



# Interaction between herbicides applied in mixtures alters the conception of its environmental impact

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## Abstract

Herbicide mixtures have often been used to control weeds in crops worldwide, but the behavior of these mixtures in the environment is still poorly understood. Laboratory and greenhouse tests have been conducted to study the interaction of the herbicides diuron, hexazinone, and sulfometuron-methyl which have been applied alone and in binary and ternary mixtures in the processes of sorption, desorption, half-life, and leaching in the soil. A new index of the risk of leaching of these herbicides has also been proposed. The sorption and desorption study has been carried out by the batch equilibrium method. The dissipation of the herbicides has been evaluated for 180 days to determine the half-life ( $t_{1/2}$ ). The leaching tests have been carried out on soil columns. The herbicides isolated and in mixtures have been quantified using ultra-high performance liquid chromatography coupled to the mass spectrometer. Diuron, hexazinone, and sulfometuron-methyl in binary and ternary mixtures have less sorption capacity and greater desorption when compared to these isolated herbicides. Dissipation of diuron alone is slower, with a half-life ( $t_{1/2}$ ) = 101 days compared to mixtures ( $t_{1/2}$  between 44 and 66 days). For hexazinone and sulfometuron-methyl, the dissipation rate is lower in mixtures ( $t_{1/2}$  over 26 and 16 days), with a more pronounced effect in mixtures with the presence of diuron ( $t_{1/2}$  = 47 and 56 and 17 and 22 days). The binary and ternary mixtures of diuron, hexazinone, and sulfometuron-methyl promoted more significant transport in depth (with the three herbicides quantified to depth P4, P7, and P7, respectively) compared to the application of these isolated herbicides (quantified to depth P2, P4, and P5). Considering the herbicides' desorption and solubility, the new index proposed to estimate the leaching potential allowed a more rigorous assessment concerning the risk of leaching these pesticides, with hexazinone and sulfometuron-methyl presenting a higher risk of contamination of groundwater.

**Keywords** Desorption · Dissipation · Mixture of herbicides · Sorption · Transport

## Introduction

Herbicides are widely used for weed control worldwide, especially in monocultures such as sugar cane (Jonsson et al. 2019). The frequent use of these compounds has increased environmental worries regarding the fate of these pesticides,

mainly when used in mixtures (Munira et al. 2018). Mixtures of herbicides have been adopted preferentially by producers, as this practice increases efficiency, expands the spectrum of weed control, and reduces application costs (Joseph et al. 2018; Webster et al. 2018).

Mixture formulations between 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)carbonyl sulfamoyl]benzoate} are widely used in the cultivation of sugarcane in Brazil (Reis et al. 2019). These herbicides can be marketed alone or in mixtures formulated in binary and ternary combinations. They are recommended herbicides to control grassy weeds, broad leaves, and perennials in pre- and initial post-emergence

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(PPDB 2021). Moreover, the three herbicides (FRONT®) formulation is indicated only for pre-emergence weed control (AGROFIT 2021).

Diuron, hexazinone, and sulfometuron-methyl have different physical and chemical properties and, therefore, it is expected that the behavior of each one in the soil will be variable. These herbicides have a medium to a long residual period in the soil, and depending on edaphoclimatic conditions, the half-life of diuron in soils could vary between 35 and 92 days (Shareef et al. 2014; Almeida et al. 2020), hexazinone (20 and 115 days) (Wang et al. 2012; Calegari et al. 2018), and sulfometuron-methyl (36 and 55 days) (Alvarez et al. 2021). There is an environmental risk associated with herbicides with a more extended residual period in the soil (Passos et al. 2018; das Chagas et al. 2019). This is because a herbicide can leach into the soil profile, and contaminated groundwater sources when exposed to events such as rain for a longer time. This fact is even more aggravating when the herbicide has high water solubility (Neto et al. 2017; Passos et al. 2019), such as hexazinone ( $33,000 \text{ mg L}^{-1}$  at  $25^\circ \text{C}$ ) (PPDB 2021).

The evaluation of the effect of herbicide mixtures in soils and their possible alteration in the main processes that act in the destination of these pesticides (sorption, desorption, persistence, and leaching) applied simultaneously is essential for more conscious and safe use of these products. Despite increasing the weed control spectrum, herbicidal mixtures generally contain molecules with more remarkable persistence in the environment (to control seeds that germinate in a more extended period) and greater mobility (to control the seed bank in-depth). Considering these factors and the different types of soil and the increasingly heterogeneous climatic conditions, the application of herbicides in mixtures can cause damage to subsequent sensitive crops. It may also increase the risk of surface and groundwater contamination (Carneiro et al. 2020).

Few studies in the literature have reported the behavior of herbicides in mixed formulations. The results found did not compare the effects of mixtures on the sorption/desorption, persistence, and leaching processes of these pesticides in the soil. For example, the sorption and desorption of diuron alone and in a mixture with hexazinone were compared in different soils, and it was found that sorption was similar. However, the availability of diuron was most significant in the mixture compared to diuron alone (Takeshita et al. 2019). The study and comparison of all these processes can bring more rich and detailed information about the complex behavior of these molecules in the environment.

Some mathematical models are currently used to assess the fate of pesticides in the environment and help understand the complex interaction of these compounds in the soil. The GUS (Groundwater Ubiquity Score Index) and the AFR (Attenuation Factor Approach) are widely used in evaluating the risk of leaching and the potential for groundwater

contamination by pesticides. These two models assess the relative leaching potential using only the measured pesticide properties, the half-life, and the normalized sorption coefficient of soil organic carbon (Gustafson 1989; Dusek et al. 2011). Thus, the ability of these models to predict the fate of pesticides in soils is limited, mainly because soils have significant variability in their attributes. Thus, the proposal of a new index to estimate the leaching potential considering desorption and solubility in the estimation model can allow a more accurate and safer assessment of the risk of pesticide leaching. However, to propose this model, it is necessary to know pesticides' sorption, desorption, and half-life. Thus, this study was conducted to (1) evaluate the retention capacity (sorption/desorption), half-life, and leaching of diuron, hexazinone, and sulfometuron-methyl isolated and in binary and ternary mixtures in the soil, and (2) propose a new model and classification to estimate the risk of contamination of these isolated and mixed herbicides.

## Material and methods

### Soil characterization

The soil used in the study was a Dystrophic Red Latosol (LVd), collected in the state of Rio Grande do Norte, Brazil, with geographical coordinates of  $5^\circ 3' 37.7'' \text{ S}$  and  $37^\circ 24' 14.4'' \text{ W}$ . The choice of this soil was based on its representativeness within the sugarcane regions of Brazil. Soil collection was carried out at a depth of 0 to 20 cm in a place with no herbicide application history (Supplementary file SI). The physical and chemical properties of the LVd soil samples (Supplementary file SII) were determined, according to Teixeira (2017). The minerals of the clay fraction (mineralogy) were characterized by chemical dispersion with sodium hexametaphosphate ( $0.025 \text{ mol L}^{-1}$ ) and mechanics using a “Wagner” type agitator for 16 h (Teixeira 2017). Minerals were identified by X-ray diffraction (XRD) using a SHIMADZU diffractometer (model XRD, 6000, Tokyo, Japan) with  $\text{K}\alpha 1$  emission of copper. The source potential was 40 kV, with 30 mA current, and a scanning speed with a step of  $0.02^\circ$  applied every second. The scanning range ( $2\theta$ ) used was from  $5$  to  $65^\circ$ . The peaks of the clay minerals were identified using the X-ray program v. 1.0.0.37, and the phases were identified according to Chen (1977) (Supplementary file SII).

### Chemicals

The reference standards used for diuron and hexazinone were achieved from Sigma-Aldrich® (Saint Louis, MO, USA) (purity of 99.6 and 99.5%, respectively). Sulfometuron-methyl was found by Supelco (Bellefonte, PA, USA) with a purity of 99.5%. These herbicides were chosen due to their wide use

in the area of sugar cane production. The structures and physical and chemical properties of these herbicides are shown in (Supplementary file [SIII](#)).

## Conducting experiments

### Sorption and desorption

**Determination of sorption kinetics** The kinetics of sorption and desorption of herbicides in the soil was determined by the method batch equilibrium (OECD 2000) at a temperature of  $25 \pm 2$  °C. A volume of 10 mL of the herbicides diuron and hexazinone solution alone and in binary and ternary mixtures at a concentration of  $1 \text{ mg L}^{-1}$  was prepared in 10-mM  $\text{CaCl}_2$  and added to Falcon tubes containing 2 g of herbicide-free soil. For sulfometuron-methyl, a 20.0-mL aliquot of the solution with this herbicide alone and in mixtures ( $1.0 \text{ mg L}^{-1}$ , prepared in 10-mM  $\text{CaCl}_2$ ) was added in Falcon tubes containing 4 g of soil. Subsequently, these tubes were shaken on a vertical shaker at different time intervals, ranging from 0 to 1440 min (Silva et al. 2019). After stirring, the samples were centrifuged at 2,640 g for 7 min. Then, the supernatant was filtered (0.22- $\mu\text{m}$  Nylon membrane) into 1.5-mL vials. The samples were quantified by ultra-high performance liquid chromatography coupled to the mass spectrometer (UHPLC-MS/MS).

