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Can soil type interfere in sorption-desorption, mobility, leaching, degradation, and microbial activity of the ^{14}C-tebuthiuron herbicide?

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ABSTRACT

Understanding the behavior in soil of herbicides applied PRE-emergence, such as tebuthiuron, is essential for more accurate weed management and less environmental impact. Thus, the objective of this research was to evaluate the effect of the physicochemical attributes of soils in ^{14}C-tebuthiuron behavior. All studies were carried out by radiometric technique. The K_f and K_d values of ^{14}C-tebuthiuron sorption were 30% and 35% higher in clay soil (1.15 $mg^{(1-1/n)}$ $L^{1/n}$ Kg^{-1} and 1.32 L Kg^{-1}) compared to loamy sand soil (0.80 $mg^{(1\text{-}1/n)}$ $L^{1/n}$ Kg^{-1} and 0.85 L Kg^{-1}, respectively). The desorbed amount was ~19% higher in loamy sand soil compared to loamy sand soil, and this process was influenced by OC and clay content. The ^{14}C-tebuthiuron leaching in clay soil was up to 10 cm depth, while in loamy sand soil was higher, up to 25 cm, and this difference can be explained by high mobility and low sorption of herbicide in loamy sand soil. ^{14}C-tebuthiuron had a long persistence in both soils (DT90 of ~385 and 334 d in loamy sand and clay soil, respectively). Although, the microbiological activity in soils differed little in the presence and absence of herbicide. Soil type interfered in ^{14}C-tebuthiuron behavior, and then the application recommendation of this herbicide as a function of the physicochemical attributes of the soil is an alternative to increase efficiency in weed control and reduce the risk of environmental contamination.

1. Introduction

Weeds are controlled by herbicides with several mechanisms of action. Among the mechanisms of action, photosystem II (PSII) inhibitors, such as tebuthiuron 1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea), which is recommended in the PRE-emergence of weeds in the sugarcane crop (Shaner, 2014), being widely used in Brazil (Tonièto and Regitano, 2014, Pereira et al., 2017).

Tebuthiuron is a systemic herbicide, absorbed by the roots, belonging to the urea group. This herbicide has a broad spectrum of action against herbaceous, woody, annual and perennial weeds (Borrel et al., 2011; Wang et al., 2019). However, tebuthiuron shows high persistence in soil and water solubility (S_w) (2500 mg L^{-1} at 20 °C), with groundwater contamination potential (Moraes et al., 2012; Tonièto et al., 2016; Qian et al., 2017).

When tebuthiuron is applied in PRE to control weeds, the final fate of the herbicide is the soil matrix (Mendes et al., 2021a). In soil, part of the herbicide may be sorbed or bioavailable in the solution to control weeds and be degraded by microorganisms. However, very soluble herbicides with high mobility, such as tebuthiuron, shows potential to be leached to deeper layers of soil (Pereira et al. 2015). Therefore, it is essential to know the interactions of the molecule with the physicochemical attributes of the soil and environmental conditions (Guimarães et al., 2018a, b).

Tebuthiuron is weakly sorbed in soil, with sorption coefficient (K_d) values of 0.1 and 0.7 mL g^{-1} in sandy and clay soil, respectively (Matallo et al., 2005). The sorption of this herbicide is 16% higher in clayey soils compared to sandy soils (Tonièto et al., 2016). In addition, the sorption of tebuthiuron is higher in soils with higher organic carbon (OC) content (Teixeira et al., 2018; Pierri et al., 2022). Therefore, the variation of herbicide behavior in soil as a function of this attribute may influence the risk of environmental contamination. A possible fate of the herbicides, with interference from soil attributes is the capacity of groundwater and nearby rivers contamination, due to the high leach-

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Table 1
Physicochemical attributes of soils used in the studies.

Attributes	Soil classification	
	Oxisol Typic Hapludox	Typic Quartzipsaments
Texture	Clay	Loamy sand
Sand (%)	15.0	89.7
Clay (%)	63.6	9.5
Silt (%)	21.4	0.8
pH ($CaCl_2$)	5.1	5.2
P (mg dm^{-3})	31	16
K ($mmol_c$ dm^{-3})	10.2	0.6
Ca ($mmol_c$ dm^{-3})	28	15
Mg ($mmol_c$ dm^{-3})	9	4
Al ($mmol_c$ dm^{-3})	2	0
H+Al ($mmol_c$ dm^{-3})	38	22
BS ($mmol_c$ dm^{-3})	47	20
CEC ($mmol_c$ dm^{-3})	85	42
V (%)	55	47
OC (%)	1.45	0.12

P: phosphorous, K: potassium, Ca: calcium, Mg: magnesium, Al: aluminum. H+Al: potential acidity, BS: base sum, CEC, cationic exchange capacity, V: saturation base, OC: organic carbon.
Source: Laboratório Agrotécnico Piracicaba Ltda., Piracicaba, SP, Brazil.

ing of tebuthiuron (Matallo et al., 2005, Cerdeira et al., 2007). The soil physicochemical attributes also directly interfere the bioavailability of tebuthiuron in the soil solution and weed control.

A study that evaluated the leaching potential of the herbicide in sandy soils, with lower clay and OC contents, showed that tebuthiuron leached up to 60 cm depth in soil columns, indicating a greater potential risk of groundwater contamination (Souza et al., 2001). Another problem is that tebuthiuron has a high degree of resistance to chemical and biological degradation processes with significant and prolonged risk to freshwater native plant species, particularly phytoplankton and floating macrophytes (Dam et al., 2004).

The sorption also affects the herbicide degradation process, i.e., when the herbicide is sorbed in the soil, it become unavailable for microbial degradation. The complexity of the molecule influences the degradation by microorganisms, characterizing the persistence of the herbicide in soil, being measured by degradation time of half-life (DT50) of the molecule (Mendes et al., 2021a). The DT50 value of tebuthiuron is high (400 d), and the residual effect in soil is ~12–14 months, with a high potential to cause injury to sensitive crops in succession to sugarcane (Blanco and Oliveira, 1987).

Therefore, understanding the behavior of the herbicide in the environment, the processes of retention, transport and degradation is essential to increase the efficiency of weed control, reduce costs, and minimize problems caused by tebuthiuron residues. The sorption-desorption process, mobility, leaching, degradation and microbial activity of this herbicide integrated in different soils cultivated with sugarcane has not been studied yet. Thus, the objective of this research was to evaluate the effect of the physicochemical attributes of soils cultivated with sugarcane in ^{14}C-tebuthiuron behavior under laboratory conditions.

