. All evaluations were performed in triplicate.

The tubes were shaken vertically at different time intervals (0.0; 10.0; 20.0; 30.0; 60.0; 120.0; 240.0; 480.0; 720.0; 960 and 1,440.0 minutes). After stirring, the samples were centrifuged at 2,640 g for seven minutes. Then the supernatant was removed and filtered through a 0.22 μm PVDF membrane into 1.5 mL vials. Subsequently, the samples contained in the vials were quantified by UHPLC to estimate the concentration of the herbicides in the aqueous and solid phases in equilibrium. The time required for equilibrium of the herbicides in the evaluated soils varied between four and 12 hours (data not shown). Thus, 12 hours was selected as the equilibrium time for the sorption and desorption experiments.

2.6. Determination of the sorption coefficients (K_f s) for diuron, hexazinone, and sulfometuron-methyl

The sorption of herbicides in soils was evaluated using working solutions containing the three isolated herbicides, in binary and ternary mixtures. These solutions were prepared from the stock solution for each herbicide, according to the recommendations of the OECD (2000). The experiment was conducted in triplicate. The concentrations of the working solutions were 0.2; 0.4; 0.73; 1.5; 3.0; 6.0, and 12 mg L^{-1} for diuron, 0.1; 0.22; 0.45; 1.0; 2.0; 3.5, and 7.0 mg L^{-1} for hexazinone, and 0.1; 0.2; 0.4; 0.8; 1.0, 1.5, and 3.0 mg L^{-1} for sulfometuron-methyl. All working solutions were prepared in 10 mM CaCl_2 . The concentrations were defined based on the highest dose recommended for commercial products (0.73, 0.45, and 0.8 mg L^{-1} for diuron, hexazinone, and sulfometuron-methyl, respectively).

In the sorption tests of the isolated diuron and hexazinone herbicides, an aliquot of 10 mL of each concentration was added to Falcon tubes containing 2.00 g of soil. For the herbicide sulfometuron-methyl, an aliquot of 20 ml of each concentration was added to each Falcon tube containing 4.00 g of soil. Then the tubes were shaken vertically at a temperature of $25\pm 2^\circ\text{C}$ for 12 hours. After stirring, the samples were centrifuged at 2,260 g for seven minutes. The supernatant was stripped and filtered through a 0.22 μm PVDF membrane into 1.5 mL vials. Subsequently, the samples contained in the vials were analyzed by UHPLC to quantify the concentration of each herbicide.

The concentrations of soil sorbed herbicides (C_s), in mg kg^{-1} , were calculated using the difference between the concentration in the standard solution initially added to the soil and the amount found in the equilibrium solution (C_e). The values of C_e and C_s

were adjusted by the Freundlich (Equation 1), Langmuir (Equation 2), and Linear (Equation 3) isotherms.

$$\text{Equation (1): } C_s = K_f * C_e^N;$$

where K_f is the soil sorption capacity, and N is the linearity coefficient of the model.

$$\text{Equation (2): } C_s = \frac{Q_{max} * K_l * C_e}{1 + K_l * C_e};$$

where Q_{max} is the maximum adsorption capacity of the soil, and K_l is the adsorption rate.

$$\text{Equation (3): } C_s = K_d * C_e;$$

where K_d is the sorption capacity.

2.7. Determination of the desorption coefficients (K_{fd}) for diuron, hexazinone, and sulfometuron-methyl

Desorption analyses were performed by removing all the supernatant from the tubes used in the sorption test. After removing all the supernatant, an aliquot of 10.0 mL of 10 mM CaCl_2 solution, free of herbicide, was added to the tubes containing the diuron and hexazinone. For the tests with sulfometuron-methyl, an aliquot of 20.0 mL of 10 mM CaCl_2 solution, free of herbicide, was added. The tubes were sealed, shaken in a vortex mixer for 10 seconds, and shaken vertically at a temperature of $25 \pm 2^\circ\text{C}$ for 12 hours. Subsequently, the supernatant was collected and filtered with a $0.22 \mu\text{m}$ PVDF membrane directly into 1.5 mL vials. After this process, the samples in the vials were analyzed by chromatography to quantify the concentration of the herbicides.

The determination of the amount of the herbicide that remained sorbed to the soil (C_s) after desorption, in mg kg^{-1} , was calculated using the difference between the concentration of the herbicide in the soil before the desorption steps and the concentration in the equilibrium solution. The C_s and C_e values obtained in the desorption test were adjusted using the Freundlich (Equation 4) and Linear (Equation 5) isotherms.

$$\text{Equation (4): } C_s = K_{fd} * C_e^N;$$

where K_{fd} is the soil desorption capacity, and N is the linearity coefficient of the model.

$$\text{Equation (5): } C_s = K_d * C_e;$$

where K_d is the desorption capacity of the soil.

The hysteresis index was calculated according to Equation 6 and described by Sander et al. (2005).

$$\text{Equation (6): } H = \frac{C_s(\text{desor}) - C_s(\text{sorption})}{C_s(\text{sorption})} T, C_e$$

where $C_s(\text{desor})$ and $C_s(\text{sorption})$ are the amount sorbed in the desorption and sorption, respectively, for a temperature (T) and concentration in the solution (C_e).

2.8. Statistical analysis

The Freundlich, Langmuir, and Linear isotherms were compared for the root mean square error (RMSE) and determination coefficient (R^2) values. The sorption and desorption capacities of isolated herbicides (diuron, hexazinone, and sulfometuron-methyl) and both binary (diuron + hexazinone; diuron + sulfometuron-methyl; sulfometuron-methyl + hexazinone) and ternary combinations (diuron + hexazinone + sulfometuron-methyl) in both soils were submitted to the Shapiro–Wilk residual normality test (SHAPIRO & WILK, 1965) and homoscedasticity (BARTLETT, 1951). After the homoscedasticity normality test, the sorption and desorption capacity data were submitted to ANOVA by the F $p \leq 0.05$, and when significant, the means were compared by the Tukey test $p \leq 0.05$. The hysteresis indexes were compared through the descriptive analysis of the means and standard error.

3. RESULTS AND DISCUSSION

3.1 Sorption and desorption of diuron isolated and mixed in binary and ternary combinations

The data for sorption of isolated and mixed diuron were adjusted for the Freundlich, Langmuir, and Linear isothermal models as shown in Figure 2. The R^2 values of the models adjusted by the Freundlich isotherm were equivalent to 0.99 for both the diuron alone and mixed in binary and ternary combinations, both in the LVA and LVD soil (Table 2). The Freundlich isotherm also provided low RMSE values, ranging from 0.07 to 0.18 mg kg⁻¹, for both the isolated and mixed diuron in both soils (Table 2). For

the Langmuir isothermal model, high values of R^2 (0.99) and low RMSE (0.06 to 0.16 mg kg^{-1}) were also observed for isolated diuron and diuron in binary and ternary combinations in LVA and LVd soils (Table 2). On the contrary, for the Linear model, R^2 values lower than 0.99 and higher RMSE values (0.21 to 0.41) were observed for diuron + hexazinone and diuron + hexazinone + sulfometuron-methyl (Table 2).

The biggest R^2 and the smallest RMSE for the Freundlich and Langmuir models demonstrated that these models show a better fit for the adsorption of isolated and mixed diuron compared to the linear model. The lower adjustment of the Linear model to the sorption data of the isolated diuron and mixed to soil is due to the non-linear characteristic of the adsorption of this herbicide to the adsorbent material. The N values observed for the Freundlich model ranged from 0.76 to 0.92 for LVA soil and 0.78 to 0.90 for LVd (Table 2), indicating the non-linearity of the adsorptive process. Regardless of the treatment (isolated or mixture) or soil (LVA and LVd), the sorption of diuron was reduced with the increase of the initial concentration tested. This behavior for diuron sorption indicates the start of saturation of the available binding sites. In addition, it is possible to infer that the sorption between the isolated and mixed diuron in the LVA and LVd soils occurs in a monolayer. Other studies have observed this non-linear pattern of diuron sorption in different soils (DAS CHAGAS et al., 2019; SILVA et al., 2019).