The time required to reach the herbicide sorption and desorption balance in the studied LVd was approximately 12 h (data not shown). Thus, 12 h was established as the equilibrium time for the sorption and desorption tests. All analyses were conducted in triplicate for each herbicide isolated, in binary mixtures and ternary mixtures.

**Determination of the sorption coefficients ( $Kfs$ ) and desorption ( $Kfd$ )** In sorption tests, working solutions containing diuron, hexazinone, and sulfometuron-methyl isolated, in binary and ternary mixtures, were prepared from the stock solution for each herbicide (OECD 2000). The working solutions were prepared in 10-mM  $\text{CaCl}_2$  in the following concentrations: 0.2, 0.4, 0.73, 1.5, 3.0, 6.0, and  $12 \text{ mg L}^{-1}$  for diuron; 0.1, 0.22, 0.45, 1.0, 2.0, 3.5, and  $7.0 \text{ mg L}^{-1}$  for hexazinone; and 0.1, 0.2, 0.4, 0.8, 1.0, 1.5, and  $3.0 \text{ mg L}^{-1}$  for sulfometuron-methyl. The choice of these concentrations was based on the highest recommended commercial dose (0.73, 0.45, and  $0.2 \text{ mg L}^{-1}$  for diuron, hexazinone, and sulfometuron-methyl, respectively).

For diuron and hexazinone, in Falcon tubes containing 2.00 g of soil, a 10-mL aliquot of each herbicide concentration was added separately. For sulfometuron-methyl, an aliquot of 20 mL of each concentration and 4.00 g of soil was used. The amount of soil used to sulfometuron-methyl was greater than the other herbicides, but the proportion of 1.00 g of soil for every

5.00 ml of herbicide solution was maintained due to the smaller dose range of sulfometuron-methyl. Previous laboratory studies showed that sulfometuron-methyl needs a larger amount to be above the limit of quantification. Subsequently, the samples were shaken vertically at a temperature of  $25 \pm 2$  °C for 12 h. After stirring, the sample solutions were centrifuged for 7 min (2,260 g). The supernatant was removed, filtered through a 0.22- $\mu\text{m}$  PVDF membrane into 1.5-mL vials. UHPLC-MS/MS analyzed the samples in the vials to quantify the concentration of each herbicide.

Through the difference between the initial standard concentration added to the soil and the amount detected in the equilibrium solution ( $Ce$ ), the concentrations of the herbicides absorbed in the soil ( $Cs$ ), in  $\text{mg kg}^{-1}$ , were calculated.  $Ce$  and  $Cs$  values were adjusted by the Freundlich isotherms (Eq. 1) to interpret the sorption process.

$$(Cs = Kfs Ce^{Ns}) \tag{1}$$

where  $Cs$  is the quantity of herbicide absorbed into the soil ( $\text{mg kg}^{-1}$ );  $Ce$  is the quantity of herbicide in the equilibrium solution ( $\text{mg L}^{-1}$ );  $Kfs$  is the sorption capacity; and  $Ns$  is the linearity.

To determine the desorption of the herbicides, all the supernatant was removed from the Falcon tubes used in the sorption tests. Soon afterward, an aliquot of 10.0 mL of 10-mM  $\text{CaCl}_2$  solution free from herbicide was added to the tubes with diuron and hexazinone. In the tests with sulfometuron-methyl, an aliquot of 20.0 mL of 10-mM  $\text{CaCl}_2$  solution without herbicide was added. The tubes were vortexed in a vortex mixer for 10 s and immediately afterward, shaken vertically at a temperature of  $25 \pm 2$  °C for 12 h. The supernatant was removed, filtered (0.22  $\mu\text{m}$ ), and analyzed by UHPLC-MS/MS to measure the amount of each herbicide extractable from the soil. All sorption and desorption analyzes were performed in triplicate.

The amount of herbicide that remained in the soil ( $Cs$ ), in  $\text{mg kg}^{-1}$ , was calculated based on the difference between the herbicide concentration in the soil (before desorption) and the concentration in the equilibrium solution. The  $Cs$  and  $Ce$  values obtained in the desorption assay were adjusted by the Freundlich isotherms (Equation 2).

$$(Cs = Kfd Ce^{Nd}) \tag{2}$$

where  $Kfd$  is a soil desorption capacity and  $Nd$  is the linearity.

The hysteresis index ( $H$ ) (Eq. 3) was designed for the reversibility of sorption and desorption (Mamy and Barriuso 2007).

$$H = Nd/Ns \tag{3}$$

where  $Ns$  and  $Nd$  are the Freundlich sorption and desorption coefficients, respectively.

## Half-life

The study was carried out in a greenhouse between February and August 2019. The experimental design used was completely randomized, and all treatments were repeated three times. The treatments were arranged in a split-plot scheme, with the parcels corresponding to the herbicides applied alone and in binary and ternary mixtures and the evaluation times subplots (1, 3, 7, 15, 30, 45, 60, 120, and 180 days after herbicide application).

The experimental units consisted of pots with a capacity of 200 mL, covered with plastic bags, and filled with 300 g of soil. Solutions were prepared to contain diuron, hexazinone, and sulfometuron-methyl isolated and in mixtures according to the recommended commercial dosage for each herbicide. The concentrations used were 0.73, 0.45, and 0.2 mg L<sup>-1</sup> for diuron, hexazinone, and sulfometuron-methyl, respectively, based on field rates. Then, the herbicide solutions (8.1 mL of solution) were sprayed directly onto the soil with a hand pump sprayer. During the conduction of the experiment, the pots were irrigated daily to moisten the soil until close to the field capacity. At each time of collection, the pots' soil was removed, and manually homogenized, and a sample of 0.05 dm<sup>3</sup> was collected to extract the herbicides.

The extraction of the herbicides in the soil samples was carried out in the laboratory by the QuEChERS method, according to Pang et al. (2016), with some modifications. In 50-mL Falcon tubes, 5.0 g of soil, 10.0 mL of acetonitrile, 100 µL of acetic acid, and 2.0 mL of distilled water were added. Soon after, the samples were submitted to an ultrasonic bath for 15 min. Subsequently, 1.0 g of NaCl and 2.0 g of MgSO<sub>4</sub> were added to each Falcon tube. These tubes were shaken on a vortex shaker and centrifuged at 2,260 g for 5 min. The supernatant (1 mL) was removed and placed in 1.5-mL microtubes containing 0.2 g of MgSO<sub>4</sub>. The samples were stirred again for 5 min, and the supernatant was removed and filtered through a 0.22-µm Nylon filter for "vials" for further analysis by UHPLC-MS/MS. Quantification was performed using the standard external method.

The half-life ( $t_{1/2}$ ) of the herbicides was calculated based on the kinetic dissipation models of pseudo-first order (Equation 4) and pseudo-second order (Equation 6).

## Pseudo-first order

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

For linear adjustment, Equation (4) was reorganized to:

$$\ln (C_e - Ct) = -kt + \ln C_e \quad (5)$$

where  $k$  is the pseudo-first order rate constant and can be estimated from the slope after plotting  $\ln (C_e - Ct)$  versus  $t$ , and  $C_e$  is the equilibrium concentration of the herbicides.

## Pseudo-second order

$$\frac{dCt}{dt} = k (C_e - Ct)^2 \quad (6)$$

For linear adjustment, Equation (6) was reorganized to:

$$\frac{t}{Ct} = \frac{t}{C_e} + \frac{1}{kC_e^2} \quad (7)$$

where  $k$  is the pseudo-second order rate constant and can be estimated from the large after plotting  $t/Ct$  versus  $1/C_e^2$ , and  $C_e$  is the equilibrium concentration of the herbicides.

The estimated values of  $t_{1/2}$  were calculated using the linear equation obtained from the regression between  $Ct$  (pseudo-first order model) and  $t/Ct$  (pseudo-second order model) of the experimental data.

## Leaching

The experiments were developed in a greenhouse, using a completely randomized design, with three replications. The treatments were arranged in a factorial scheme (7 × 7), with the first factor representing the isolated herbicides (diuron, hexazinone, and sulfometuron-methyl) and in binary mixtures (diuron + hexazinone; diuron + sulfometuron-methyl; sulfometuron-methyl + hexazinone) and ternary (diuron + hexazinone + sulfometuron-methyl) and the second factor referring to soil depths 0–5 (P1); 5–10 (P2); 10–15 (P3); 15–20 (P4); 20–25 (P5); 25–30 (P6); and 30–35 (P7) cm.

The methodology used for the leaching experiment followed was Guidelines for Testing of Chemicals of OECD, test number 312: Leaching in Soil Columns (OECD 2004). Polyvinyl chloride (PVC) columns with 10 cm in diameter and 35 cm in length were used. The PVC columns were coated internally with a thin layer of paraffin to ensure uniformity in the water flow. To retain the soil and allow drainage at the column base, a 2-cm layer of glass wool was placed. The columns were filled with soil and weighed against maintaining uniformity. Subsequently, the columns were placed in a container with water for 24 h to saturate the soil by capillarity. After saturation, the columns were placed in support for the flow of water for 24 h.