2. Material and methods

2.1. Soil collection and analysis

The two types of soil used in the studies were collected from sugarcane fields in the region of Piracicaba, SP, Brazil. Soil was collected in 0-0.10 m deep layer, after cleaning the litter layer in the top soil. The soil samples were air dried and sieved on 2.0 mm sieves and stored at room temperature in plastic bags.

The analyses of the physicochemical attributes of the soils are presented in Table 1. Soils were classified as Oxisol Typic Hapludox (*Latossolo Vermelho eutrófico*), clay texture (22°43′38″S and 47°34′25″W) and Typic Quartzipsaments (*Neossolo Quartzarênico órtico*) (Empresa Brasileira de Pesquisa Agropecuária – EMBRAPA, 2018), loamy sand texture (22°14′36 ″S and 47°43′10 ″W).

2.2. Herbicide

Analytical standards (99.5% of chemical purity) and radiolabeled forms (^{14}C-UL) of tebuthiuron (specific activity = 3.01 MBq mg^{-1}, radiochemical purity > 98%) were adopted and applied in all studies. The solvent used was methanol.

2.3. Sorption–desorption studies

Sorption-desorption studies were done under batch equilibrium conditions of the herbicide in the aqueous phase and sorbed to the soil, according to guidelines “Adsorption – Desorption Using a Batch Equilibrium Method” of the Organization for Economic Cooperation and Development-106 (OECD - Organization for economic co-operation and development, 2000a). Each Teflon tube (in duplicate) with 50-mL screw cap received 10 g of soil and 10 mL of an aqueous solution containing radiolabeled herbicide (5 concentration: 1/4, 1/2, 1, 2, and 4-fold the recommended dose of 1200 g ha^{-1}), resulting in a 1:1 ratio (w v^{-1}), and were shaken on a horizontal pendulum table (Technical Scientific Equipment, model I-240, Piracicaba, SP, Brazil) at 38 *g*, 20 °C for 24 h, in the dark.

After equilibrium for 24 h, the tubes were centrifuged at 755 *g* for 15 min (Hitachi CF16RXII, Hitachi Koki Co., Ltd., Indaiatuba, SP, Brazil). A 1 μL-aliquot of the supernatant of each tube was transferred in duplicate to scintillation vials containing 10 mL of scintillation solution and analyzed by Liquid Scintillation Counting (LSC) (Tri-Carb 2910 TR LSA counter, PerkinElmer, Waltham, MA, USA) to determine the concentrations of ^{14}C-tebuthiuron. The concentration of herbicide sorbed in soil was determined by calculating the difference between the initial concentration applied and the final concentration in the supernatant after equilibration (24 h).

Immediately after the sorption studies, the desorption studies were carried out on the same Teflon tubes as the sorption analyses. First, $CaCl_2$ old solution was removed and 5 mL of 0.01 mol L^{-1} $CaCl_2$ solution was added, and the tubes were shaken for 24 h under the same conditions of the sorption experiment until equilibrium was reached. After re-centrifugation (755 *g* for 15 min), 1 mL aliquots of the supernatants were transferred in duplicate to scintillation vials containing 10 mL of the scintillation solution, for LSC analysis. The amount of herbicide desorbed was calculated from the difference between the concentrations of the solution before and after desorption.

The sorption-desorption coefficients were calculated according to the equation of linear model: K_d=Cs/Ce, where Cs is the concentration of sorbed herbicide in soil (mg g^{-1}), and Ce is the herbicide concentration in the liquid phase at equilibrium (mg mL^{-1}). To normalize the sorption coefficient for a more real situation, the OC content was considered in calculating the K_{oc}, using the following equation: K_{oc}=(K_d/%OC) × 100%.

The Freundlich model, in the linearized form, and its coefficient were derived from the equation: K_f=Cs/$Ce^{1/n}$, where n (dimensionless value) can range from 0 to 1, depending on the heterogeneity of the sorption sites. The same coefficient was also standardized, considering the OC content of the soil (K_{foc}). The index of hysteresis (H) was calculated by the equation, $H = 1/n_{(desorption)}/1/n_{(sorption)}$.

2.4. Mobility study

The mobility study of the herbicide was developed according to the method described in the EPA standard OPPTS 835.1210: "Soil Thin Layer Chromatography" (EPA- Environmental Protection Agency, 1998). The method is based on the ability to drag a substance radiolabeled with ^{14}C in a thin layer of soil, eluted in water, following the principles of the soil Thin Layer Chromatography (soil TLC) technique, with soil as the stationary phase of the system.

For the preparation of the soil plates, a semi-fluid paste of each of the studied soils was prepared by adding about 100 g of soil in a 0.2-L beaker plus deionized water, which was spread in a homogeneous layer of 5.10^{-4} to $7.5\text{–}10^{-4}$ m on glass plates measuring $0.15 \times 0.9 \times 1.5\text{–}10^{-3}$ m. The soil sample plates were prepared with an acrylic plate holder ($0.3 \times 0.12 \times 0.28$ m) suitable for plate preparation. After air-drying, a straight line was drawn 0.12 m from the base in order to separate the top soil layer, thus avoiding the continuity of elution by capillarity after the water reached the height of 0.12 m.

A 10-μL of the working solution was applied using a microsyringe at 0.02 m from the base of the soil TLC at a single point, with two points applied for each plate; using three repetitions (three plates) for each soil sample type. The working solution contained 70.72 Bq μL^{-1} of ^{14}C-tebuthiuron.

An acrylic support ($0.013 \times 0.11 \times 0.22$ m) was used for the application of the radiolabeled herbicide, positioning a plastic blade properly cut in the application position (0.2 m from the base) above the support in order to apply the solution in the correct position.

Then the TLC soils were placed in the vertical position inside a chromatographic tank containing 0.1-L of deionized water, removing the plates when the water reached the elution limit line (0.1 m above the application point).

After dried in air (23 ± 5 °C), the soils of the two soil sample classes were read in the radio-scanner (PerkinElmer® Storage Phosphor System, model Cyclone Plus, Shelton, WA, USA), which provides the retention factor (R_f) being the ratio between the distance traveled by the product in the soil TLC and the solvent (H_2O) displacement front.

The Rf were calculated by the equipment through the radiograms presented by the plates using the following equation: $R_f = D_p / D_a$, where: D_p means distance traveled by the herbicide and D_a distance traveled by the water.

2.5. Leaching study

The leaching study of tebuthiuron herbicide followed the "Leaching in soil Columns" methodology of the OECD – Organisation for economic co-operation and development (2002a).