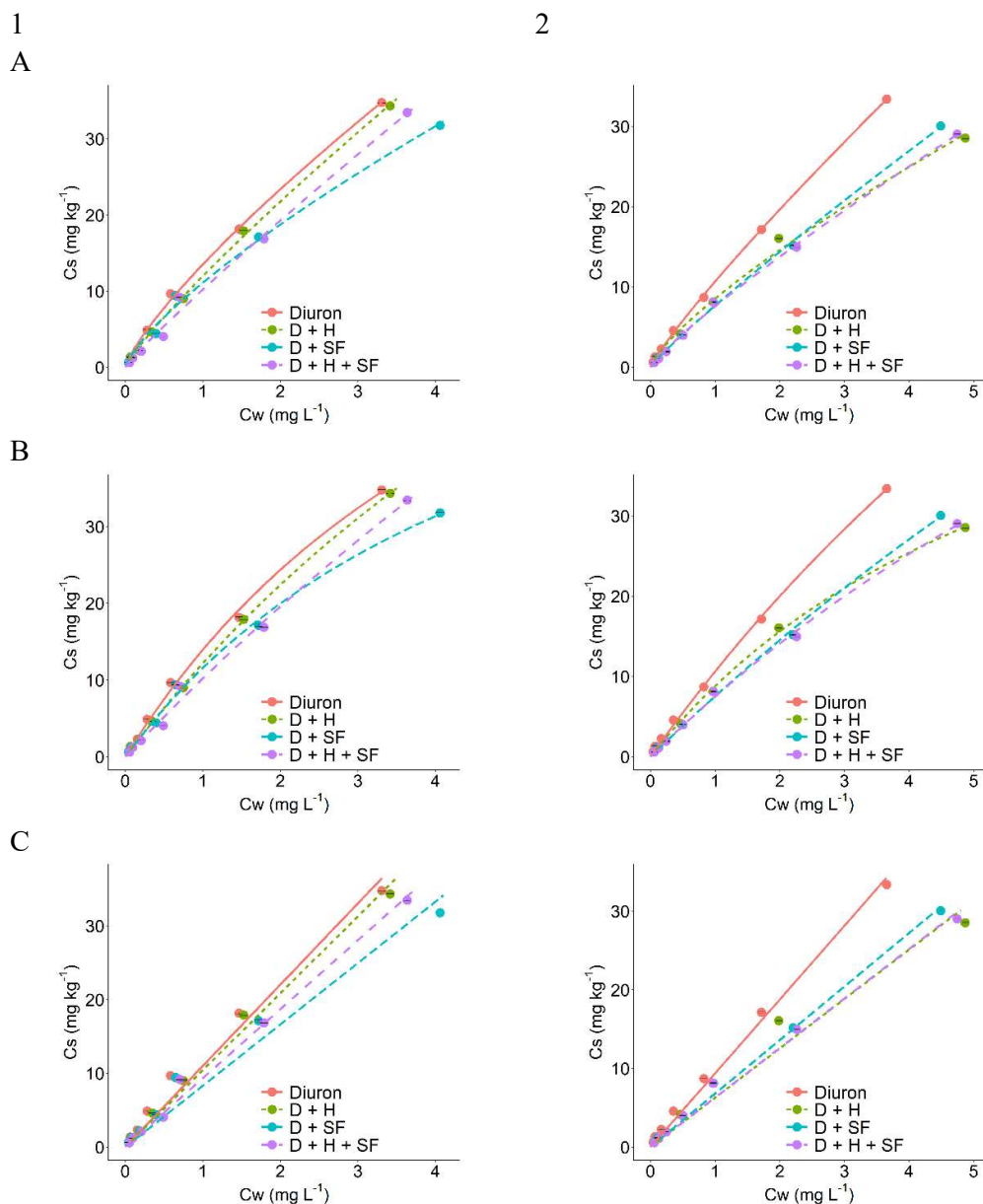
In the Langmuir model, the parameters Q_{max} and KL indicate the maximum sorption capacity and the rate at which it occurs. The Q_{max} values for diuron isolated and in binary and ternary combinations ranged between 72.89 to 235 mg kg^{-1} and 68.65 to 200.80 mg kg^{-1} for LVA and LVd soil, respectively (Table 2).

1 **Table 2.** Parameters (mean \pm standard error) of the Freundlich, Langmuir, and Linear isotherms for the sorption of isolated diuron and its binary
 2 and ternary mixtures with the herbicides hexazinone and sulfometuron-methyl in two soils (LVA and LVd).

FV	Soil LVA										
	Freundlich				Langmuir				Linear		
	K_f	N	R^2	RMSE	Q_{max}	K_L	R^2	RMSE	K_d	R^2	RMSE
Diuron	13.5 Aa (± 0.19)	0.79 \pm 0.01	0.99	0.12	95.73 \pm 7.14	0.17 \pm 0.02	0.99	0.14	11.03 \pm 0.21	0.99	0.1
D + H	11.97 Ba (± 0.14)	0.86 \pm 0.01	0.99	0.09	139.02 \pm 7.28	0.09 \pm 0.01	0.99	0.06	10.43 \pm 0.20	0.97	0.35
D + SF	11.11 Ba (± 0.29)	0.76 \pm 0.02	0.99	0.18	72.89 \pm 4.90	0.19 \pm 0.02	0.99	0.16	8.32 \pm 0.08	0.99	0.11
D + H + SF	10.21 Ca (± 0.30)	0.92 \pm 0.03	0.99	0.2	235.95 \pm 82.28	0.05 \pm 0.02	0.99	0.2	9.35 \pm 0.11	0.98	0.21

FV	Soil LVd										
	Freundlich				Langmuir				Linear		
	K_f	N	R^2	RMSE	Q_{max}	K_L	R^2	RMSE	K_d	R^2	RMSE
Diuron	10.67 Ab (± 0.10)	0.87 \pm 0.01	0.99	0.07	170.74 \pm 19.64	0.07 \pm 0.01	0.99	0.09	9.01 \pm 0.21	0.99	0.12
D + H	8.55 Bb (± 0.26)	0.78 \pm 0.02	0.99	0.17	68.65 \pm 2.32	0.15 \pm 0.01	0.99	0.07	6.27 \pm 0.20	0.97	0.41
D + SF	7.67 Cb (± 0.12)	0.90 \pm 0.01	0.99	0.09	200.80 \pm 36.17	0.04 \pm 0.01	0.99	0.1	6.80 \pm 0.01	0.99	0.15
D + H + SF	7.57 Cb (± 0.13)	0.86 \pm 0.01	0.99	0.08	121.12 \pm 13.38	0.06 \pm 0.01	0.99	0.1	6.3 \pm 0.11	0.98	0.21

3 D + H = Diuron + hexazinone; D + SF = Diuron + sulfometuron-methyl; D + H + SF = Diuron + hexazinone + sulfometuron-methyl. K_f and N =
 4 Sorption constant and Freundlich linearity coefficient. Q_{max} and K_L = Maximum amount of adsorption and velocity constant. K_d = Linear
 5 adsorption constant. R^2 = Coefficient of determination. RSME = Root of the mean square error. Lower case letters compare soils within each
 6 herbicide association and upper case letters compare herbicide associations within each soil using the Tukey test p -value ≤ 0.05 .



7 **Figure 2.** Freundlich (A), Langmuir (B), and Linear (C) isotherms for the sorption of
 8 diuron isolated and mixed in binary and ternary combinations with the herbicides
 9 hexazinone and sulfometuron-methyl in LVA (1) and LVd (2) soils). D + H = Diuron +
 10 hexazinone; D + SF = Diuron + sulfometuron-methyl; D + H + SF = Diuron + hexazinone
 11 + sulfometuron-methyl.

12

13 Although Q_{max} and KL demonstrate differences for diuron sorption alone and in
 14 combinations, the estimated values were much higher than the absorbed concentrations
 15 (C_s) measured in the assay (maximum 35 mg kg^{-1} absorbed in the soil, Figure 2). The
 16 highest estimated value of Q_{max} by the Langmuir model compared to the tested range is

17 commonly observed when maximum adsorption is not achieved by the tested data range
18 (HINZ et al., 2001). Maximum adsorption is achieved when the values for C_s become
19 constant with an increase in C_w , and this behavior was not observed for diuron in the
20 ranges of concentrations studied and estimated based on the rate used in sugarcane crops.
21 To avoid false interpretations of the treatments, the Freundlich model and its K_f and N
22 parameters, which represent the adsorption capacity and affinity, proved to be more
23 reliable.

24 The K_f value for diuron in the LVA soil, regardless of the combinations, was
25 higher than the LVd (Table 2). The higher sorption of diuron in the LVA soil can be
26 attributed to the higher TOC content (9.46 g kg^{-1}) compared to the LVd soil—properties
27 that increase the number of sites for adsorption of the diuron. A study evaluating diuron
28 sorption in 27 different Brazilian soils showed that those with the highest TOC allowed
29 the greatest adsorption of this herbicide (DAS CHAGAS et al., 2019).

30 The greater amount of clay may also allow greater sorption of diuron; however,
31 the difference in clay contents between the LVA and LVd soils was low (4%). However,
32 the LVA soil showed a greater amount of clay fractions that favor the occurrence of
33 adsorptive processes, such as kaolinite and gibbsite (see Figure 2). Carbo et al. (2007)
34 reported an increase in the adsorption of diuron in the Bw2 horizon compared to Bw1 for
35 an oxisol, attributing this increase to the greater presence of kaolinite and gibbsite in the
36 Bw2 horizon.

37 The K_f for the diuron isolated in the LVA soil was 13, 22, and 32% higher than
38 the combinations D + H, D + SF, and D + H + SF, respectively (Table 2). There were no
39 differences between binary combinations in the LVA soil for the K_f value (Table 3).
40 However, the K_f diuron in the mixture of the three herbicides in the solution differed from
41 the other treatments, presenting the lowest K_f value (Table 3). For LVd soil, K_f for diuron
42 was also higher compared to binary (25 and 39% for D + H and D + SF, respectively) and
43 ternary (41%) combinations (Table 2). The mixture of D + SF and D + H + SF had the
44 lowest K_f values in the LVd soil (Table 2).