The herbicide treatments were applied at the top of each column (10 mL of solution) according to the highest recommended commercial dose (0.73, 0.45, and 0.2 mg L<sup>-1</sup> for diuron, hexazinone, and sulfometuron-methyl, respectively). After applying the herbicides, the upper end of the column was protected with aluminum foil to prevent herbicides by light. A 60-mm rain sheet, divided into 4 h, was applied to the columns 24 h after herbicide application so that in each hour of rain, the columns received an average volume of 15 mm. The percolated water from the columns was collected at 1-h intervals after the precipitation simulation in each soil

column. The collected water was stored at  $-20\text{ }^{\circ}\text{C}$  for later quantification of the herbicides.

The reading of the herbicides in the leachate samples was for each hour of simulated and collected rain. In 1.5-mL microtubes, 1 mL of the leached water was placed for centrifugation at 2,260 g for 5 min. Soon after, all the supernatant was removed and filtered through Nylon filters ( $0.22\text{ }\mu\text{m}$ ) for “vials” and analyzed by LC-MS/MS. The soil columns were sectioned longitudinally every 5 cm in depth (0–0.05; 0.05–0.10; 0.10–0.15; 0.15–0.20; 0.20–0.25; 0.25–0.30; 0.30–0.35 m) 24 h after the last simulated rain to evaluate the herbicide leaching capacity.

The soil samples from each depth of the columns were dried in the shade, ground, sieved in a 2-mm mesh, and stored at  $-20\text{ }^{\circ}\text{C}$ . The extraction of herbicides in the soil was carried out by the QuEChERS method according to Pang et al. (2016), with some modifications, as previously reported in the topic of half-life. After extraction, the samples were analyzed by LC-MS/MS to quantify the herbicides. For samples that were outside the calibration curve, dilutions were made as necessary for adequacy.

### Chromatographic and mass spectrometry conditions

Quantification of diuron, hexazinone, and sulfometuron-methyl was performed using the ultra-high performance liquid chromatography (UHPLC) coupled to a triple quadrupole mass spectrometer (LCMS-8040, Shimadzu, Tokyo, Japan) (liquid chromatography/spectroscopy of tandem mass, LC-MS/MS). The UHPLC is equipped with a Restek column (Pinnacle DB AQ C18, size  $50 \times 2.1\text{ mm}$ , with  $1.9\text{-}\mu\text{m}$  particles), including two LC-30AD pumps, a DGU-20A<sub>5R</sub> degasser, a SIL-30AC autosampler, a CTO-30AC column oven, and a CBM-20A controller.

To obtain the best resolution during the analysis, the chromatographic system's operating conditions were isocratic elution with the flow of  $0.3\text{ mL min}^{-1}$ , injection volume of  $5\text{ }\mu\text{L}$ , and the temperature of the automatic sampler of  $15\text{ }^{\circ}\text{C}$ . The mobile phase A was constituted of water with 0.1% of formic acid and the mobile phase B by acetonitrile in the proportion of 30 to 70%. The column oven temperature was adjusted to  $40\text{ }^{\circ}\text{C}$ .

The electrospray ionization source (ESI) mass spectrometer was operated in positive ionization mode with parameters for multiple reaction monitoring (MRM) (Supplementary file SIV). The interface voltage was adjusted to 4.5 kV, with the temperature of the desolvation line of  $250\text{ }^{\circ}\text{C}$  and with a nitrogen gas flow of nebulization of  $3\text{ L min}^{-1}$ ; block temperature of  $400\text{ }^{\circ}\text{C}$  and drying nitrogen gas flow with  $15\text{ L min}^{-1}$ ; and collision argon gas at a pressure of 230 kPa. Considering the MRM transitions ( $m/z$ ), the absence of signals from the interfering matrix compounds simultaneously as the retention

of diuron, hexazinone, and sulfometuron-methyl confirmed the method's selectivity (Supplementary file SV).

### Validation of the extraction method

To assess the reliability of the results provided by the herbicide extraction method, the method was validated through the parameters of performance, selectivity, linearity, the limit of detection and quantification, precision, accuracy, and matrix effect (ANVISA 2020). The method's selectivity was evaluated by comparing the chromatograms obtained by the blank extracts and the fortified samples for the concentration of  $10\text{ }\mu\text{g kg}^{-1}$  in the soil matrix. Linearity for the herbicides diuron, hexazinone, and sulfometuron-methyl was evaluated by calibration levels with concentrations of 0.5, 1, 2.5, 5, 10, 25, 50, and  $100\text{ }\mu\text{g L}^{-1}$ , prepared by successive dilutions of the working solution.

The detection limit (LD) and the quantification limit (LQ) were calculated based on the calibration curve parameters. The LD and LQ were 3 and 10 times the value of the ratio of the standard deviation of the linear regression coefficient to the slope of the analytical curve. The repeatability of the method was calculated by the relative standard deviation (RSD) for six consecutive measurements at three concentration levels (1, 10, and  $100\text{ }\mu\text{g L}^{-1}$ ) of solutions containing the diuron, hexazinone, and sulfometuron-methyl standards (Supplementary file SVI).

Calibration curves evaluated matrix effects. Two different calibration curves were prepared, one in solvent and another in matrix at the same concentrations for the points of the calibration curves. Each calibration curve comprised eight concentration points, within the range from 1 to  $100\text{ }\mu\text{g L}^{-1}$ . The matrix effect was evaluated comparing the slopes of the calibration curves in solvent and matrix. The matrix effect values were in the range of  $-20$  to  $+20\%$  (Supplementary file SVI), a condition in which the matrix does not cause suppression or amplification of the signal (Ferrer et al. 2011; Łozowicka et al. 2017; Kaczyński 2017).

### Recovery study

The recovery of diuron, hexazinone, and sulfometuron-methyl in the soil was evaluated at the fortification levels of 1, 10, and  $100\text{ }\mu\text{g kg}^{-1}$ . Samples at each concentration level were performed in triplicate. In 50-mL Falcon tubes, 5.00 g of soil and 1 mL of the incorporation solution were added, and these samples were left to stand in the dark for complete evaporation of the solvent. The non-fortified samples (control) were submitted to the same conditions. After extraction, the fortified and non-fortified samples' solutions were used to quantify the recovery of the herbicides (Supplementary file SVII).

## Statistical analysis

The data were analyzed using RStudio software (version 3.6.1, Team R Core 2019). The sorption ( $K_f$ ) and desorption ( $K_d$ ) coefficients of the isolated herbicides (diuron, hexazinone, and sulfometuron-methyl) and in binary mixtures diuron + hexazinone (D + H), diuron + sulfometuron-methyl (D + S), sulfometuron-methyl + hexazinone (S + H), and ternary diuron + hexazinone + sulfometuron-methyl (D + H + S) were compared regarding the values of the square root of the mean error (RMSE) and determination coefficient ( $R^2$ ). For the leaching tests, the data were compared by the mean confidence interval ( $p \leq 0.05$ ). The half-life values ( $t_{1/2}$ ) were calculated using the pseudo-first order (PPO) and pseudo-second order (PSO) model and compared for the values of RMSE,  $R^2$ , and Akaike test (AIC).

## Results and discussion

### Sorption, desorption, half-life, and leaching of diuron alone and in binary and ternary mixtures

The sorption and desorption data of the diuron isolated in binary and ternary mixtures were described by Freundlich's isotherms (Supplementary file SVIII). The values of the determination coefficient were equivalent to 0.99, and the values of the square root of the mean error (RMSE) varied between 0.07 and 0.17 mg kg<sup>-1</sup> for diuron sorption (Table 1). For desorption isotherms,  $R^2$  values were more significant than 0.90 and with RMSE less than 0.64 mg kg<sup>-1</sup> (Table 1), indicating that the estimated curves could explain the experimental data of sorption and desorption diuron isolated and in mixtures. The linearity values ( $N_s$ ) varied between 0.87 and 0.90 for the sorption of diuron alone and in mixtures, showing a non-linear

relationship between the concentrations of the herbicides in equilibrium and the amount absorbed in the soil. This behavior shows that the sorption isotherms are classified as type L curves (convex), indicating a progressive soil saturation with an increase in the concentration of herbicides (Yavari et al. 2020).

Isolated diuron showed higher  $K_f$ s (10.67 mg l<sup>-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>) compared to mixtures D + H (8.55 mg l<sup>-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>), D + S (7.67 mg l<sup>-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>), and D + H + S (7.57 mg l<sup>-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>) (Table 3). The lowest sorption of diuron was observed in the presence of sulfometuron-methyl, either in the binary or ternary mixture, with a reduction of 29%. The effect of hexazinone on the adsorption of diuron was less, with a reduction of 19%. The lower sorption capacity of diuron due to sulfometuron-methyl or hexazinone suggests a competition between these molecules for similar binding sites in the soil colloids. Similar behavior was observed for some antibiotics when incorporated into different soil classes (Schmidtová et al. 2020). Besides, the greater physicochemical similarity between diuron and sulfometuron-methyl, such as low water solubility and the presence of an aromatic ring (Supplementary file SII), intensified the competition, probably, for the hydrophobic regions of the soil that adsorb organic molecules (Fang et al. 2010). A similar effect has already been observed for other molecules. For example, the lower adsorption of clindamycin occurred due to competitive sorption through hydrophobic partitioning in mixtures with other antibiotics (Schmidtová et al. 2020).