Glass columns of 0.50 m packed with the two soil types selected for the study (clay and loamy sand soil) were used for the study. Three columns were prepared per soil (three repetitions), for a total of 6 columns for the entire study.

The soil columns were prepared by weighing the amount of soil required and then closing the tip of the columns with glass wool, filling the conical part with quartz sand, washed and dried in an oven at 100 °C and packing the column until the height of 0.30 m, placing small portions of air-dried soil at the bottom of the column, vibrating the set to accommodate the soil sample, thus avoiding the formation of air bubbles.

The soils conditioned in the columns were weighed to control the reproducibility of the packing process of the columns, thus 675.2 g were used for the clay soil and 914.18 g for the loamy sand soil.

The soil columns were placed inside a 2-L beaker and slowly moistened with an upward flow (mobility of the solution up the columns) of a 0.01 mol L^{-1} $CaCl_2$ solution so that the solution level was not 0.10 m higher than the wetting front of the soil sample. The soil sample was flooded for approximately 30 min. After the flooding process of the columns, when the $CaCl_2$ solution reached by upward flow the top of the columns, the columns were removed from the beaker and installed on the stand waiting for 1 or 2 h to drain the $CaCl_2$ solution.

Then, the columns were attached to the stand and beakers were placed under each column to drain all the $CaCl_2$ solution until the time of herbicide application. The mouth of each column was covered with film paper.

The herbicide (^{14}C-tebuthiuron + analytical standard) was applied at the highest dose recommended for the sugarcane crop (1200 g ha^{-1}) using Nichiryo micropipette, corresponding to 236 μg a.i. of tebuthiuron per soil column, directly on the moist soil at the top of each column. A radioactivity of 15,330.34 Bq per soil column was applied. The soil was then covered with a glass wool disk and an inverted funnel was fitted, where the peristaltic pump hose through which the 0.01 mol L^{-1} $CaCl_2$ solution was passed was connected.

A flow rate of approximately 8 mL h^{-1} for 48 h was simulated using the $CaCl_2$ solution, resulting in a rainfall simulation of approximately 200 mm for 48 h. Every 12 h, the leachate was collected in a labeled Erlenmeyer flask and the volume was measured. Three aliquots of 5 mL were taken for the first 12 h and 10 mL for 24, 36, and 48 h after herbicide application, placed in scintillation vials pre-counted with scintillation solution (Insta-gel plus) and counted in LSC for measurement of leached radioactivity in the liquid medium.

After 48 h, the peristaltic pump was turned off and the soil columns were removed from the stand and placed on a tray supported by foam so that they were slightly inclined. To remove the soil from the column, air was injected into the tip of the glass column to force out the soil, which was cut into 6 depth of approximately 5 cm each (0–5, 5–10, 10–15, 15–20, 20–25, and 25–30 cm). The soil samples were placed in aluminum trays, air dried, and then weighed.

When the soil samples were completely dry, they were weighed again. The milling process was started with the use of a grinder (Marconi®, Piracicaba, SP, Brazil) and homogenization of the soils. The process was carried out inside the chapel lined with plastic and exhaust fan on. The ground samples were transferred to plastic bags properly labeled for further oxidation.

Sub-samples of 0.2 g from each layer of the clay and loamy sand soils were weighed in porcelain beakers, with three repetitions for each layer of the columns.

The samples were burned in a biological oxidizer (R.J. Harvey Instrument Corporation OX500, Tappan, NY, USA), this procedure was used to obtain the radioactivity measurement in each soil layer, thus obtaining the total radioactivity of the study.

2.6. Degradation studies

The degradation study was conducted according to the method described in the standard "Aerobic and Anaerobic Transformation in Soil" (OECD – Organisation for economic co-operation and development, 2002b). The method is based on the use of radiometric techniques, to measure degradation rates as well as the metabolism of the test substance by soil microorganisms. These processes are quantified through the evolution of $^{14}C\text{-}CO_2$ trapped in 0.2 mol L^{-1} NaOH solution and quantification and identification of the radioactivity extracted by LSC. The amount of soil bound residue was quantified by oxidation of soils and quantification of radioactivity by LSC.

Prior to the start of the study, moisture (0.248 and 0.054 Kg^{-1} in the clay and loamy sand soil, respectively), and field capacity adjusted to 75% (32.36 and 25.36% in the clay and loamy sand soil, respectively) were determined in 50 g of soil on a dry basis and packed in the biometric bottles.

The experimental design used for the study was entirely randomized with three repetitions, and eleven extractions (0,7,14,28,42,56,70,84,98,112, and 126 d after application) were performed in 300 mL biometric bottles for each soil type. All the biometric flasks were pre-incubated in the dark for a period of 10 d at a temperature of 20 ± 2 °C to reestablish the soil microbiota.

Aliquots of 200 L of the tebuthiuron working solution were applied to the soil samples in the biometric bottles, corresponding to the maximum recommended dose (1200 g ha^{-1}) of the herbicide, assuming soil density was equal to 1200 kg m^{-3} and depth equal to 0.10 m. Each biometric bottle received the application of 200 μL of the working solution containing a radioactivity of 17,226.17 Bq.

After application of the working solution to the soil, the soil was mixed carefully with the help of a spatula to ensure complete homogenization of the samples, and then the bottles were closed with a rubber stopper attached to a soda lime filter with a stopper between the filter and the bottle. The atmospheric CO_2 entering the flask was blocked by the soda lime filter, ensuring that the CO_2 collected was only from soil respiration. A 10 mL aliquot of a 0.2 mol L^{-1} NaOH solution was added to the side tube of each biometric bottle for trapping and determination of the amount of mineralized ^{14}C-CO_2.

The soils conditioned in the biometric flasks were incubated for 126 d in a semi-dark room air-conditioned at 20 °C, and the temperature was monitored daily. During the study, periodic checks of the water content of the soils in the biometric flasks were done by weighing the flask + soil. If the difference between the initial and the determined water content was more than 5%, adjustments were made by adding deionized water in order to maintain the initial soil moisture value.

For the degradation and mineralization study (^{14}C-CO_2), NaOH solution samples were collected weekly at 7,14,21,28,35,42,49,56,63,70,84,98,112, and 126 d after the application of the working solution providing values on respiration rate for a total period of 126 d, The results are expressed as evolved ^{14}C-CO_2, which is the amount of carbon dioxide, consisting of radioactive carbon fourteen, released from the tebuthiuron molecule after its degradation and mineralization.