45 The presence of hexazinone and sulfometuron-methyl in the solution reduced the
46 sorption of diuron in the two soils evaluated. In LVA soil, the lower sorption for the
47 ternary mixture compared to binary mixtures indicates an additive effect in reducing the
48 adsorption of diuron. The addition of a larger number of herbicide molecules (D + H +
49 SF) possibly increased the competition between herbicides for the binding sites available
50 in the LVA soil, reducing the number of diuron molecules adsorbed to the soil. For LVd,

51 the additive effect due to the mixture of the three herbicides was not observed, since the
52 binary mixture D + SF did not differ from the ternary mixture. In addition, hexazinone
53 has not shown the same ability to reduce sorption of diuron compared to sulfometuron-
54 methyl.

55 Diuron and sulfometuron-methyl have some similarities in terms of their physical
56 and chemical properties that may allow greater affinity for similar sites for the adsorption
57 of these herbicides. For example, the presence of an aromatic ring and less solubility of
58 diuron and sulfometuron-methyl in relation to hexazinone are properties that allow a
59 greater affinity of these pollutants to hydrophobic binding sites, generating greater
60 competition between the molecules of diuron and sulfometuron-methyl. In LVd, this
61 interaction between diuron and sulfometuron-methyl was more evident, probably due to
62 the lower sorption capacity of diuron compared to LVA.

63 Other studies have already demonstrated the occurrence of competitive sorption
64 between different organic compounds, similar to that observed in our work among the
65 herbicides diuron, hexazinone, and sulfometuron-methyl. For example, Xing et al. (1996)
66 reported the occurrence of competitive sorption between atrazine and other organic
67 compounds (e.g., Cyanazine and prometon) in silicate and organic matter—adsorbents
68 with a physical-chemical structure similar to those identified in soils. These authors also
69 reported a greater competition between atrazine and prometon or cyazine, which are
70 herbicides with the presence of the 1,3,5-triazine group. Fernández-Calviño et al. (2015)
71 also observed the competitive effect between the antibiotics tetracycline (TC),
72 oxytetracycline (OTC), and chlortetracycline (CTC) in two acidic soils, showing the most
73 intense competition between the antibiotics TC and CTC.

74 The desorption data of the diuron adjusted to the Freundlich and Linear model, as
75 shown in Figure 3. However, the Freundlich model showed a better fit with higher R^2
76 values (0.98 to 0.99) and lower RMSE (0.06 to 0.64 mg kg⁻¹) for all treatments tested
77 (Table 4). The best fit of the Freundlich models compared to the Linear one is the result
78 of the non-linearity of the desorption for the tested concentrations. Only for diuron
79 isolated in the LVA and LVd soils was there similarity in the adjustment capacity of the
80 Freundlich and Linear models due to the greater linear tendency in desorption ($N = 1.03$
81 and $N = 0.98$ for LVA and LVd, Table 3). For binary and ternary combinations, the
82 linearity coefficients (N) for diuron ranged between 0.80 and 0.90, indicating the highest
83 desorption ratio at higher concentrations.

84 **Table 3.** Parameters (mean \pm standard error) of isotherms (Freundlich and Linear) for desorption and hysteresis index (H) of isolated diuron and
 85 its binary and ternary mixtures with the herbicides hexazinone and sulfometuron-methyl in two soils (LVA and LVd)

FV	Solo LVA										
	Freundlich				Linear			Hysteresis index (H) mg L ⁻¹			
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	0,1	0,2	0,5	1,5
Diuron	30.97 Aa (± 0.20)	1.03 \pm 0.01	0.99	0.09	30.76 \pm 0.21	0.99	0.1	0.33 \pm 0.03	0.57 \pm 0.03	0.95 \pm 0.03	1.52 \pm 0.02
D + H	14.71 Ba (± 0.19)	0.86 \pm 0.02	0.98	0.12	15.23 \pm 2.02	0.97	0.4	0.40 \pm 0.08	0.40 \pm 0.02	0.40 \pm 0.05	0.40 \pm 0.06
D + SF	14.65 Ba (± 0.21)	0.78 \pm 0.03	0.99	0.13	13.91 \pm 1.23	0.98	0.26	-0.10 \pm 0.03	-0.07 \pm 0.02	-0.02 \pm 0.03	0.05 \pm 0.05
D + H + SF	11.44 Ba (± 0.53)	0.81 \pm 0.03	0.99	0.19	12.99 \pm 0.98	0.96	0.5	-0.02 \pm 0.05	0.10 \pm 0.04	0.28 \pm 0.03	0.54 \pm 0.03

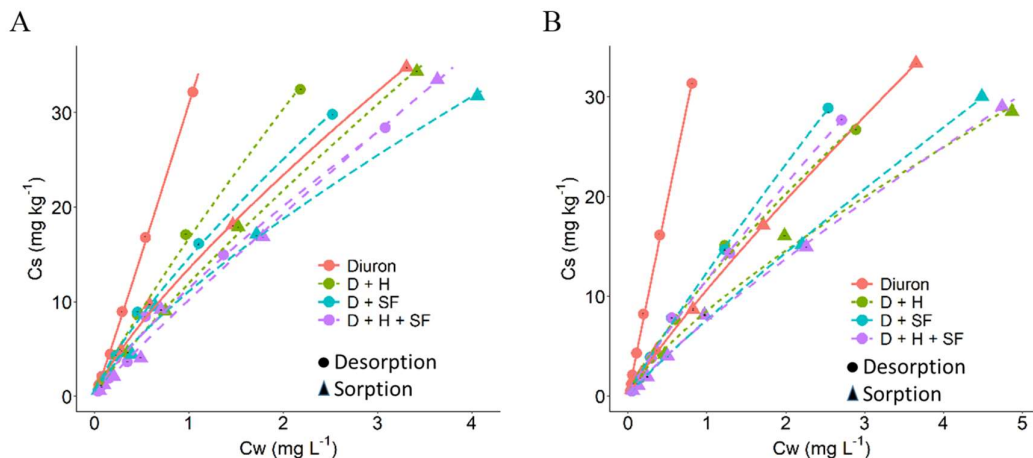
FV	Solo LVd										
	Freundlich				Linear			Hysteresis index (H) mg L ⁻¹			
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	0.1	0.2	0.5	1.5
Diuron	38.69 Ab (± 0.54)	0.98 \pm 0.02	0.99	0.14	39.04 \pm 0.40	0.99	0.14	1.89 \pm 0.22	2.10 \pm 0.20	2.40 \pm 0.17	2.79 \pm 0.18
D + H	11.64 Ba (± 0.25)	0.80 \pm 0.02	0.99	0.17	12.86 \pm 0.90	0.99	0.18	0.29 \pm 0.08	0.31 \pm 0.05	0.34 \pm 0.02	0.38 \pm 0.04
D + SF	12.44 Ba (± 0.19)	0.90 \pm 0.02	0.91	0.64	13.43 \pm 5.60	0.89	0.71	0.67 \pm 0.09	0.62 \pm 0.06	0.56 \pm 0.01	0.49 \pm 0.04
D + H + SF	11.68 Ba (± 0.14)	0.87 \pm 0.01	0.99	0.22	10.88 \pm 1.76	0.98	0.26	0.52 \pm 0.04	0.55 \pm 0.02	0.60 \pm 0.02	0.66 \pm 0.06

86 D + H = Diuron + hexazinone; D + SF = Diuron + sulfometuron-methyl; D + H + SF = Diuron + hexazinone + sulfometuron-methyl. *Kfd* and N=

87 Desorption constant and Freundlich linearity coefficient. *Kdd* = Linear desorption constant. R² = Coefficient of determination. RSME = Root of

88 the mean square error. Lower case letters compare soils within each herbicide association and upper case letters compare herbicide associations

89 within each soil using the Tukey test p-value ≤ 0.05 .



91 **Figure 3.** Freundlich isotherms for desorption of isolated and mixed diuron in binary and
 92 ternary combinations with the herbicides hexazinone and sulfometuron-methyl in the
 93 LVA (A) and LVd (B) soils. D + H = Diuron + hexazinone; D + SF = Diuron +
 94 sulfometuron-methyl; D + H + SF = Diuron + hexazinone + sulfometuron-methyl.

95

96 The K_{fd} of the diuron isolated in the LVd soil (38.69) was higher than the LVA
 97 soil (30.97) (Table 3). Despite the higher sorption capacity of diuron in LVA compared
 98 to LVd, in the first, part of the sorbed herbicide managed to return to solution due to
 99 greater desorption. The lower stability between part of the diuron molecules sorbed by
 100 LVA resulted in a lower hysteresis (0.33 to 1.52) compared to LVd (1.89 to 2.79). The
 101 higher hysteresis value for LVd indicates the possibility that a sorbed portion of the diuron
 102 in this soil is unlikely to return to solution, reaching a metastable state with the aging of
 103 the herbicide in the LVd soil. For LVA, the probability of the formation of a bound
 104 residue between diuron and soil particles is lower in relation to LVd.

105 The K_{fd} for diuron in binary (14.71 and 14.64 for D + H and D + SF, respectively)
 106 and ternary combinations (11.44) were lower compared to diuron alone (30.97) in LVA
 107 soil (Table 3). In LVd, the same behavior was observed—lower K_{fd} values for diuron in
 108 binary (11.64 and 12.44 for D + H and D + SF, respectively) and ternary combinations
 109 (11.68) compared to isolated diuron (Table 3). There was no difference for K_{fd} between
 110 mixtures and soils (Table 3).