Hydrogen bonds between these herbicides and the soil can also promote competition for similar adsorption sites (El-Nahhal and Hamdona 2017; dos Santos et al. 2019), explaining the lower sorption of diuron mixed with hexazinone and sulfometuron-methyl. Diuron, hexazinone, and sulfometuron-methyl have 2, 4, and 9 hydrogen bond acceptors and donors, respectively (Supplementary file SII). These regions allow hydrogen bonds with carboxylic and

**Table 1** Parameters (mean ± standard error) of the Freundlich isotherms for sorption and desorption and hysteresis index ( $H$ ) of the isolated diuron and its binary and ternary mixtures with the herbicides hexazinone and sulfometuron-methyl in a Dystrophic Red Latosol (LVd)

	Sorption				Desorption				Hysteresis index ( $H$ )		
	$K_f$	$N_s$	$R^2$	RMSE	$K_d$	$N_d$	$R^2$	RMSE	mg kg <sup>-1</sup>		
									0.1	0.5	1.5
Diuron	10.67 (±0.10)	0.87 (±0.01)	0.99	0.07	38.69 (±0.54)	0.98 (±0.02)	0.99	0.14	1.89 ±0.22	2.40 ±0.17	2.79 ±0.18
D + H	8.55 (±0.26)	0.78 (±0.02)	0.99	0.17	11.64 (±0.25)	0.80 (±0.02)	0.99	0.17	0.29 ±0.08	0.34 ±0.02	0.38 ±0.04
D + S	7.67 (±0.12)	0.90 (±0.01)	0.99	0.09	12.44 (±0.19)	0.90 (±0.02)	0.91	0.64	0.67 ±0.09	0.56 ±0.01	0.49 ±0.04
D + H + S	7.57 (±0.13)	0.86 (±0.01)	0.99	0.08	11.68 (±0.14)	0.87 (±0.01)	0.99	0.22	0.52 ±0.04	0.60 ±0.02	0.66 ±0.06

$D + H$  diuron + hexazinone;  $D + S$  diuron + sulfometuron-methyl;  $D + H + S$  diuron + hexazinone + sulfometuron-methyl.  $K_f$ s and  $N_s$ , sorption constant and Freundlich linearity coefficient.  $K_d$  and  $N_d$ , desorption constant and Freundlich linearity coefficient.  $R^2$  coefficient of determination. RMSE square root of the average error

phenolic groups of organic matter (García-Delgado et al. 2020) or hydroxyls of the kaolinite mineral fraction (Olu-Owolabi et al. 2017; Khairy et al. 2018). Consequently, hexazinone and especially sulfometuron-methyl limited the establishment of hydrogen bonds between diuron and soil.

The linearity of desorption for isolated diuron ( $Nd = 0.98$ ) was greater than the binary ( $Nd = 0.8$  and  $0.90$ , hexazinone and sulfometuron-methyl, respectively) and ternary ( $Nd = 0.87$ ) mixtures. This suggests a greater tendency towards desorption of the adsorbed diuron when in higher concentrations and mixed with binary and ternary combinations. The highest desorption coefficient for isolated diuron ( $Kfd = 38.69 \text{ mg l}^{-1/2} \text{ kg}^{-1} \text{ L}^{1/2}$ ) indicated a lower desorption compared to D + H mixtures ( $Kfd = 11.64 \text{ mg l}^{-1/2} \text{ kg}^{-1} \text{ L}^{1/2}$ ), D + S ( $Kfd = 12.44 \text{ mg l}^{-1/2} \text{ kg}^{-1} \text{ L}^{1/2}$ ), and D + H + S ( $Kfd = 11.68 \text{ mg l}^{-1/2} \text{ kg}^{-1} \text{ L}^{1/2}$ ) (Table 1). The values of the  $H$  indexes varied between 1.89 and  $2.79 \text{ mg kg}^{-1}$  for the diuron alone (Table 1). When in binary and ternary mixtures, the  $H$  values were close to 0 (Table 1).

The presence of hexazinone and sulfometuron-methyl increased the desorption of diuron compared to the isolated condition, eliminating the hysteresis effect. Hysteresis occurs for molecules strongly adsorbed to the soil and indicates the formation of residue-bound bonds (Kaur and Kaur 2018). This phenomenon has been observed for diuron alone; however, the hysteresis effect was canceled in combinations with other herbicides (values close to or less than 1). The presence of hexazinone and sulfometuron-methyl in the aqueous phase during desorption probably displaced the weakly adsorbed diuron molecules, intensifying the return of the herbicide to the soil solution. The removal of molecules adsorbed to the soil by allosteric competition has already been identified between pyrene and phenanthrene in soils with contrasting properties (White and Pignatello 1999).

The adequacy of the dissipation kinetic models to the experimental data is demonstrated in Supplementary file SIX, and Table 2 shows the parameters of these models. The kinetic model of pseudo-second order (PSO) fitted better to the data compared to the model of pseudo-first order (PPO), both for diuron alone and in binary mixtures, with higher values of  $R^2$  (0.98, 0.97, and 0.96), lower RMSE values (0.56, 0.74, and 0.98), and lowered AIC (157.54, 174.1, and 191.3) (Table 2). For the ternary mixture, the best fit was observed for the PPO model ( $R^2 = 0.98$ ; RMSE = 0.74; and AIC = 173.8) (Table 2).

The  $C_e$  values for the isolated and mixed diuron varied between 95.10 and 97.91 for the models with the best fit (Table 2). For  $k$  ( $\text{d}^{-1}$ ), the isolated diuron ( $9.67\text{E-}05$ ) showed a lower value than the combinations D + H ( $2.09\text{E-}04$ ), D + S ( $2.35\text{E-}04$ ), and D + H + S ( $1.00\text{E-}02$ ). The  $C_e$  parameter indicates the relative concentration of diuron in the soil in the initial periods. For diuron, the relative concentration was very close between the isolated conditions and mixed with other herbicides. However, the rate of dissipation of the diuron alone was lower than in its binary and ternary combination. This fact increased the half-life for diuron alone ( $t_{1/2} = 101$  days) compared to the mixture D + H (47), D + S (44), and D + H + S (66) (Table 2). Diuron persisted in the LVd during the 180 days of evaluation for all treatments, with values greater than 25% of the initial concentration applied in isolated conditions.

Higher sorption and more negligible desorption of diuron when applied alone reduced the number of molecules available in the soil solution, that is, limited the access of physical, chemical (Villaverde et al. 2017), and biological agents (de Araújo Fiore et al. 2019) capable of degrading the diuron. This limitation directly affected the rate of dissipation of the diuron. Conversely, the lower sorption and greater desorption, provided by the mixture with hexazinone and sulfometuron-methyl,

**Table 2** Parameters of the kinetic dissipation models (pseudo-first order (PPO) and pseudo-second order (PSO)), Akaike test value (AIC), and half-life ( $t_{1/2}$ ) for the isolated and mixed diuron in binary and ternary combinations with the herbicides hexazinone and sulfometuron-methyl in a Dystrophic Red Latosol (LVd)

Combination	Model	Parameters				$R^2$	RMSE	AIC	$t_{1/2}$ (days)
		$C_e$	Std. Error	$K$	Std. Error				
Diuron	PPO	95.55	0.92	6.26E-03	2.45E-04	0.97	0.63	164.57	103
	PSO	97.91	0.91	9.67E-05	3.95E-06	0.98	0.56	157.54*	101
D + H	PPO	92.74	1.71	1.12E-02	7.10E-04	0.95	1.10	197.7	55
	PSO	97.29	1.32	2.09E-04	1.03E-05	0.97	0.74	174.1*	47
D + S	PPO	90.00	2.17	1.18E-02	9.60E-04	0.92	1.37	211.1	50
	PSO	95.10	1.79	2.35E-04	1.58E-05	0.96	0.98	191.3*	40
D + H + S	PPO	96.60	1.14	1.00E-02	4.30E-04	0.98	0.74	173.8*	66
	PSO	99.90	1.97	1.76E-04	1.30E-05	0.96	1.12	198.9	57