On each collection date two 1-mL aliquots of 0.2 mol L^{-1} NaOH solution were sampled into liquid scintillation flasks free of any external contamination for the determination of total ^{14}C activity by LSC. "Background" readings (flasks containing only scintillator solution without the presence of any radiolabeled substance) were also performed. The remaining 0.2 mol L^{-1} NaOH solution (8 mL) was removed from the side tube, which was then filled with 10 mL of a new 0.2 mol L^{-1} NaOH solution. For radioactivity identification, the extraction process was done with appropriate solvents 0,7,14,21,28,35,42,49,56,63,70,84,98,112, and 126 d after the application of the test substance.

The soil samples went through a process characterized by three extractions: in the first extraction, 50 g soil samples were removed from the biometric bottles and transferred to centrifuge tubes (250 mL) where 100 mL of methanol was added, which were stirred for 30 min at 38 *g* in a horizontal shaker. Then the tubes were centrifuged at 4000 rpm for 15 min and the supernatant was collected and transferred to 500 mL flasks. For the second and third extraction, the volume of methanol added was 80 and 70 mL, respectively, and the rest of the procedures were the same as the first extraction, and the three extracts were pooled.

Aliquots of 1 mL of the extract from the three extractions were pipetted into liquid scintillation vials with 10 mL of scintillator solution for measurement in the LSC. Subsequently, the extracts of the three extractions were rotary evaporated at 40 °C and 1 mL aliquots were pipetted for measurement in the LSC.

Extraction was performed to evaluate the presence of undegraded herbicide remaining in the soil using TLC. To do this, 100 μL of the concentrated extracts and the herbicide standards were applied to silica plates, previously activated at 250 °C for 2 h. The plates were placed in a flask containing 100 mL of methanol solution for tebuthiuron. After solvent elution, the plate was withdrawn from the cube and remained exposed until the solvent completely evaporated.

The analysis of tebuthiuron was performed using phosphorescent plates. The TLC plates were kept in contact with the film for at least 24 h and after this period, the film was read on a radio-scanner. The formation of metabolites and parental product were quantified by the value of $R_{f.}$

After the extractions, the soils were dried at room temperature and homogenized in a soil mill. Three soil subsamples (0.2 g) were weighed and oxidized in a biological oxidizer. The recovered radioactivity balance was determined by adding up the radioactivity detected in the total ^{14}C released, in the extracts and the residues recovered from the soils, after oxidation.

Based on the results obtained with TLC of the extracted residue, we were able to define the degradation time of half-life (DT50) of the herbicide in the two studied soils, as well as to quantify the resulting metabolites from the degradation of the herbicide during incubation. The data on the amount of ^{14}C-herbicide were suitable for the first order kinetic model $C=C_0e^{-kt}$, where C is the herbicide concentration in incubation time (%); C_0 is the concentration of herbicide at time zero (%); k is a degradation constant (d^{-1}); and t is the incubation time (d). The DT50, defined as the time required for 50% of the applied herbicide to be degraded, was calculated using the following equation: DT50 = ln2/k. The DT90, defined as the time required for 90% of the applied herbicide to be degraded, was calculated using the following equation: DT90 = ln10/k.

2.7. Microbial activity (mineralization of ^{14}C-glucose)

The ^{14}C-glucose mineralization study was conducted according to the OECD – Organization for economic co-operation and development, 2000b using the carbon transformation test "Soil Microorganisms: Carbon Transformation Test".

Prior to the start of the studies, moisture content was determined, field capacity adjusted to 75% as per the degradation study, and 300 g of soil on a dry basis packed into the 3-L glass jars for both soils. The glass jars were pre-incubated in the dark for a period of 10 d at 20 ± 2 °C for reestablishment of the soil microbiota.

After the pre-incubation period, the treatments applied were: maximum recommended dose (1200 g ha^{-1}), 5-fold the maximum recommended dose (6000 g ha^{-1}) and control (no tebuthiuron application). The experimental design used was entirely random with three repetitions.

After applying the tebuthiuron doses to the soil samples, they were mixed carefully with the help of a spatula, assuring a complete homogenization of the samples. After application and homogenization of the soil samples a 10 g aliquot was taken from each 300 g sample and transferred to biometric vials.

A 1-mL aliquot of ^{14}C-glucose solution (D-[U-^{14}C] glucose) plus analytical standard glucose, with specific activity of 11 GBq $mmoL^{-1}$ and total activity of 37 MBq mC-1, was added the soil samples from each biometric vial at 0, 7, 14, and 28 d after tebuthiuron application with approximately 8813.63 Bq mL^{-1} of ^{14}C-glucose.

After application of the ^{14}C-glucose solution, each biometric flask was closed with a rubber cap attached to a "soda lime" filter; containing a stopper between the filter and the flask. Atmospheric CO_2 entering the bottle was blocked by the soda lime filter, ensuring that the CO_2 collected was only from respiration. A 10 mL aliquot of a 0.2 mol L^{-1} NaOH solution was added to the all side of each biometric bottle.

The NaOH solution was collected 12 h after the application of the ^{14}C-glucose solution, and the results were expressed as evolved ^{14}C-CO_2, which is the amount of CO_2, consisting of ^{14}C, released from glucose after its degradation and mineralization. The two 1 mL aliquots of NaOH solution were sampled into liquid scintillation flasks free of any external contamination for the determination of total ^{14}C activity by LSC. "Background" readings (vials containing only scintillating solution, without the presence of the radiolabeled herbicide) were also performed. The remaining NaOH solution (8 mL) was removed from the side tube which was then filled with 10 mL of a new NaOH solution.

The biometric flasks were placed in the incubation room in the dark with a temperature of 20 °C being recorded daily. During the study periodic checks of the water content of the soils in the 4 L flasks were made by weighing the flask + soil. If the difference between the initial and the determined water content was greater than 5% adjustments were made by adding water in order to maintain the initial soil moisture value.

2.8. Statistical analysis

Sorption-desorption, mobility, leaching, degradation, and microbial activity data of herbicide were expressed as mean and standard devia-

Table 2
Freundlich sorption parameters and linear distribution coefficients for ^{14}C-tebuthiuron in the clay and loamy sand soil.

Soil	Freundlich model				Linear model			Sorbed herbicide(%)
	$K_{f\ (sorption)}$ ($mg^{(1-1/n)}$ $L^{1/n}$ Kg^{-1})	$K_{foc\ (sorption)}$	$1/n_{\ (sorption)}$	R^2	$K_{d\ (sorption)}$ (L Kg^{-1})	$K_{oc\ (sorption)}$	R^2	
Clay	1.15	79.31	0.90	0.99	1.32	91.03	0.99	60.02 ± 2.14[a]
Loamy sand	0.80	666.67	0.95	0.99	0.85	708.33	0.99	48.15 ± 2.20

[a] Mean followed by standard deviation (±SD) of the mean ($n = 3$).