111 The presence of the herbicides hexazinone and sulfometuron-methyl increased the
 112 desorption of diuron in LVA and LVd soils. The intense desorption of diuron in binary
 113 and ternary combinations eliminated the hysteresis effect for diuron in LVd soil, with
 114 values close to zero for this index (Table 3). In addition to impairing the sorption process

115 of diuron to soil, the herbicides hexazinone and sulfometuron-methyl also reduced the
116 stability of the interactions between diuron and soil colloids, allowing the greater return
117 of the herbicide to the aqueous phase of the soil. The hexazinone and sulfometuron-
118 methyl still present in the soil solution during desorption may have displaced part of the
119 diuron that was poorly adsorbed to the soil solution, and this effect did not occur for
120 diuron conditions alone. This behavior in binary and ternary solutions has already been
121 reported. For example, White & Pignatello (1999) have already demonstrated that a solute
122 through competition can exclude a solute already adsorbed to the soil. These authors
123 observed this effect by comparing the competing solute (pyrene) with the primary solute
124 (phenanthrene) for two soils with contrasting organic carbon content.

125

126 **3.2 Sorption and desorption of hexazinone isolated and mixed in binary and ternary** 127 **combinations.**

128 The sorption data of isolated and combined hexazinone with the other herbicides
129 in the LVA and LVd soils were adjusted to the isothermal models of Freundlich,
130 Langmuir, and Linear (Figure 4, Table 4). The R^2 values were equivalent to 0.99 for the
131 Freundlich, Langmuir, and Linear models in tested treatments (Table 4). The RMSE value
132 was low for all models and treatments, ranging from 0.01 to 0.02 mg kg⁻¹ (Table 4).

133 Despite the good fit of the three models tested for isothermal adsorption of
134 hexazinone, the Freundlich model proved to be more suitable for interpreting the
135 differences between treatments (combinations of herbicides and soils). Again, the
136 Langmuir model provided very high values that were outside the data range
137 experimentally tested for the Q_{max} parameter when hexazinone was evaluated separately
138 in the LVA (165.10 mg kg⁻¹) and LVd (162.30 mg kg⁻¹) soils.

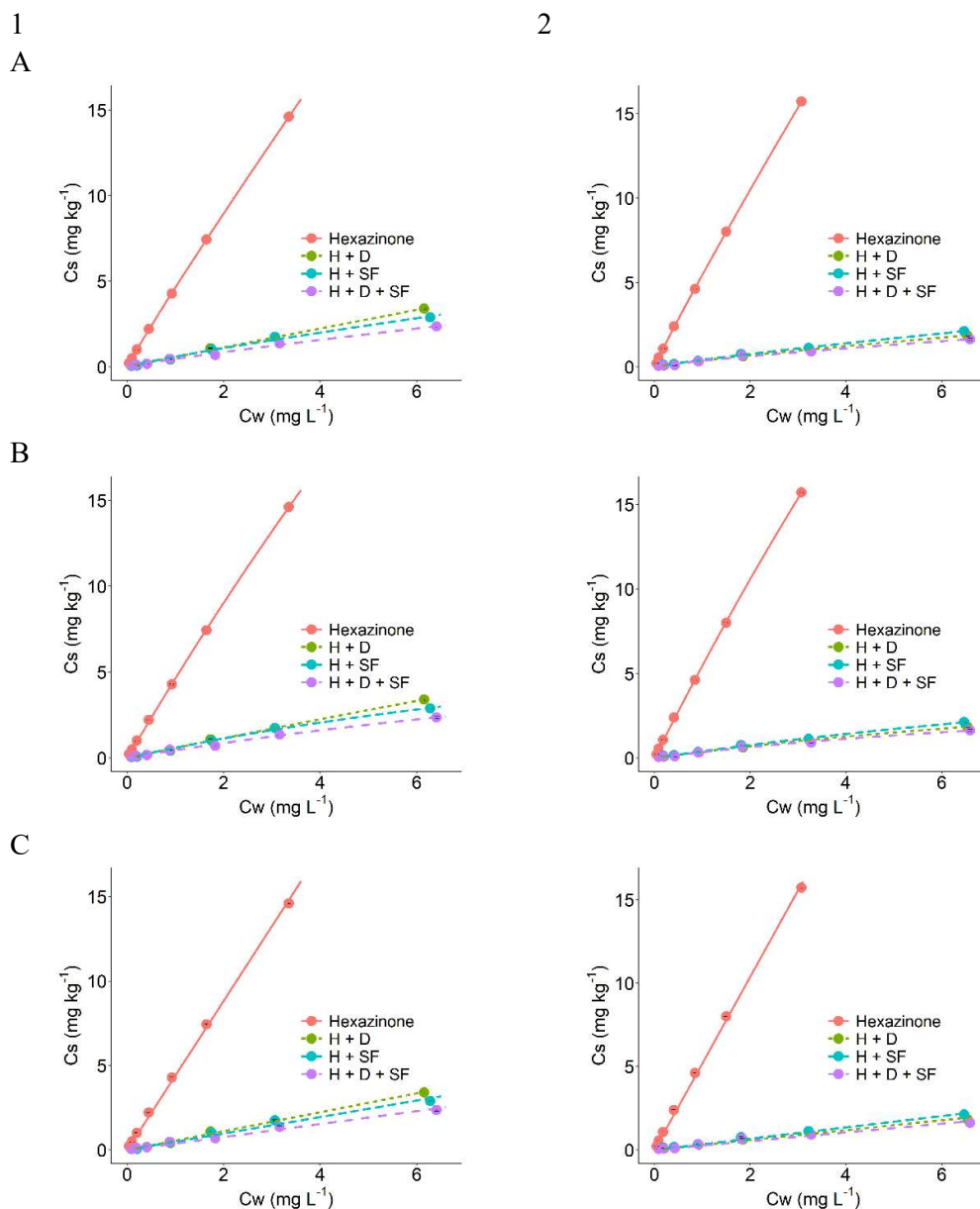
139 In the H + D mixture in the LVA, the Q_{max} value was also higher than the
140 maximum limit tested experimentally. For the other herbicide mixtures, both in the LVA
141 and LVd soil, the Q_{max} values varied between 4.76 to 10.65 mg kg⁻¹, remaining below
142 the tested upper limit of 15 mg kg⁻¹. The ability of the Langmuir model to provide Q_{max}
143 values within the tested concentration limits indicates an L-type adsorption; that is, the
144 sorption rate is reduced due to the increase in the concentration of hexazinone in the soil
145 solution.

146 **Table 4.** Parameters (mean \pm standard error) of the Freundlich, Langmuir, and Linear isotherms for the sorption of isolated hexazinone and its
 147 binary and ternary mixtures with diuron and sulfometuron-methyl in two soils (LVA and LVd).

FV	LVA Soil										
	Freundlich				Langmuir				Linear		
	K_f	N	R ²	RMSE	Qmax	K _L	R ²	RMSE	Kd	R ²	RMSE
Hexazinone	4.65 Ab (± 0.02)	0.94 ± 0.01	0.99	0.01	165.10 ± 18.85	0.03 ± 0.01	0.99	0.02	4.42 ± 0.02	0.99	0.02
H + D	0.57 Ba (± 0.03)	0.97 ± 0.03	0.99	0.01	55.77 ± 33.20	0.01 ± 0.01	0.99	0.02	0.55 ± 0.01	0.99	0.01
H + SF	0.60 Ba (± 0.03)	0.86 ± 0.03	0.99	0.02	10.60 ± 1.41	0.06 ± 0.01	0.99	0.02	0.48 ± 0.01	0.99	0.01
H + D + SF	0.47 Ba (± 0.02)	0.86 ± 0.03	0.99	0.02	10.65 ± 2.17	0.04 ± 0.01	0.99	0.02	0.38 ± 0.01	0.99	0.01

FV	LVd Soil										
	Freundlich				Langmuir				Linear		
	K_f	N	R ²	RMSE	Qmax	K _L	R ²	RMSE	Kd	R ²	RMSE
Hexazinone	5.46 Aa (± 0.02)	0.94 ± 0.01	0.99	0.02	162.30 ± 16.91	0.01 ± 0.01	0.99	0.02	5.19 ± 0.03	0.99	0.04
H + D	0.38 Bb (± 0.01)	0.85 ± 0.02	0.99	0.01	6.51 ± 0.71	0.06 ± 0.01	0.99	0.02	0.30 ± 0.01	0.99	0.02
H + SF	0.43 Bb (± 0.01)	0.86 ± 0.02	0.99	0.01	9.35 ± 0.01	0.05 ± 0.01	0.99	0.01	0.34 ± 0.02	0.99	0.02
H + D + SF	0.36 Bb (± 0.02)	0.80 ± 0.03	0.99	0.01	4.76 ± 0.64	0.08 ± 0.01	0.99	0.01	0.26 ± 0.01	0.99	0.02

148 H + D = Hexazinone + diuron; H + SF = Hexazinone + sulfometuron-methyl; H + D + SF = Hexazinone + diuron + sulfometuron-methyl. K_f and
 149 N = Sorption constant and Freundlich linearity coefficient. Qmax and KL = Maximum amount of adsorption and velocity constant. Kd = Linear
 150 adsorption constant. R² = Coefficient of determination. RSME = Root of the mean square error. Lower case letters compare soils within each
 151 herbicide association and upper case letters compare herbicide associations within each soil using the Tukey test p -value ≤ 0.05 .