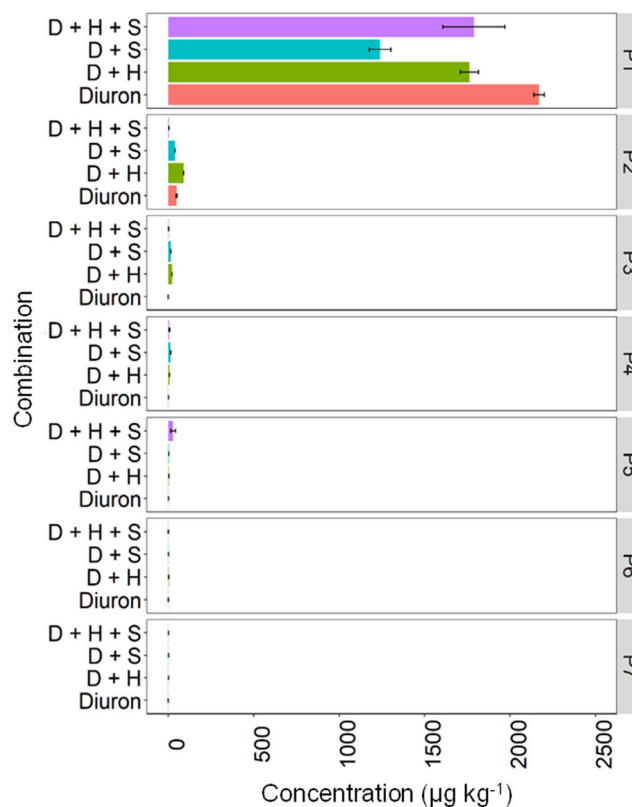
\*Best model according to Akaike test for each solo. Std. Error, standard error of the mean.  $R^2$ , coefficient of determination. RMSE square root of the average error.  $C_e$ , balance concentration of herbicides.  $k$ , dissipation rate of herbicides. D + H diuron + hexazinone; D + S diuron + sulfometuron-methyl; D + H + S diuron + hexazinone + sulfometuron-methyl

increased the bioavailability of the diuron molecules in the aqueous phase of the soil, allowing their transformation into the soil. The immediate response to this lower sorption and more excellent desorption ratio due to mixing was the reduction in diuron  $t_{1/2}$ , and this correlation has already been reported for other pesticides such as imazapyr (Gianelli et al. 2014; Yavari et al. 2019), glyphosate (Zhelezova et al. 2017), tebuconazole (Siek and Paszko 2019), and imazapyr (Yavari et al. 2019). The lowest  $t_{1/2}$  for a herbicide in binary and ternary mixtures was also observed for nicosulfuron (nicosulfuron + mesotrione and nicosulfuron + mesotrione + S-metolachlor) when applied to the soil (Carles et al. 2018).

Despite the relative values for diuron sorption in the binary and ternary mixture (ranging from 7.57 to 8.55), a higher  $t_{1/2}$  was measured for the ternary mixture (66 days) compared to the binary D + H (47) and D + S (44) (Table 2). This behavior seems to contradict the relationship between sorption and persistence. However, dissipation is also linked to the degrading mechanisms available in the soil. The microbial community is primarily responsible for the dissipation of diuron (Villaverde et al. 2017), and often, the imposition of stressors can restrict the presence of degrading microorganisms or the functional degradation pathway (Zhan et al. 2018; Dobrzanski et al. 2018). Possibly, the application of the D + H + S mixture selected a community highly adapted to the presence of these three xenobiotics, however, with limited diuron dissipation capacity. Similar to our results, Swarczewicz and Gregorczyk (2012) reported less dissipation of the herbicide pendimethalin in a ternary mixture (pendimethalin + thiamethoxam + mancozebe) compared to binaries (pendimethalin + thiamethoxam and pendimethalin + mancozeb).

The mixture of the herbicides also directly affected the vertical mobility of the diuron. However, only small differences were observed between treatments, as major majorities of isolated diuron ( $2,253.6 \mu\text{g kg}^{-1}$ ) and mixtures D + H ( $1,781.7 \mu\text{g kg}^{-1}$ ), D + S ( $1,245.1 \mu\text{g kg}^{-1}$ ), and D + H + S ( $1,796.2 \mu\text{g kg}^{-1}$ ) were quantified in P1 (Figure 1). The highest concentration in P1 was observed for the diuron alone, followed by D + H = D + H + S > D + H (Figure 4). The isolated diuron was quantified only up to P2, and this herbicide was no longer detected (Figure 1). The diuron was quantified up to the P4 layer for binary mixtures, with extremely low introductions, equivalent to 12.3 and  $9.5 \mu\text{g kg}^{-1}$  for D + S and D + H, respectively (Figure 1). The highest layer reached by diuron in binary mixtures was P5 but below the limit of quantification. In the ternary mixture, diuron was quantified in P5 at a concentration equivalent to  $32.8 \mu\text{g kg}^{-1}$ ; however, in layers P2, P3, and P4, diuron was detected below the limit of quantification (Figure 1).

The higher yield of diuron, both isolated and mixed, is due to the high sorption values determined for this soil, ranging from 10.67 to  $7.57 \text{ mg l}^{-1/n} \text{ kg}^{-1} \text{ L}^{1/n}$ . Herbicides with high adsorption to the soil tend to remain in systems in the



**Fig. 1** Leaching of isolated and mixed diuron in binary and ternary mixtures with hexazinone and sulfometuron-methyl in a Dystrophic Red Latosol (LVd) after simulating a 60-mm rain applied in 4 h. Bars indicate the confidence interval of the mean ( $p \leq 0.05$ ). D + H, diuron + hexazinone; D + S, diuron + sulfometuron-methyl; D + H + S, diuron + hexazinone + sulfometuron-methyl

superficial layers of the soil (Pérez-Lucas et al. 2020; Fernandes et al. 2021). Other studies have already demonstrated behavior similar to diuron, even in soils with different properties to that used in this study; diuron was detected in large systems only on surfaces between 0 and 10 cm (Mendes et al. 2016; El-Nahhal and Hamdona 2017). However, mixing the herbicides hexazinone and sulfometuron-methyl increased the leaching of the diuron to deeper layers, reaching up to 25 cm. Even if the norms percolated by the soil are small, the binary and ternary mixtures increase the risk of groundwater contamination (Passos et al. 2015). Constant inputs of low pesticide practices can gradually raise levels in water sources, making their potential for use unfeasible (LI et al. 2018). This more significant leaching is caused by the lower sorption of diuron to the LVd soil when applied together with hexazinone or sulfometuron-methyl, as the default in sorption tests.

### Sorption, desorption, half-life, and leaching of hexazinone alone and in binary and ternary mixtures

The curves for sorption and desorption of hexazinone alone and in mixtures in LVd are shown in Supplementary file SX.  $R^2$  values were higher than 0.97, and RMSE values were low,



ranging from 0.01 to 0.1 mg kg<sup>-1</sup> for all treatments in the sorption and desorption tests (Table 3). Like diuron, the sorption isotherms were not linear ( $N_s \leq 1$ ), suggesting an adsorption curve type L; that is, the sorption rate to the soil is reduced due to the increase in the concentration of hexazinone in the soil solution. The  $K_f s$  for hexazinone alone (5.46 mg kg<sup>-1</sup>) was higher than the mixed treatments H + S (0.43 mg kg<sup>-1</sup>), H + D (0.38 mg kg<sup>-1</sup>), and H + D + S (0.36 mg kg<sup>-1</sup>) (Table 3).

Hexazinone showed 2× less affinity to the soil about diuron, a fact quickly confirmed by the difference in sorption between the isolated application of these herbicides. The tendency of hexazinone to remain in the soil’s aqueous phase reflects its high hydrophilicity ( $S = 33,000 \text{ mg L}^{-1}$  and  $Kow = 1,7$ ). Also, the pH of LVd (4.7) is higher than the pKa (2.2) of hexazinone, increasing the number of molecules in the neutral form of this herbicide. This soil pH condition prevents hexazinone from assuming its protonated form, reducing the attraction (Coulomb strength) to the negative charges of organic colloids and minerals in the soil (dos Santos et al. 2019). This lower affinity also explains the more significant effect of the mixture on the sorption of hexazinone compared to diuron.

The  $K_f s$  values for hexazinone were highly reduced due to mixtures with diuron and sulfometuron-methyl, showing a reduction more significant than 92% compared to the isolated condition. For diuron, the maximum reduction was 29%. Once the diuron, a compound with greater affinity for the solid phase of the soil, was added to the mixture, the hexazinone molecules were easily displaced into the soil solution, offering little resistance to bind to the adsorptive sites. This fact also justifies the lesser competition exerted by hexazinone on diuron in the results mentioned above. Studies show that adsorbates’ hydrophilic and hydrophobic nature is crucial in determining adsorption intensity in different materials (Masson et al. 2016; Carneiro et al. 2020; García-Delgado et al. 2020).

The isolated hexazinone showed the highest  $K_f d$  (39.9 mg<sup>1-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>), followed by the mixture H + S (0.66 mg<sup>1-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>), H + D (0.54 mg<sup>1-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>), and H + D + S (0.49 mg<sup>1-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>) (Table 3). Hexazinone showed positive hysteresis in the isolated condition (Table 3). However, mixing with diuron or sulfometuron-methyl eliminated the hysteresis effect, with  $H$  values close to 0 (Table 3).

A lower value for the  $K_f d$  parameter when the hexazinone was mixed with other herbicides indicates greater desorption of the herbicide; that is, the adsorbed hexazinone quickly returns to the aqueous phase the soil. The absence of apparent hysteresis confirmed the lower stability of the connections between hexazinone in the presence of diuron and sulfometuron-methyl. The diuron and sulfometuron-methyl present in the aqueous soil phase during desorption quickly replaced the hexazinone adsorbed to the soil. This mechanism can also be driven by the hydrophilic strength of the solution that attracts hexazinone. This mechanism has already been reported for atrazine, carbendazim, and imidacloprid, where co-adsorbed solutes promoted greater desorption of the compound with less affinity with the soil matrix (Jin et al. 2013).