Table 3
Freundlich desorption parameters, linear distribution coefficients and hysteresis coefficient (H) for ^{14}C-tebuthiuron in the clay and loamy sand soil.

Soil	Freundlich model					Linear model			Desorbed herbicide(%)
	$K_{f\ (desorption)}$ (mg $^{(1-1/n)}$ $L^{1/n}$ Kg^{-1})	$K_{foc\ (desorption)}$	$1/n_{\ (desorption)}$	R^2	H	$K_{d\ (desorption)}$ (L Kg^{-1})	$K_{oc\ (desorption)}$	R^2	
Clay	3.45	237.93	0.90	0.99	1.00	4.51	311.03	0.99	26.40 ± 1.52[a]
Loamy sand	2.81	2341.67	0.90	0.99	0.95	3.64	3033.33	0.99	35.29 ± 1.84

[a] Mean followed by standard deviation (±SD) of the mean ($n = 3$).

tion ($n = 3$). All figures were plotted using Sigma Plot (version 10.0 for Windows, Systat Software, Inc., Point Richmond, CA, USA).

3. Results

3.1. Physicochemical attributes of soils

Clay and OC content were 7 and 12-fold higher in clay soil than in loamy sand soil, respectively (Table 1). The pH in these soils were very close (5.1 and 5.2 in clay and loamy sand soil, respectively), indicating the acidic nature of the soils. CEC in clay soil was 50% higher when compared to loamy sand soil. In turn, loamy sand soil presented a sand content 6-fold higher than clay soil. These physicochemical attributes of soil and herbicide have great interference in the product behavior in soils, weed control efficiency, and prevent the occurrence of environmental problems.

3.2. ^{14}C-tebuthiuron sorption–desorption

The parameters derived from the Freundlich and Linear models and the sorption and desorption isotherms of the ^{14}C-tebuthiuron adapted for the two models are presented in Table 2 and Fig. 1, respectively. In the two models evaluated, great fit of the data were observed, according to the analysis of the coefficient of determination (R^2) close to 1, this indicates that the estimated curves were able to explain the observed values (Table 2). Sorption and desorption isotherms adjusted by the Freundlich and Linear model for ^{14}C-tebuthiuron in different soils are shown in Fig 1. Isotherm was L type, showing that the more sites of soil colloids are filled, the greater the difficulty of filling vacant sites by other solute molecules. The solute molecules are not oriented vertically. The higher the herbicide concentration in the soil, the greater is the phenomenon of desorption.

Values of 1/n close to 1 in the sorption and desorption of ^{14}C-tebuthiuron indicated that the process was irreversible to soil solution (Tables 2 and 3). The K_f and K_d values of sorption were 30% and 35% higher in clay soil (1.15 $mg^{(1-1/n)}$ $L^{1/n}$ Kg^{-1} and 1.32 L Kg^{-1}) when compared to loamy sand soil (0.80 $mg^{(1-1/n)}$ $L^{1/n}$ Kg^{-1} and 0.85 L Kg^{-1}, respectively) (Table 2). The sorption coefficients normalized according to the OC content (K_{foc} and K_{oc}) were 8-fold higher in loamy sand soil than in clay soil for both coefficients. Overall, both the sorption isotherm adjusted by the Freundlich and Linear model obtained similar results, with a higher sorption coefficient (K_d and K_f) in the clay soil when compared to loamy sand soil. The sorbed percentage of the herbicide in clay soil was 60%, while in loamy sand soil was 48% (Table 2).

The K_f and K_d values of ^{14}C-tebuthiuron desorption were similar, in which it was 19% higher in loamy sand than in clay soil (Table 3). The K_{foc} and K_{oc} values of ^{14}C-tebuthiuron desorption were 9-fold higher in loamy sand than in clay soil (Table 3). Of the herbicide quantity of 60% sorbed in clay soil, only 26% returned to the soil solution, while in the sandy soil, of the 48% sorbed, 35% was desorbed to soil solution. These results indicated greater desorption in loamy sand than in clay soil.

3.3. ^{14}C-tebuthiuron mobility and leaching

The values of the mobility coefficients (R_f) for ^{14}C-tebuthiuron were 0.92 and 1.00 in clay and loamy sand soil, respectively (Fig. 2), and these results indicate high herbicide mobility.

The ^{14}C-tebuthiuron had a slightly increase mobility in the loamy sand soil when compared to soil clay. In the leaching study, the recovery (mass balance) of ^{14}C-tebuthiuron (sum of herbicide percentages at different soil depths and leachate) was 105% and 104% in clay and loamy sand soil, respectively, within the recommended range for radiolabel substances (90%−110%) (OECD, 2002a).

The percentages of ^{14}C-tebuthiuron distributed in soil columns and leachate after 200 mm rain simulation over 48 h in clay and loamy sand soil are presented in Fig. 3. ^{14}C-tebuthiuron amounts of ~54% and 99% were observed on the soil surface of 0–5 cm, ~16% and 6% in the 5–10 cm of soil depth, in loamy sand and clay soil, respectively. From the depth 10–15 cm, only in the loamy sand soil was detected the ^{14}C-tebuthiuron. The amount of ^{14}C-tebuthiuron detected in the soil profile decreased according to deeper layers, being ~4-fold higher in the 10–15 cm layer than to 20–25 cm. At the depth of 25–30 cm and in the leachate solution the herbicide was not detected. This found collaborate with mobility studies, in which it was observed that ^{14}C-tebuthiuron has greater mobility in loamy sand soil (Fig. 3). This greater mobility is consistent with the high leaching in the soil profile.

3.4. ^{14}C-tebuthiuron degradation

3.4.1. Mass balance

The mass balance values of ^{14}C-tebuthiuron in the studied soils were 107 and 108% in clay and loamy sand soil, respectively, within the recommended range to radiolabeled substances (90%−110%) (OECD, 2002b).

The distributions of ^{14}C tebuthiuron in the degradation study are shown in Fig. 4, by the quantification of extractable residues, bound residues (non-extractable) and mineralized to $^{14}C\text{-}CO_2$, in the two soils studied.