162 the Langmuir model performs a very high extrapolation to the maximum adsorption
163 capacity due to the linear tendency of adsorption to the concentrations used in the work.
164 Differences in linear and non-linear behavior for adsorption of isolated and mixed
165 hexazinone, as well as in LVA and LVd soils, led the authors to choose the Freundlich
166 model to describe the behavior of hexazinone between treatments.

167 The K_f value for hexazinone alone was higher in LVd soil (5.46) compared to
168 LVA (4.65) (Table 4). Contrary to the behavior observed for diuron, the LVd soil showed
169 a greater capacity to adsorb hexazinone. Despite the lower TOC and clay content present
170 in LVd—properties that increase hexazinone sorption as reported by Smernik and
171 Kookana (2015), the pH in LVd (4.58) is lower than LVA (5.84) and can increase
172 hexazinone sorption. The lower pH of the LVd soil may allow protonation of the
173 hexazinone molecules due to the higher concentration of H^+ in the soil solution. In the
174 protonated state, the affinity between hexazinone and negative soil loads increases,
175 allowing for greater sorption of this herbicide. A similar effect of pH on the sorption
176 capacity of hexazinone in different soils has been reported by dos Santos et al. (2019).
177 These authors observed that by increasing the pH of different soils, the sorption of
178 hexazinone was considerably reduced, even in soils with a high TOC and clay content.

179 In the LVA soil, the K_f for H + D, H + SF, and H + D + SF were 0.57, 0.60, and
180 0.47, respectively (Table 4). For LVd soil, K_f values were 0.38, 0.43, and 0.36 for H + D,
181 H + SF, H + D + SF, respectively (Table 4). There were no differences between the K_f
182 values for hexazinone in the binary and ternary mixtures and in the LVA and LVd soils
183 (Table 4). The K_f value for hexazinone in the presence of the herbicides diuron and
184 sulfometuron-methyl in binary and ternary combinations was lower compared to
185 hexazinone isolated in the LVA (88%, average value between mixtures) and LVd (92%,
186 average value between mixtures) soils (Table 4).

187 The herbicides diuron and sulfometuron-methyl reduced the sorption of
188 hexazinone in the evaluated soils in the same intensity. In the same way as observed for
189 diuron, competitive sorption among herbicides by the adsorption sites in LVA and LVd
190 prevented the sorption of hexazinone to soils. However, hexazinone was more affected
191 due to the presence of other herbicides in the solution when compared to diuron.
192 Hexazinone showed reductions in higher sorption rates of between 88% and 96% for LVA
193 and LVd, respectively, compared to diuron, with maximum reduction values equal to 24
194 and 27%. The greater tendency of hexazinone to remain dissolved in solution compared
195 to diuron is due to its high hydrophilicity ($S_w = 33,000 \text{ mg L}^{-1}$). This property of

196 hexazinone displaces a larger number of herbicide molecules to the soil solution instead
197 of competing with the most hydrophobic herbicides for the adsorption sites available in
198 LVA and LVd soils.

199 Another mechanism that may be involved in the lower sorption of hexazinone in
200 LVA and LVd soils is the solvation of soil colloids, especially those associated with
201 organic matter, by the molecules of diuron and sulfometuron-methyl. The aromatic rings
202 present in the molecule of diuron and sulfometuron-methyl when creating a solvation
203 layer in the organic and mineral particles of the soil can prevent the approach and the
204 establishment of interactions capable of adsorbing hexazinone. This effect between
205 organic molecules was evidenced by Teklebrhan et al. (2016) when studying the
206 adsorption of polychromatic molecules (PA) in the presence of naphthenic acids (NA).
207 These authors observed that higher concentrations of NA promoted the solvation of C5pe
208 nanoaggregates and prevented the sorption of PA molecules to the nanoaggregate.

209 The Freundlich and Linear models showed good adjustments for the hexazinone
210 desorption data, both when it was alone and in mixture in the LVA and LVd soils (Table
211 5). The Freundlich model showed lower values of RMSE (0.01 to 0.10) and higher R^2
212 (0.97 to 0.98) compared to the Linear model (RSME between 0.83 to 1.14 and R^2 between
213 0.83 and 0.97) in the evaluated soils (Table 5). The Freundlich model showed greater
214 adjustment to the data compared to the Linear one. For treatments in binary and ternary
215 combinations, the difference in relation to RMSE and R^2 was greater compared to the
216 isolated system due to the lower linearity (N between 0.92 and 0.79) when hexazinone
217 was mixed. Therefore, Freundlich parameters were used to detect the differences between
218 herbicide and soil combinations.

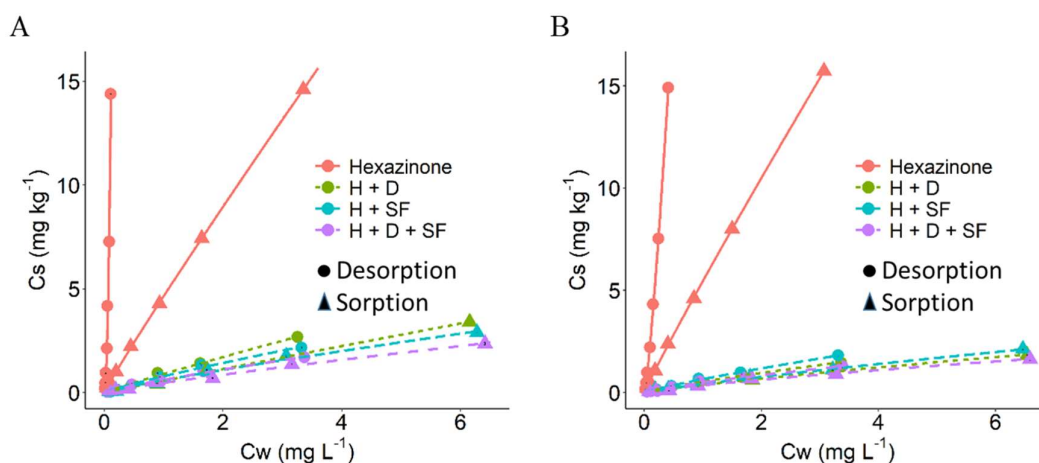
219 The Kfd for hexazinone alone was higher in the LVA soil (103.33) than in LVd
220 (39.90) (Table 5). The H for hexazinone isolated in the LVA soil (15.09 to 22.60) was
221 higher than in the LVd (4.58 to 6.51) (Table 5). Despite the higher sorption of hexazinone
222 under isolated conditions in LVd soil compared to LVA, a greater desorption was
223 observed for LVd soil, with a difference between the soils of up to 2.5 times. Studies have
224 already shown that soils with greater sorption capacity also show less herbicide
225 desorption (DOS SANTOS et al. 2019; OZBAY et al. 2018; MUKHERJEE et al. 2016;
226 AZCARATE et al., 2015). However, soils with lower sorption capacity may have low
227 herbicide desorption, such as for hexazinone and LVA, as long as the interactions between
228 soil-herbicide particles demonstrate high stability.

229 **Table 5.** Parameters (mean \pm standard error) of isotherms (Freundlich and Linear) and hysteresis index (H) for desorption of isolated hexazinone
 230 and its binary and ternary mixtures with diuron and sulfometuron-methyl in two soils (LVA and LVd).

FV	LVA Soil										
	Freundlich				Linear			Hysteresis index (H) mg L ⁻¹			
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	0,1	0,2	0,5	1,5
Hexazinone	103.33 Aa (± 37.74)	1.08 \pm 0.10	0.99	0.12	100.40 \pm 7.30	0.99	1.08	15.09 \pm 0.74	16.74 \pm 1.11	19.20 \pm 1.72	22.60 \pm 2.64
H + D	0.90 Ba (\pm 0.02)	0.92 \pm 0.03	0.99	0.03	1.1 \pm 0.07	0.95	0.83	0.80 \pm 0.46	0.71 \pm 0.29	0.61 \pm 0.01	0.51 \pm 0.13
H+ SF	0.79 Ba (\pm 0.02)	0.86 \pm 0.05	0.98	0.03	0.89 \pm 0.09	0.96	0.94	0.38 \pm 0.15	0.35 \pm 0.12	0.32 \pm 0.14	0.31 \pm 0.07
H + D + SF	0.62 Ba (\pm 0.02)	0.94 \pm 0.03	0.99	0.03	0.56 \pm 0.08	0.94	0.87	0.13 \pm 0.10	0.17 \pm 0.11	0.24 \pm 0.10	0.34 \pm 0.14

FV	LVd Soil										
	Freundlich				Linear			Hysteresis index (H) mg L ⁻¹			
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	0.1	0.2	0.5	1.5
Hexazinone	39.90 Ab (\pm 1.84)	1.15 \pm 0.03	0.99	0.1	33.35 \pm 0.74	0.97	1.15	4.58 \pm 1.30	5.00 \pm 1.06	5.62 \pm 0.67	6.51 \pm 0.12
H + D	0.54 Ba (\pm 0.02)	0.84 \pm 0.03	0.97	0.02	0.68 \pm 0.03	0.96	0.95	0.49 \pm 0.09	0.47 \pm 0.10	0.45 \pm 0.13	0.42 \pm 0.16
H+ SF	0.66 Ba (\pm 0.01)	0.85 \pm 0.02	0.97	0.03	0.60 \pm 0.03	0.97	0.91	0.65 \pm 0.27	0.63 \pm 0.22	0.60 \pm 0.16	0.58 \pm 0.12
H + D + SF	0.49 Ba (\pm 0.02)	0.79 \pm 0.03	0.98	0.03	0.55 \pm 0.04	0.96	0.9	0.29 \pm 0.10	0.30 \pm 0.07	0.31 \pm 0.10	0.33 \pm 0.15

231 H + D = Hexazinone + diuron; H + SF = Hexazinone + sulfometuron-methyl; H + D + SF = Hexazinone + diuron + sulfometuron-methyl. *Kfd* and
 232 N = Desorption constant and Freundlich linearity coefficient. *Kdd* = Linear desorption constant. R² = Coefficient of determination. RSME = Root
 233 of the mean square error. Lower case letters compare soils within each herbicide association, and upper case letters compare herbicide associations
 234 within each soil using the Tukey test p -value \leq 0.05.