The fit of the kinetic models to the experimental data is shown in Supplementary file SXI. The PSO kinetic model fitted the data better for all treatments, with higher  $R^2$  values and lowered RMSE and AIC than PPO (Table 4). The rate of dissipation  $k$  (d<sup>-1</sup>) of hexazinone in the presence of diuron (with or without sulfometuron-methyl) was 2 times lower than that of hexazinone alone (Table 4). The lower dissipation rate for hexazinone applied in the mixtures H + D and H + D + S increased  $t_{1/2}$  in 33 and 24 days, respectively, compared to hexazinone alone. The total  $t_{1/2}$  for H + D and H + D + S was 56 and 47 days, respectively (Table 4). In isolated conditions mixed only with sulfometuron-methyl, the  $t_{1/2}$  for hexazinone was 23 and 26 days, respectively (Table 4). At

**Table 3** Parameters (mean ± standard error) of Freundlich isotherms for sorption and desorption, and hysteresis index (H) of isolated hexazinone and binary and ternary mixtures with the herbicides diuron and sulfometuron-methyl in a Dystrophic Red Latosol (LVd)

	Sorption				Desorption				Hysteresis index (H)		
	$K_f s$	$N_s$	$R^2$	RMSE	$K_f d$	$N_d$	$R^2$	RMSE	mg kg <sup>-1</sup>		
									0.1	0.5	1.5
H	5.46 (±0.02)	0.94 (±0.01)	0.99	0.02	39.9 (±1.84)	1.15 (±0.03)	0.99	0.10	4.58 (±1.30)	5.62 (±0.67)	6.51 (±0.12)
H + D	0.38 (±0.01)	0.85 (±0.02)	0.99	0.01	0.54 (±0.02)	0.84 (±0.03)	0.97	0.02	0.49 (±0.09)	0.45 (±0.13)	0.42 (±0.16)
H + S	0.43 (±0.01)	0.86 (±0.02)	0.99	0.01	0.66 (±0.01)	0.85 (±0.02)	0.97	0.03	0.65 (±0.27)	0.60 (±0.16)	0.58 (±0.12)
H + D + S	0.36 (±0.02)	0.80 (±0.03)	0.99	0.01	0.49 (±0.02)	0.79 (±0.03)	0.98	0.03	0.29 (±0.10)	0.31 (±0.10)	0.33 (±0.15)

H Hexazinone; H + D hexazinone + diuron; H + S hexazinone + sulfometuron-methyl; H + D + S hexazinone + diuron + sulfometuron-methyl.  $K_f s$  and  $N_s$ , sorption constant and Freundlich linearity coefficient.  $K_f d$  and  $N_d$ , desorption constant and Freundlich linearity coefficient.  $R^2$ , coefficient of determination.  $RSME$  square root of the mean square error

**Table 4** Parameters of the kinetic dissipation models (pseudo-first order (PPO) and pseudo-second order (PSO)), Akaike test value (AIC), and half-life ( $t_{1/2}$ ) for isolated and mixed hexazinone in binary and ternary combinations with the herbicides diuron and sulfometuron-methyl in a Dystrophic Red Latosol (LVd)

Combination	Model	Parameters				$R^2$	RMSE	AIC	$t_{1/2}$ (days)
		$C_e$	Std. Error	$k$	Std. Error				
Hexazinone	PPO	88.05	2.63	2.00E-02	1.75E-03	0.92	1.55	218.4	28
	PSO	94.42	2.19	4.14E-04	3.18E-05	0.96	1.10	197.8*	23
H + D	PPO	94.28	1.45	1.01E-02	5.42E-04	0.96	0.94	188.7	63
	PSO	98.02	1.10	1.74E-04	7.33E-06	0.98	0.62	164.1*	56
H + S	PPO	91.70	2.45	1.80E-02	1.50E-03	0.94	1.45	214.2	34
	PSO	97.90	1.35	3.79E-04	1.74E-05	0.98	0.68	169.2*	26
H + D + S	PPO	95.80	1.05	1.22E-02	4.48E-04	0.98	0.66	168.5	53
	PSO	99.60	1.22	2.11E-04	9.30E-06	0.99	0.67	167.4*	47

\*Best model according to Akaike test for each solo. Std. Error, standard error of the mean.  $R^2$ , coefficient of determination. RMSE square root of the average error.  $C_e$ , balance concentration of herbicides.  $k$ , dissipation rate of herbicides. *H + D* hexazinone + diuron; *H + S* hexazinone + sulfometuron-methyl; *H + D + S* hexazinone + diuron + sulfometuron-methyl

180 days after application, hexazinone concentrations were less than 10% to the initial concentration applied for all treatments (Supplementary file SXI).

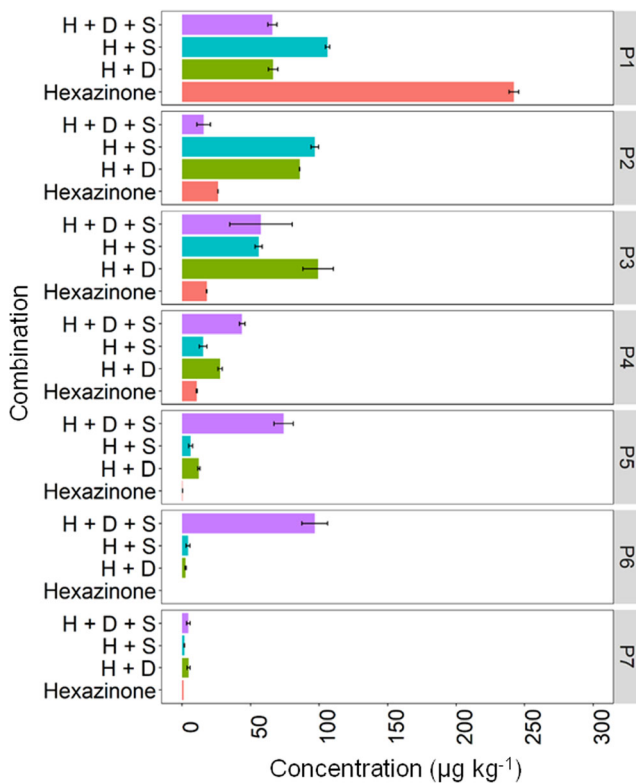
Theoretically, the lower availability of isolated hexazinone due to greater sorption and more negligible desorption should increase its persistence; however, this effect was not observed, resulting in  $t_{1/2}$  similar to the H + S mixture. The existence of favorable conditions for the dissipation of the hexazinone mitigated the differences between the adsorption rates of hexazinone isolated and mixed with sulfometuron-methyl. For example, pH conditions below 5, as observed for LVd soil, favor the hydrolysis of hexazinone (Zhonglin et al. 1998). The effect of soil pH was reported by Lalah et al. (2009). They conferred the rapid dissipation of hexazinone to the lower pH of the soil compared to other soils from Canada, the USA, and Australia. Besides, the presence of a microbial community highly adapted to degrade hexazinone may have accelerated the dissipation of the herbicide in the soil before its adsorption to the soil. Indeed, the hexazinone  $t_{1/2}$  in LVd for isolated applications was lower with other soils already studied in the literature (Michael et al. 1999; Guimarães et al. 2018).

When mixed with diuron (without or with sulfometuron-methyl) with its isolated application, the lower sorption of hexazinone did not allow a faster dissipation of hexazinone. Contrary to diuron, the combination of H + D and H + D + S increased the  $t_{1/2}$  of hexazinone. This behavior shows that the mere presence of the herbicide in the solution is not a sufficient condition for it to be dissipated. Studies have already shown that the mixture of pesticides can synergize (Xiaoqiang et al. 2008) or antagonistic (Pino and Peñuela 2011) effect dissipation of pollutants. The mixture of hexazinone + diuron possibly changed the composition or functional metabolism of soil microorganisms, impairing the

dissipation of hexazinone. Another possibility may be associated with the preference of the soil microbiota when using diuron as a source of carbon and nitrogen instead of hexazinone. A similar example was observed for the herbicide linuron, where the mixture with thiamethoxam and mancozeb reduced the dissipation of the herbicide, extending its half-life (Swarcewicz and Gregorczyk 2013).

In evaluating the leaching potential, the highest hexazinone concentration in P1 (242.6  $\mu\text{g kg}^{-1}$ ) was observed (Figure 2). Lower concentrations of hexazinone alone were quantified up to P4. The concentration of hexazinone in the binary Mixture (H + S) was 103.4  $\mu\text{g kg}^{-1}$  in P1; however, higher concentrations than the isolated condition were quantified up to P5 (Figure 2). In the H + D mixture, the concentration in the upper layer was lower than for hexazinone alone and H + S; however, a high concentration was observed in P3 (99.8  $\mu\text{g kg}^{-1}$ ). Hexazinone in the H + D + S mixture leached up to P7, with a more significant amount recovered in P6 (98.3  $\mu\text{g kg}^{-1}$ ) (Figure 2). Hexazinone alone and in mixtures was not detected in the soil leachate; however, it was detected up to the P7 layer for all combinations of mixtures (Figure 2).