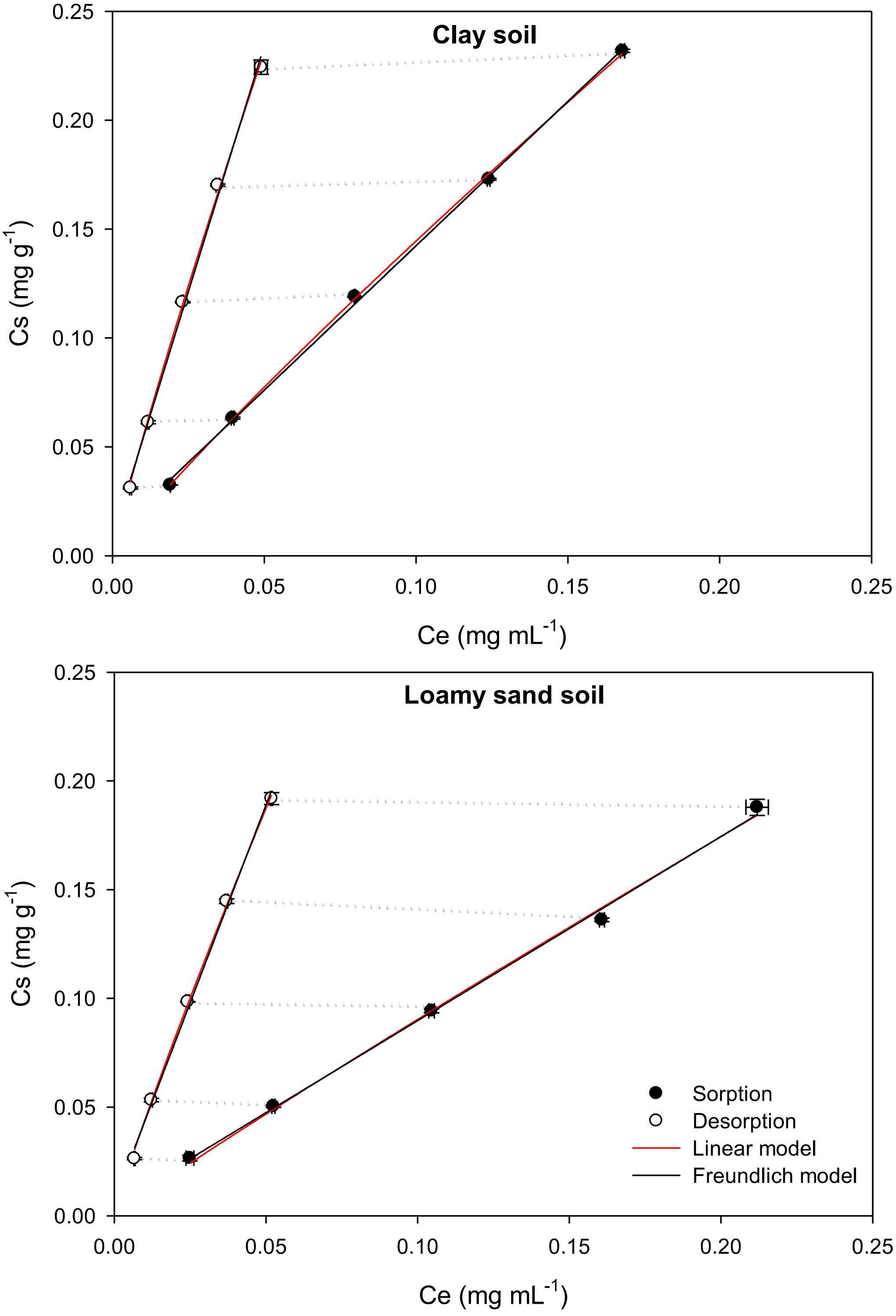

Fig. 1. Freundlich and linear sorption (●) and desorption (○) isotherms of ^{14}C-tebuthiuron in the clay and loamy sand soil. Error bars represent standard deviation (± SD) of the mean (n = 3). Symbols may cover error bars.

3.4.2. ^{14}C-tebuthiuron mineralization to $^{14}C\text{-}CO_2$

The mineralization of ^{14}C-tebuthiuron accumulated to $^{14}C\text{-}CO_2$ ranged from 0.44 (0 d) to 3.22% (126 d) in loamy sand. At the same time, in clay soil, herbicide mineralization ranged from 0.44 to 2.55% (Fig. 4).

Over the incubation time of the soil, the mineralization of ^{14}C-tebuthiuron increased in both soils (accumulated total of $^{14}C\text{-}CO_2$) (Fig. 4), probably due to the greater activity of microorganisms capable of degrading this molecule. On the other hand, during the incubation period, there was an increase in bound residues in the two soils, thus, a smaller amount of herbicide was bioavailable in the soil solution to be mineralized, because much of the herbicide adhered strongly to the soil colloids, in the form of bound residue. When the herbicide molecule is retained to the soil, it becomes unavailable to be degraded by microorganisms.

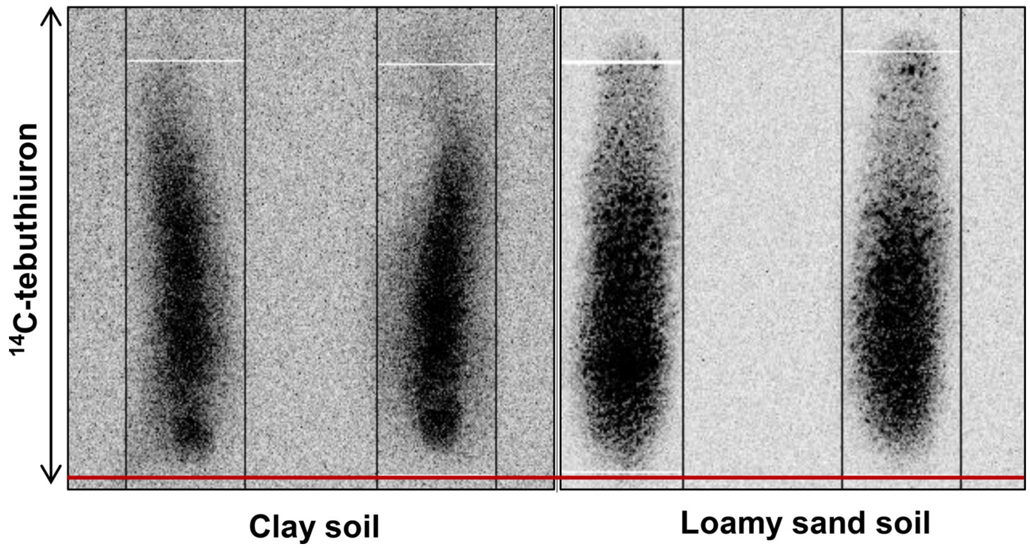

Fig. 2. Visualization of the mobility of ^{14}C-tebuthiuron in clay (left, Retention factor (R_f)=0.92 ± 0.10) and loamy sand soil (right, R_f=1.00 ± 0.00) in two applications. Mean R_f value standard deviation (± SD) of the mean (n = 3). The red line is the basis of the herbicide application. The panels show the autoradiographs of the soil profiles with the localization ^{14}C-tebuthiuron after mobility in the soil with artificial rainfall. Dark gray to black regions in the autoradiographies indicates intensity of radioactive signal on a scale from low to high levels ^{14}C activity.