235 **Figure 5.** Freundlich isotherms for desorption of isolated and mixed hexazinone in binary
 236 and ternary combinations with the herbicides diuron and sulfometuron-methyl in the LVA
 237 (A) and LVd (B) soils. H + D = Hexazinone + diuron; H + SF = Hexazinone +
 238 sulfometuron-methyl; H + D + SF = Hexazinone + diuron + sulfometuron-methyl.

239

240 The LVA has a greater amount of kaolinite than LVd, and this property can
 241 increase the number of stable bonds, reducing hexazinone desorption. Kaolinite has
 242 hydroxyl groups (OH) on its surface (WANG et al., 2017), which are capable of
 243 establishing hydrogen bonds with four regions of the hexazinone molecule. Hydrogen
 244 bonds are more stable compared to surface interaction (Van der Waals) and can increase
 245 adsorption stability in LVA soil. The higher amount of TOC in the LVA possibly also
 246 favored the occurrence of hydrogen bonds due to the presence of carboxylic groups and
 247 phenols in the organic matter. In addition, the TOC of the soil can allow other types of
 248 interactions (i.e., Van der Waals, dipole-induced, and electrostatic) that, when they occur
 249 simultaneously, increase the stability of adsorption. The strong adhesion of hexazinone
 250 to LVA compared to LVd can be evidenced by the calculated hysteresis indexes. The
 251 sorption of this herbicide in isolated conditions showed an average hysteresis three times
 252 higher in LVA compared to LVd, indicating a lesser tendency of hexazinone to return to
 253 the solution.

254 There were no significant differences between binary and ternary mixtures and
 255 between soils for the *Kfd* value (Table 5). The presence of diuron and sulfometuron-
 256 methyl, whether in binary or ternary associations, reduced the hexazinone *Kfd* in the LVA
 257 and LVd soil compared to the hexazinone alone (Table 5). The reductions in the *Kfd*
 258 values were 144, 130, and 166 times for the mixtures H + D, H + SF, and H + D + SF,
 259 respectively, and in the LVd, the reductions were 72, 60, and 82 times for H + D, H + SF,

260 and H + D + SF, respectively (Table 5). The H values for the binary and ternary mixtures
261 in the soils approached zero, with the maximum and minimum values varying between
262 0.13 and 0.80 (Table 5).

263 The mixture of hexazinone and the herbicides diuron and sulfometuron-methyl
264 dramatically increased the desorption of hexazinone in the two soils studied. In isolated
265 conditions and despite the differences between LVA and LVd soils, hexazinone once
266 adsorbed had a low capacity to return to the soil solution, reaching a possible metastable
267 state. However, the combinations between hexazinone and diuron or sulfometuron-
268 methyl impaired the formation of more stable bonds. The hysteresis effect observed for
269 hexazinone alone was not evidenced for the treatments mixed with the other herbicides,
270 approaching zero. Clearly, isolated hexazinone prefers to remain adsorbed into the soil,
271 and this scenario changed when diuron or sulfometuron-methyl was added to the system,
272 resulting in an almost overlap of the sorption and desorption curves (see Figure 5).

273 Even with the lower sorption of hexazinone in binary and ternary combinations,
274 the presence of other herbicides favored the return of hexazinone already adsorbed to the
275 aqueous phase of the soil. The diuron and sulfometuron-methyl molecules, which were
276 also adsorbed to the LVA and LVd soil, possibly reduced the formation of bi- or
277 multidentified complexes between hexazinone and soil particles due to hysterical
278 impediment, weakening the adsorbent and adsorbate bonds. Consequently, hexazinone
279 was easily removed after the desorption step. Studies have shown the importance of bi-
280 or multidentate complexes as a crucial phenomenon to reduce desorption of herbicides,
281 such as picloram (MARCO-BROWN et al. 2019; MARCO-BROWN et al., 2015) and
282 atrazine, (GONZÁLEZ-MÁRQUEZ et al. 2018) in mineral and organic fractions of the
283 soil.

284 **3.3 Sorption and desorption of sulfometuron-methyl isolated and mixed in binary** 285 **and ternary combinations.**

286 The R^2 values for the Freundlich and Langmuir isotherms for the sulfometuron-
287 methyl alone and in combinations were 0.99, both for the LVA and LVd soil (Table 6).
288 The RMSE values of the Freundlich model varied between 0.01 and 0.03 (Table 6). For
289 the Langmuir model, the RMSE varied between 0.01 and 0.07 (Table 6). The R^2 values
290 for the Linear model were 0.99 for the LVA soil, whereas in LVd, the R^2 varied between
291 0.97 and 0.98 (Table 6). Similar to diuron and hexazinone, the Freundlich model was

292 preferable for assessing the differences between treatments due to the better fit and ability
293 of the parameters to reproduce the behavior of the data range used in the tests.

294 The K_f for LVA (2.66) was higher than for LVd (2.30) under isolated conditions
295 of sulfometuron-methyl (Table 6). Sulfometuron-methyl has nine hydrogen bond
296 acceptors/donors, and in soils with a higher content of TOC and kaolinite (similar to
297 LVA), adsorption is favored due to the hydrogen bonds between soil particles and the
298 herbicide. However, the difference between soils for K_f was small. It is important to
299 consider that the pH of LVA (pH = 5.85) is higher than the pKa of sulfometuron-methyl
300 (pKa = 5.2), unlike LVd, and this fact can reduce the attraction between soil and herbicide.
301 In the pH range of the LVA, a greater number of sulfometuron-methyl molecules are in a
302 dissociated state with a negative residual charge (similar to a weak acid), generating a
303 greater repulsion of the herbicide to the negatively charged colloids of the LVA soil. The
304 deprotonation of the weak acidic herbicides, imazethapyr and 2,4-D, due to the increase
305 in pH, caused less adsorption of these molecules to the soil, with more intense effects in
306 pH ranges higher than the pKa of the herbicides (LIU et al. 2018).

307 Regardless of the evaluated soil, the K_f value for sulfometuron-methyl in binary
308 and ternary mixtures was lower than for isolated conditions (Table 6). In the LVA soil,
309 the combinations SF + D (0.90) and SF + D + H (0.91) did not differ and were lower
310 compared to SF + H (1.16) (Table 6). However, the combinations SF + D (0.33) and SF
311 + D + H (0.44) did not differ from each other and were lower compared to SF + H (0.32)
312 in the LVd soil (Table 6). The presence of the herbicides diuron and hexazinone reduced
313 the sorption of sulfometuron-methyl. When diuron is mixed with sulfometuron-methyl, a
314 greater reduction (66 and 85% for LVA and LVd, respectively) is observed compared to
315 the combination of sulfometuron-methyl and hexazinone (56 and 80% for LVA and LVd,
316 respectively). The presence of diuron affected the sorption process of sulfometuron-
317 methyl more intensely, similar to what was observed when we compared the influence of
318 sulfometuron-methyl on diuron. This relationship between sulfometuron-methyl and
319 diuron reinforces the premise that greater similarity in molecular structure and
320 hydrophobicity raises the competition between these herbicides for available adsorption
321 sites.

322 **Table 6.** Parameters (mean \pm standard error) of the Freundlich, Langmuir, and Linear isotherms for the sorption of isolated sulfometuron-methyl
 323 and its binary and ternary mixtures with diuron and hexazinone in two soils (LVA and LVd).