The deeper leaching of hexazinone in the mixtures compared to the isolated application is directly related to the lower sorption of this herbicide in the presence of other herbicides. Compared to diuron, hexazinone's lower sorption and major solubility make the first compound much more prone to leach to deeper layers and contaminate groundwater. Consequently, factors that reduce sorption and increase desorption, such as mixtures between herbicides, are potentially more severe for hydrophilic pesticides. Dos Reis et al. (2017) also detected more significant leaching of hexazinone in a mixture with diuron and sulfometuron-methyl; however, our work allowed us to confirm the participation of the lower sorption as responsible for this behavior.



**Fig. 2** Leaching of isolated hexazinone and binary and ternary mixtures with the herbicides diuron and sulfometuron-methyl in a Dystrorphic Red Latosol (LVd) after simulating a 60-mm rain applied in 4 h. Bars indicate the confidence interval of the mean ( $p \leq 0.05$ ). H + D, hexazinone + diuron; H + S, hexazinone + sulfometuron-methyl; H + D + S, hexazinone + diuron + sulfometuron-methyl

**Sorption, desorption, half-life, and leaching of sulfometuron-methyl isolated and in binary and ternary mixtures**

The sorption and desorption isotherms of sulfometuron-methyl isolated and in mixtures in LVd are shown in Supplementary file SXII. The performance indicators of the adjustment were satisfactory for all treatments, with  $R^2$  values greater than 0.9 and low RMSE values (Table 5). The sorption isotherms obtained for all herbicide combinations were of the “L” type ( $N_s \leq 0.97$ ), similar to the diuron and hexazinone herbicides, with implications similar to the behavior of the highest concentrations.

The  $K_f$ s for sulfometuron-methyl was lower in the mixtures compared to isolate herbicide (Table 5). More significant reductions in  $K_f$ s occurred for mixtures containing diuron (66 and 65% in S + D and S + D + H, respectively) compared to the mixture with sulfometuron-methyl (56%) (Table 5). The molecules of sulfometuron-methyl and diuron compete intensely for the same adsorptive sites in the soil, resulting in less sorption of both herbicides compared to mixtures with hexazinone. This fact reinforces the theory that competitive adsorption is associated with a greater physicochemical

similarity between molecules (Li et al. 2017; Kraus et al. 2018; Conde-Cid et al. 2019; Maitlo et al. 2019).

Sulfometuron-methyl isolated and binary mixtures showed similar  $Kfd$  values, ranging from 0.29 to 0.37  $mg\ kg^{-1}$  (Table 5). Also, both the condition alone and mixed with other herbicides resulted in negative  $H$  values (Table 5). The main difference between sulfometuron-methyl to diuron and hexazinone was the similar desorption capacity for isolated and mixed conditions. The non-interference of the mixture on the desorption of sulfometuron-methyl may be correlated to the negative hysteresis observed for this herbicide, even for conditions of isolated application. Negative hysteresis suggests a greater tendency for the herbicide to return to the soil solution after its adsorption (Carneiro et al. 2020); Sulfometuron-methyl does not have high water solubility; however, the most significant polar surface of this herbicide (Supplementary file SIII) can be attracted by cations and anions dissolved in the solution, resulting in its easy desorption. The low  $Kow$  value may also favor the return of sulfometuron-methyl molecules to the aqueous phase of the soil. Singh and Singh (2012) reported that the herbicide sulfosulfuron, with the lowest  $Kow$  (0.73), showed greater desorption than metsulfuron-methyl (2.2) in five soils in India.

At 180 days after applying the herbicides, the presence of sulfometuron-methyl in the LVd was not detected, regardless of the evaluated treatment (Supplementary file SXIII). The dissipation of sulfometuron-methyl isolated and in the mixtures adjusted to the PSO kinetic model (Table 6 and Supplementary file SXIII). The rate of dissipation rate  $k$  ( $d^{-1}$ ) for mixtures S + H, S + D, and S + D + H was lower than sulfometuron-methyl alone (Table 6). The lower dissipation rate of sulfometuron-methyl in the mixtures resulted in higher  $t_{1/2}$ . However, the difference for  $t_{1/2}$  between treatments was not significant (Table 6).

All the mixtures caused a higher  $t_{1/2}$  of sulfometuron-methyl than the isolated application, contradicting the theory that establishes a shorter half-life for conditions of lower sorption. However, the desorption of sulfometuron-methyl is the most significant influence on the availability of this herbicide in the aqueous soil phase. This herbicide quickly returns to the soil solution, regardless of isolated or mixed applications, allowing the dissipation of molecules in their metabolites. This fact is evident since the differences for  $t_{1/2}$  of sulfometuron-methyl are small between the isolated and mixed application of this herbicide, making available the molecules of the sorption data evaluated in that same soil. Therefore, the desorption of herbicides must be considered in models that seek to determine the potential for contamination of herbicides. However, most models currently applied, such as the GUS (*Groundwater Ubiquity Score Index*) (Gustafson 1989) and AFR (*Attenuation Factor Approach*) (Dusek et al. 2011), do not take this process into account.

**Table 5** Parameters (mean ± standard error) of Freundlich isotherms for sorption and desorption, and hysteresis index (H) for isolated sulfometuron-methyl and in binary and ternary mixtures with the herbicides diuron and hexazinone in a Dystrophic Red Latosol (LVd)

	Sorption				Desorption				Hysteresis index (H)		
	<i>K<sub>fs</sub></i>	<i>N<sub>s</sub></i>	<i>R</i> <sup>2</sup>	RMSE	<i>K<sub>fd</sub></i>	<i>N<sub>d</sub></i>	<i>R</i> <sup>2</sup>	RMSE	mg kg <sup>-1</sup>		
									0.1	0.5	1.5
S	2.66 (±0.03)	0.72 (±0.01)	0.99	0.02	0.29 (±0.01)	0.38 (±0.04)	0.97	0.01	-0.77 (±0.01)	-0.84 (±0.01)	-0.89 (±0.01)
S + D	0.90 (±0.02)	0.91 (±0.03)	0.99	0.02	0.36 (±0.01)	0.91 (±0.07)	0.93	0.01	-0.16 (±0.12)	-0.17 (±0.10)	-0.18 (±0.07)
S + H	1.16 (±0.03)	0.87 (±0.03)	0.99	0.02	0.37 (±0.01)	0.88 (±0.05)	0.94	0.03	-0.17 (±0.10)	-0.18 (±0.07)	-0.20 (±0.08)
S + D + H	0.91 (±0.02)	0.97 (±0.03)	0.99	0.02	0.32 (±0.01)	0.72 (±0.05)	0.94	0.02	-0.20 (±0.21)	-0.12 (±0.20)	-0.04 (±0.22)

*S* sulfometuron-methyl; *S + D* sulfometuron-methyl + diuron; *S + H* sulfometuron-methyl + hexazinone; *S + D + H* sulfometuron-methyl + diuron + hexazinone. *K<sub>fs</sub>* and *N<sub>s</sub>*, sorption constant and Freundlich linearity coefficient. *K<sub>fd</sub>* and *N<sub>d</sub>*, desorption constant and Freundlich linearity coefficient. *R*<sup>2</sup>, coefficient of determination. *RSME* square root of the average error

The binary and ternary mixtures affected the leaching of sulfometuron-methyl compared to the isolated application (Figure 3). The highest concentrations of sulfometuron-methyl isolated and in the mixtures were observed in P1. Sulfometuron-methyl isolated showed the highest concentration (12.3 μg kg<sup>-1</sup>), followed by the mixture S + D (7.5 μg kg<sup>-1</sup>), S + H (4.97 μg kg<sup>-1</sup>), and S + D + H (4.2 μg kg<sup>-1</sup>) (Figure 3). In P2 and P3, the highest concentrations of sulfometuron-methyl were found for S + D (4.7 μg kg<sup>-1</sup> and 3.8 μg kg<sup>-1</sup>) compared to the isolated application and other mixtures. Sulfometuron-methyl isolated was quantified in low concentrations up to P5. The S + H mixture was quantified up to P6; however, in the deepest layers of the soil, the detected concentration was below the limit of quantification (Figure 3). In the ternary mixture,

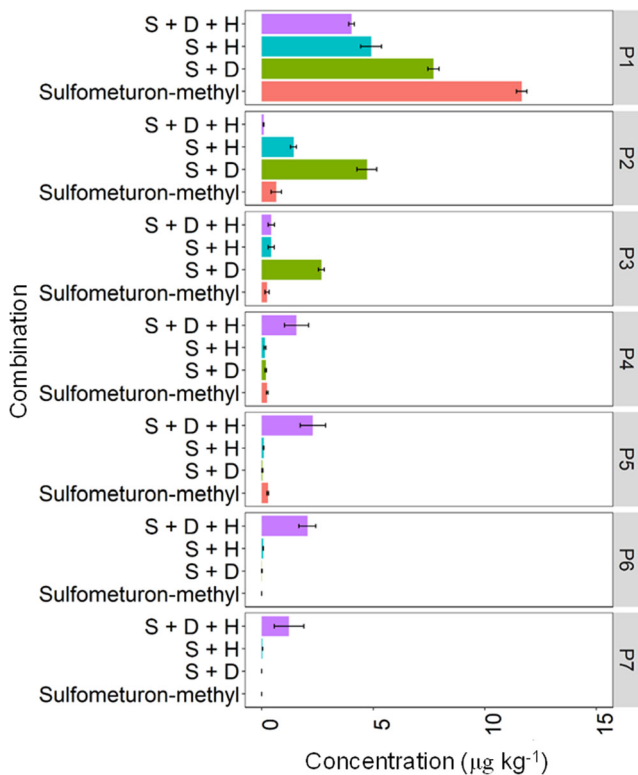
sulfometuron-methyl showed greater leaching than all treatments, reaching high concentrations (1.2 μg kg<sup>-1</sup>) up to the P7 layer (Figure 3). Despite the high concentrations in the P7 layer for the ternary mixture, the presence of this herbicide was not detected in the soil leachate from all evaluated treatments.