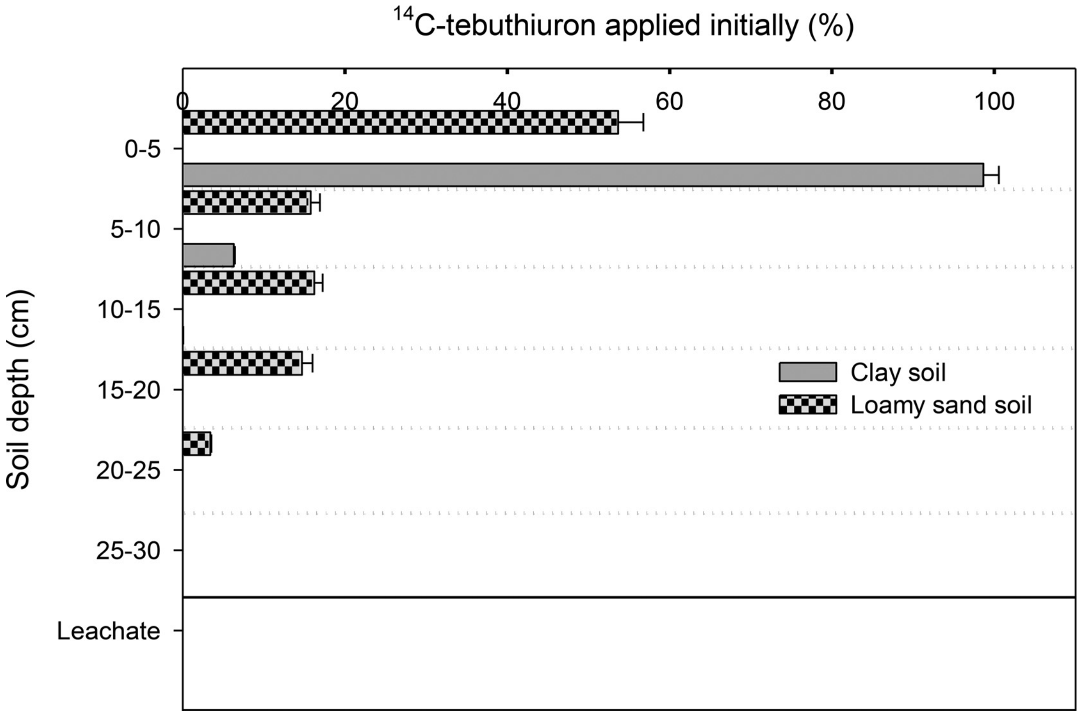

Fig. 3. Percentages of ^{14}C-tebuthiuron distributed in soil columns and leachate after 200 mm rainfall simulation over 48 h in clay and loamy sand soil. Error bars represent the standard deviation (+ SD) of mean (n = 3).

3.4.3. ^{14}C-tebuthiuron extractable residues

The total amount of herbicide applied was initially extracted (0 d). In the loamy sand soil had the highest amount of residue extracted from ^{14}C-tebuthiuron at the end of incubation (126 d), with a value of ~48%. In clay soil, in turn, it had a slight difference in relation to loamy sand soil, with 46% of extractable residue from ^{14}C-tebuthiuron at 126 d (Fig. 4). In the two soils studied, there was the same decreasing trend of the residue extracted from the herbicide over incubation time, as there was an increasing in complete microbial degradation (mineralization) and also an increasing in the formation of bound residues.

3.4.4. ^{14}C-tebuthiuron bound residues

Higher amount (8%) of ^{14}C-tebuthiuron bound residue was found in the soil clay initially (0 d), while 4% of ^{14}C-tebuthiuron bound residue was detected in the loamy sand soil. ^{14}C-tebuthiuron bound residues more intensely in clay soil compared to loamy sand soil, at 0 d In clay soil, at 126 d, it was formed less bound residue (54%) compared to loamy sand soil (56%) (Fig. 4). The formation of ^{14}C-tebuthiuron bound residues was faster in clay soil, while in loamy sand soil, the formation of ^{14}C-tebuthiuron was slightly slower and more constant.