FV	Soil LVA										
	Freundlich				Langmuir				Linear		
	K_f	N	R ²	RMSE	Qmax	K _L	R ²	RMSE	K_d	R ²	RMSE
Sulfometuron-methyl	2.66 Aa (± 0.03)	0.72 \pm 0.01	0.99	0.02	10.31 \pm 1.1	0.37 \pm 0.06	0.99	0.04	2.42 \pm 0.09	0.99	0.07
SF + D	0.90 Ca (± 0.02)	0.91 \pm 0.03	0.99	0.02	11.35 \pm 2.45	0.09 \pm 0.02	0.99	0.01	0.89 \pm 0.02	0.99	0.02
SF + H	1.16 Ba (± 0.03)	0.87 \pm 0.03	0.99	0.02	8.33 \pm 1.21	0.15 \pm 0.03	0.99	0.02	0.98 \pm 0.02	0.99	0.03
SF + D + H	0.91 Ca (± 0.02)	0.97 \pm 0.03	0.99	0.02	21.24 \pm 10.92	0.05 \pm 0.02	0.99	0.02	0.9 \pm 0.02	0.99	0.02

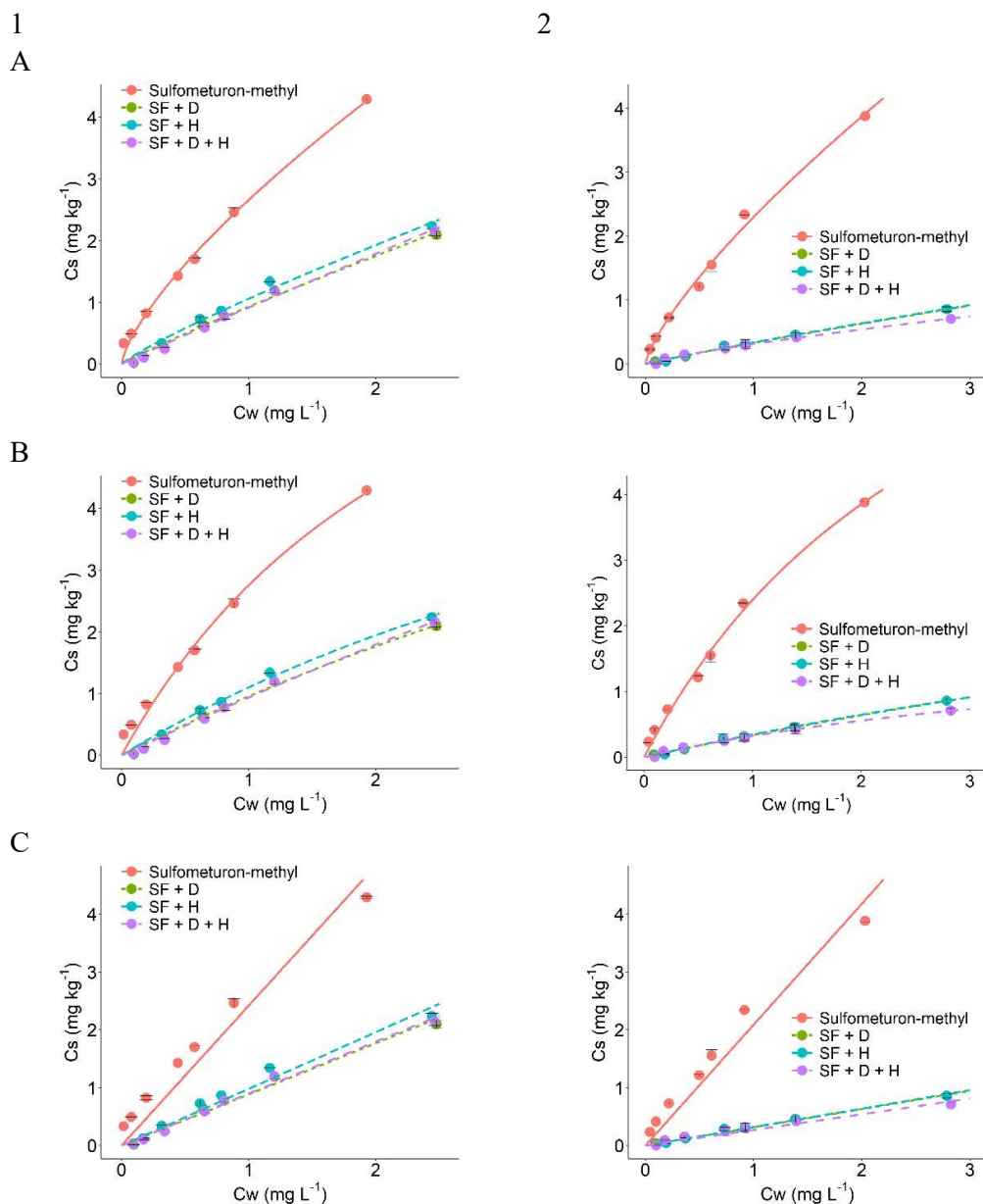
FV	Soil LVd										
	Freundlich				Langmuir				Linear		
	K_f	N	R ²	RMSE	Qmax	K _L	R ²	RMSE	K_d	R ²	RMSE
Sulfometuron-methyl	2.30 Bb (± 0.03)	0.75 \pm 0.02	0.99	0.03	9.81 \pm 0.86	0.32 \pm 0.04	0.99	0.03	2.09 \pm 0.07	0.97	0.07
SF + D	0.33 Cb (± 0.01)	0.92 \pm 0.04	0.99	0.01	6.50 \pm 3.56	0.05 \pm 0.03	0.99	0.01	0.32 \pm 0.01	0.98	0.01
SF + H	0.44 Bb (± 0.01)	0.91 \pm 0.04	0.99	0.01	5.13 \pm 2.08	0.07 \pm 0.03	0.99	0.01	0.32 \pm 0.01	0.98	0.01
SF + D + H	0.31 Cb (± 0.01)	0.79 \pm 0.05	0.99	0.01	2.00 \pm 0.19	0.43 \pm 0.07	0.99	0.01	0.27 \pm 0.01	0.98	0.01

324 SF + D = Sulfometuron-methyl + diuron; SF + H = Sulfometuron-methyl + hexazinone; SF + D + H = Sulfometuron-methyl + diuron + hexazinone.

325 K_f and N = Sorption constant and Freundlich linearity coefficient. Qmax and K_L = Maximum amount of adsorption and velocity constant. K_d =

326 Linear adsorption constant. R² = Coefficient of determination. RSME = Root of the mean square error. Lower case letters compare soils within

327 each herbicide association, and upper case letters compare herbicide associations within each soil using the Tukey test p -value ≤ 0.05 .



328 **Figure 6.** Freundlich (A), Langmuir (B), and Linear (C) isotherms for the sorption of
 329 sulfometuron-methyl isolated and mixed in binary and ternary combinations with the
 330 herbicides diuron and hexazinone in the LVA (1) and LVd (2) soils. SF + D =
 331 Sulfometuron-methyl + diuron; SF + H = Sulfometuron-methyl + hexazinone; SF + D +
 332 H = Sulfometuron-methyl + diuron + hexazinone.

333

334 For the LVd soil, the K_f value was lower than the LVA for the sulfometuron-
 335 methyl in mixture (Table 6). The difference in sorption capacity between the LVA and
 336 LVd soils did not change for sulfometuron-methyl in binary or ternary mixtures. The

337 greater affinity of sulfometuron-methyl to LVA may explain the greater sorption in this
338 soil even when mixed with diuron and/or hexazinone.

339 The values of R^2 and RMSE for the Freundlich model adjusted for desorption
340 varied between 0.84 to 0.98 and 0.01 to 0.04, respectively (Table 7). For the Linear model,
341 the values of R^2 and RMSE ranged between 0.71 to 0.97 and 0.01 to 0.5, respectively
342 (Table 8). The highest values of R^2 and lowest RMSE were observed for the Freundlich
343 model, indicating a better fit of this model to the desorption data.

344 The K_{fd} value in the LVA soil was higher than the LVd, regardless of the
345 combination of herbicides (Table 7). Despite the difference between soils, the K_{fd} values
346 for sulfometuron-methyl were very low for all treatments tested (Table 7). The lower
347 desorption of sulfometuron-methyl in the LVA soil compared to LVd indicates that soil
348 properties such as the higher TOC and kaolinite may allow the establishment of more
349 stable hydrophilic bonds. Báez et al. (2015) observed the lower desorption of
350 metsulfuron-methyl—an herbicide with physicochemical properties similar to
351 sulfometuron-methyl—in soils with a greater amount of kaolinite in its mineralogical
352 composition. The role of COT in the lower desorption of sulfometuron-methyl is related
353 to the ability of this adsorbent to establish more complex interactions of different natures
354 (i.e., dipole-dipole, electrostatics and Van der Waals), similar to other carbonaceous
355 compounds (TONG et al. 2019; PIGNATELLO et al. 2017; DAOUK et al., 2015).

356 In general, sulfometuron-methyl proved to be an herbicide that has a high capacity
357 to return the aqueous phase of the soil compared to the other herbicides in the mixture
358 (diuron and hexazinone). The desorption of sulfometuron-methyl in the isolated form
359 resulted in negative H values, both for LVA (-0.61 to -0.66) and for LVd (-0.70 to -0.89),
360 showing that this herbicide does not tend to remain adsorbed to the soil (see Figure 6).
361 This behavior may be related to its low octanol-water partition coefficient (K_{ow}) and
362 greater polar surface area that favors the displacement of molecules to polar solutions.
363 Cristale et al. (2017) demonstrated that organophosphate contaminants with lower K_{ow}
364 showed a higher percentage of desorption (>58.1%) in two soils with contrasting physical
365 and chemical properties. Another interesting report on the effect of the octanol/water ratio
366 was reported by Gang et al. (2018), testing new possible ionic forms of picloram. These
367 authors observed that ionic forms of picloram with higher K_{ow} had greater affinity with
368 the soil compared to forms of lesser K_{ow} , reducing the mobility of this pesticide. The
369 mixing with diuron and/or hexazinone reduced the negative effect of hysteresis; however,

370 this effect is probably due to less sorption of sulfometuron-methyl than in mixing with
371 diuron and/or hexazinone.