The higher concentration of sulfometuron-methyl isolated found in P1 when compared to the mixtures is due to its greater sorption to the soil. However, this herbicide leached up to the P5 layer, probably because this herbicide showed high desorption even for isolated conditions. Even if the lower sorption did not affect the dissipation of sulfometuron in mixed treatments, mobility was affected, allowing the leaching of this herbicide to the last evaluated layer when in the ternary mixture.

**Table 6** Parameters of the dissipation kinetic models (pseudo-first order (PPO) and pseudo-second order (PSO)), Akaike test value (AIC), and half-life (*t*<sub>1/2</sub>) for isolated sulfometuron-methyl and in binary and ternary mixtures with the herbicides diuron and hexazinone in a Dystrophic Red Latosol (LVd)

Combination	Model	Parameters				<i>R</i> <sup>2</sup>	RMSE	AIC	<i>t</i> <sub>1/2</sub> (days)
		<i>C<sub>e</sub></i>	Std. Error	<i>k</i>	Std. Error				
S	PPO	92.43	2.64	3.30E-02	2.80E-03	0.95	1.42	213.4	19
	PSO	100.5	1.74	7.45E-04	4.02E-05	0.98	0.77	176.5*	13
S + D	PPO	97.1	1.25	2.46E-02	9.50E-04	0.99	0.71	181.3	27
	PSO	102.3	1.85	4.67E-04	2.73E-05	0.99	0.89	175.3*	22
S + H	PPO	93.3	2.18	2.80E-02	1.90E-03	0.97	1.21	203.3	22
	PSO	100.2	1.52	6.10E-04	2.94E-05	0.99	0.70	170.9*	16
S + D + H	PPO	97.5	1.54	3.10E-02	1.40E-03	0.99	0.84	181.8	22
	PSO	103.6	1.62	6.06E-04	2.99E-05	0.99	0.74	174.2*	17

\*Best model according to Akaike test for each solo. Std. Error, standard error of the mean. *R*<sup>2</sup>, coefficient of determination. *RMSE* square root of the mean error. *C<sub>e</sub>*, balance concentration of herbicides. *k*, dissipation rate of herbicides. *S* sulfometuron-methyl; *S + D* sulfometuron-methyl + diuron; *S + H* sulfometuron-methyl + hexazinone; *S + D + H* sulfometuron-methyl + diuron + hexazinone



**Fig. 3** Leaching of sulfometuron-methyl isolated and mixed in binary and ternary mixtures with the herbicides diuron and hexazinone in a Dystrophic Red Latosol (LVd) after simulating a 60-mm rain applied in 4 h. Bars indicate the confidence interval of the mean ( $p \leq 0.05$ ). S + D, sulfometuron-methyl + diuron; S + H, sulfometuron-methyl + hexazinone; S + D + H, sulfometuron-methyl + diuron + hexazinone

**Potential risk of contamination of diuron, hexazinone, and sulfometuron-methyl applied alone and in mixtures**

The results of this work bring new insights into the behavior of herbicides in the soil, considering the application mixed with

other molecules. The vast majority of previous studies addressed the isolated condition of herbicides to determine their sorption, desorption, persistence, and leaching in different soils. However, our results reveal that some extrapolations may not represent the real scenario about the behavior of herbicides in the soil. First, the behavior of the herbicides diuron, hexazinone, and sulfometuron-methyl, commonly applied in binary and ternary formulations in sugarcane crops, cannot be based only on isolated studies to estimate the potential for contamination. The lower sorption of these herbicides in mixtures suggests that isolated studies may underestimate the risk of leaching these herbicides.

The risk of contamination for diverse applications of these herbicides is even more remarkable because the half-life and persistence of these molecules do not follow the standard theoretically addressed so far. Our results showed that the lower sorption of hexazinone and sulfometuron-methyl due to binary and ternary mixtures did not reflect a shorter half-life. Studies report a shorter half-life of herbicides due to more negligible sorption to soils (Su et al. 2019; Wu et al. 2019; Chin-Pampillo et al. 2021); this condition is not observed for mixing the herbicides diuron, hexazinone, and sulfometuron-methyl. This fact may increase the carryover risk on crops planted in succession and groundwater contamination.

The complexity of the interactions between soil and the herbicide molecules applied in mixtures is most evident when we apply our results to prediction models for the risk of leaching. The GUS index, commonly used for herbicide studies, indicated a low risk of contamination for diuron, both in isolated and mixed applications. This classification corroborated our leaching results. However, for the applications of hexazinone and sulfometuron-methyl alone, the GUS model indicated low risk, contradicting the results found here for the leaching of these herbicides. These herbicides were detected up to 20 to 35 cm in the leaching tests with only a simulated

**Table 7** Risk of contamination of the herbicides diuron, hexazinone, and sulfometuron-methyl based on the GUS index and the new index proposed for studies of herbicides in the soil

Treatment	$Kfs$	$Kfd$	$K_{foc}$	$t_{1/2}$	Solubility (mg L <sup>-1</sup> )	GUS	Leaching risk	New index	New rating
D	10.7	38.7	1994.8	101	34.7	1.4	Low	2.2	Positive values
D + H	8.6	11.6	1598.5	47	34.7	1.3	Low	0.8	(lower risk)
D + S	7.7	12.4	1434.0	40	34.7	1.4	Low	0.7	
D + H + S	7.6	11.7	1415.3	66	34.7	1.5	Low	0.7	
H	5.5	39.9	1020.8	23	33000.0	1.3*	Low *	-3.0	Negative values
H + D	0.4	0.5	71.0	56	33000.0	3.8	High	-9.1	(highest risk)
H + S	0.4	0.7	80.4	26	33000.0	3.0	High	-7.2	
H + D + S	0.4	0.5	67.3	47	33000.0	3.6	High	-8.8	
S	2.7	0.3	497.3	13	244.0	1.5*	Low *	-2.8	
S + D	0.9	0.4	168.3	22	244.0	2.4	Moderate	-3.9	
S + H	1.2	0.4	216.9	16	244.0	2.0	Moderate	-3.3	
S + D + H	0.9	0.3	170.1	17	244.0	2.2	Moderate	-3.6	

60-mm rain. For example, the most studied herbicide, hexazinone, is frequently detected in groundwater close to agricultural areas (Di Bernardo et al. 2011; Santos et al. 2015). The GUS index disregards the desorption and solubility of the molecules makes the model prone to error. Therefore, considering desorption and solubility in the estimation model can allow a safer assessment of the risk of leaching. We propose the following considerations to the GUS model as a new Equation (8):

$$\text{New index} = \frac{Kfs * Kfd}{S} * \log_{10} \left( t_{1/2} \right)$$

where Kfs and Kfd are the desorption sorption coefficients for the Freundlich isotherm, S is the solubility of the molecule in  $\text{mg L}^{-1}$ , and  $t_{1/2}$  is the half-life in days (Table 7).

Our equation allows, in a simple way, the desorption and solubility values to the GUS model. When defining new thresholds for the herbicides diuron, hexazinone, and sulfometuron-methyl, the recommendation of these herbicides becomes more rigorous. This greater control for applications in conditions more prone to leaching of these herbicides can minimize environmental contamination. We hope that new studies will consider this model to estimate the leaching risk for validation and compare it with other models in different scenarios.

## Conclusions

Diuron, hexazinone, and sulfometuron-methyl in binary and ternary mixtures have less sorption capacity and greater desorption when compared to these herbicides isolated in Dystrophic Red Latosol. Dissipation of isolated diuron is slower compared to mixtures. For hexazinone and sulfometuron-methyl, the dissipation rate is lower in mixtures, especially in mixtures with diuron presence. The binary and ternary mixtures of diuron, hexazinone, and sulfometuron-methyl promote more significant leaching than the application of these isolated herbicides. The new index proposed to estimate the leaching potential, considering the desorption and solubility of the herbicides, allows a more rigorous assessment of the leaching risk.

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**Author contribution** TSS and MFS: interpretation, writing original draft, review and editing. RCAM: methodology. DVS: conceptualization, methodology, and review. PSFC, HAL, and CCS: methodology and analysis. CMMS and VM: suggestions in methodology framework and review.

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## Declarations

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

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