372 **Table 7.** Parameters (mean \pm standard error) of isotherms (Freundlich and Linear) and hysteresis index (H) for the desorption of isolated
 373 sulfometuron-methyl and its binary and ternary mixtures with diuron and hexazinone in two soils (LVA and LVd).

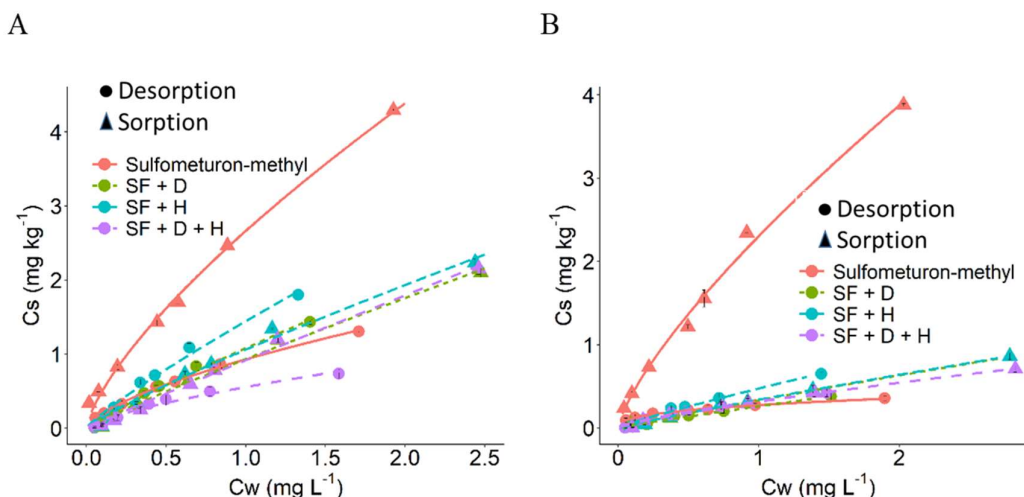
FV	LVA Soil											
	Freundlich				Linear			Hysteresis index (H)				
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	mg L ⁻¹				
								0.1	0.2	0.5	1.5	
Sulfometuron- methyl	0.93 Aa (± 0.01)	0.65 ± 0.02	0.98	0.01	1.94 ± 0.07	0.97	0.03	-0.61 ± 0.03	-0.62 ± 0.02	-0.64 ± 0.02	-0.66 ± 0.01	
SF + D	0.76 Ba (± 0.02)	0.89 ± 0.03	0.96	0.02	1.62 ± 0.07	0.95	0.03	0.22 ± 0.01	0.20 ± 0.02	0.17 ± 0.03	0.14 ± 0.04	
SF + H	0.77 Ba (± 0.12)	0.86 ± 0.03	0.90	0.04	1.56 ± 0.09	0.88	0.05	0.39 ± 0.10	0.38 ± 0.07	0.3 ± 0.02	0.35 ± 0.03	
SF + D + H	0.55 Ba (± 0.02)	0.70 ± 0.06	0.92	0.02	1.02 ± 0.07	0.85	0.03	0.15 ± 0.1	-0.06 ± 0.09	-0.27 ± 0.05	-0.46 ± 0.05	

FV	LVd Soil											
	Freundlich				Linear			Hysteresis index (H)				
	<i>Kfd</i>	N	R ²	RMSE	<i>Kdd</i>	R ²	RMSE	mg L ⁻¹				
								0.1	0.2	0.5	1.5	
Sulfometuron- methyl	0.29 Ab (± 0.01)	0.38 ± 0.04	0.87	0.01	0.30 ± 0.04	0.83	0.02	-0.70 ± 0.01	-0.77 ± 0.01	-0.84 ± 0.01	-0.89 ± 0.01	
SF + D	0.36 Ab (± 0.01)	0.91 ± 0.07	0.93	0.01	0.27 ± 0.02	0.92	0.01	-0.14 ± 0.15	-0.16 ± 0.12	-0.17 ± 0.10	-0.18 ± 0.07	
SF + H	0.37 Ab (± 0.01)	0.88 ± 0.05	0.84	0.03	0.52 ± 0.03	0.74	0.03	-0.16 ± 0.12	-0.17 ± 0.10	-0.18 ± 0.07	-0.20 ± 0.08	
SF + D + H	0.32 Ab (± 0.01)	0.72 ± 0.05	0.84	0.02	0.38 ± 0.04	0.71	0.02	0.26 ± 0.18	0.20 ± 0.21	0.12 ± 0.20	0.04 ± 0.22	

374 SF + D = Sulfometuron-methyl + diuron; SF + H = Sulfometuron-methyl + hexazinone; SF + D + H = Sulfometuron-methyl + diuron + hexazinone.

375 *Kf* and N = Desorption constant and Freundlich linearity coefficient. *Kd* = Linear desorption constant. R² = Coefficient of determination. RSME =

376 Root of the mean square error.



377 **Figure 7.** Freundlich isotherms for desorption of sulfometuron-methyl, isolated and
 378 mixed in binary and ternary combinations with the herbicides diuron and hexazinone in
 379 the LVA (A) and LVd (B) soils. SF + D = Sulfometuron-methyl + diuron; SF + H =
 380 Sulfometuron-methyl + hexazinone; SF + D + H = Sulfometuron-methyl + diuron +
 381 hexazinone.

382

383 4. FINAL CONSIDERATIONS

384 The sorption and desorption of the herbicides diuron, hexazinone, and
 385 sulfometuron-methyl are lower in binary and ternary combinations when compared to
 386 these isolated herbicides. The sorption and desorption of hexazinone in soils is most
 387 affected by mixing with other herbicides. Sulfometuron-methyl promotes greater
 388 reduction in the sorption of diuron in relation to hexazinone. In general, sulfometuron-
 389 methyl proved to be an herbicide that has a high capacity to return the aqueous phase of
 390 the soil compared to the other herbicides in the mixture (diuron and hexazinone). The
 391 mixture between diuron, hexazinone, and sulfometuron-methyl increases the availability
 392 of these herbicides in the aqueous phase of the soil, and mixed doses should be lower
 393 compared to doses for isolated applications.

394

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544 **FINAL CONSIDERATIONS**

545 The results of this work provide new information on the behavior of the mixture
546 of the herbicides diuron, hexazinone, and sulfometuron-methyl in soil. This information
547 helps to understand the efficiency of this mixture in the control of weeds and what
548 precautions must be taken regarding the risk of environmental contamination. The
549 mixture of diuron, hexazinone, and sulfometuron-methyl, whether in binary or ternary
550 combinations, reduced the sorption of the three herbicides compared to the isolated tests.
551 The adsorption of hexazinone was most affected due to mixing, followed by
552 sulfometuron-methyl and diuron.

553 The lower capacity of the soils to adsorb the herbicides when mixed increases the
554 probability of absorption by the seeds or stem of the plants, explaining the high efficiency
555 of the mixture in the control of weeds. Studies have already reported the greatest pre-
556 emergence efficiency of weeds for the mixture of diuron + hexazinone and diuron +
557 hexazinone + sulfometuron-methyl in relation to the isolated application of these
558 herbicides.

559 Another important point to be considered is the greater tendency of hexazinone
560 and sulfometuron-methyl to percolate to greater depths compared to diuron due to the
561 lower retention, evidenced in this work, of the first two in the ternary mixture. The greater
562 leaching of hexazinone and sulfometuron-methyl can exert greater control over the seed
563 bank located at greater depths of the soil, making the mixture even more efficient. The
564 reduction of the weed seed bank is a strategic practice that helps in integrated
565 management and reduces costs with post-emergency control.

566 Despite the greater efficiency of the mixture of herbicides in the control of weeds,
567 some caveats must be considered in relation to the risk of environmental contamination.
568 The lower sorption of these herbicides in mixture can increase the risk of contamination
569 of surface and groundwater due to the greater mobility of the molecules. Conditions that
570 reduce the adsorption of herbicides in the soil increase the mobility of the molecule in the
571 environment, mainly its leaching.

572 To avoid contamination of water resources, the doses of the combinations between
573 diuron, hexazinone, and sulfometuron-methyl should be lower. In fact, the
574 recommendations for combined diuron + hexazinone (Velpar K[®] and Hexaron[®]) and
575 diuron + hexazinone + sulfometuron-methyl (Front[®]) formulations apply a lower amount
576 of active ingredient to these herbicides compared to their isolated formulations (Diuron

577 Nortox® and Hexazinone Nortox® and Oust® [available only in the United States as an
578 herbicide]).

579 However, a precaution should be taken when recommending the mixing these
580 herbicides based on the dose of the formulations isolated from each. This scenario can
581 increase the risk of environmental contamination due to the greater amount of molecules
582 available to undergo leaching or surface runoff, reaching ground and surface water
583 sources.

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