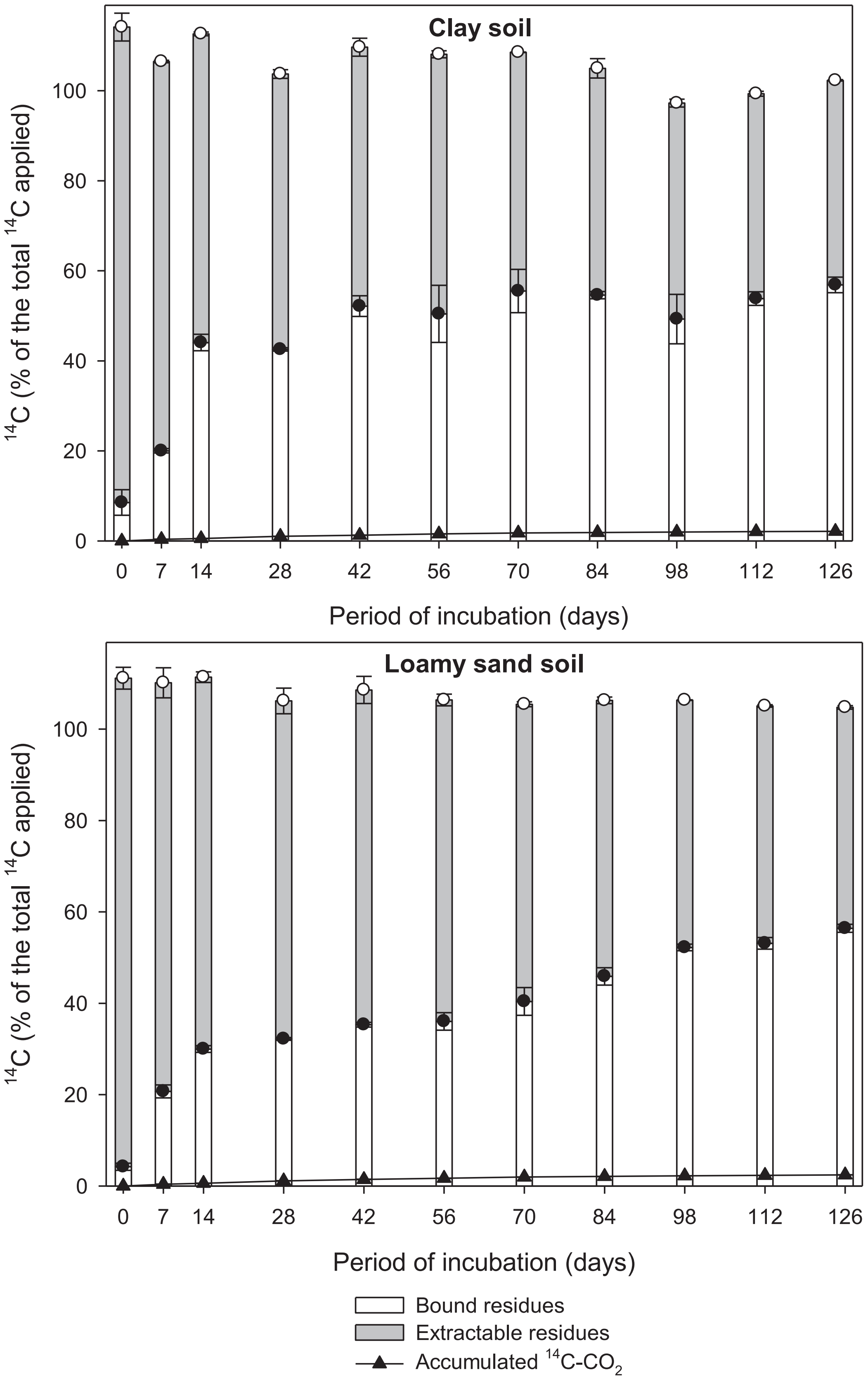

Fig. 4. Distribution of ^{14}C-tebuthiuron applied in clay and loamy sand soils among extractions with solvent, mineralized ^{14}C-CO$_2$, and bound residues (%) as a function of incubation time (126 d) in soil samples. Vertical bars represent standard deviations (± SD) of means (*n* = 3).

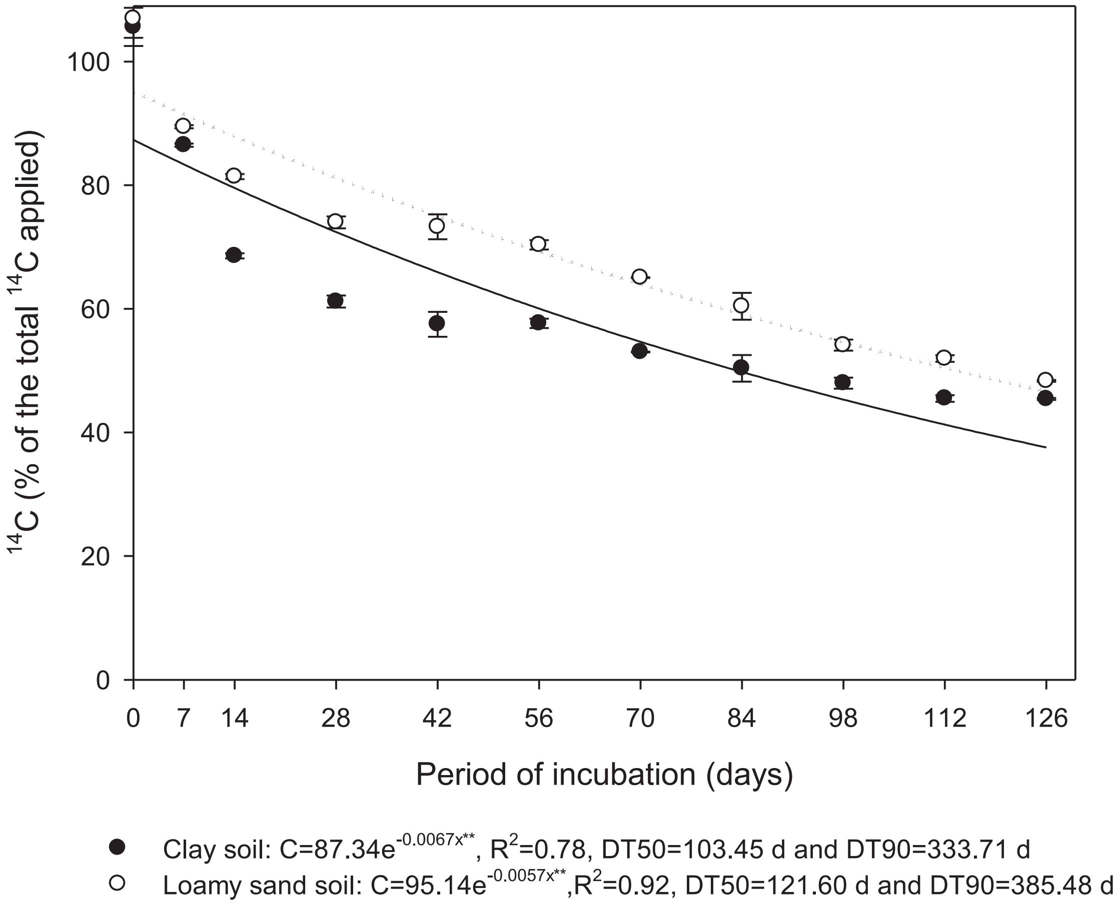

Fig. 5. Degradation of the solvent-extracted ^{14}C-tebuthiuron separated by TLC plates in parental compound (%) when applied in clay and loamy sand soil, as a function of incubation time (126 d) in soil samples. The vertical bars inserted in the symbols and bars represent the standard deviation (±SD) of the mean (n = 3). $^{**}p < 0.01$ by the F test.

The tendency of increasing formation of bound residues was opposed to the decreasing order formed by soils in the mineralization of ^{14}C-tebuthiuron, since the greater the amount of bound residues, the lower is the bioavailability of the herbicide in the soil solution to the activity of microorganisms and weed absorption.

3.4.5. *Degradation time of ^{14}C-tebuthiuron*

R^2 values were 0.78 and 0.92 for clay soil and loamy sand soil, respectively, and this indicated that the estimated first-order curves were able to explain the observed values (Fig. 5). ^{14}C-tebuthiuron degradation was faster in clay soil than in loamy sand soil, with DT50 values of ~103 and 122 d, respectively. DT90 showed that the amount close to the totality of ^{14}C-tebuthiuron initially applied can persist for a long time in both soils, with ~385 and 334 d in loamy sand soil and clay soil, respectively. On the other hand, the presence of metabolites from the ^{14}C-herbicide in the degradation process was not found.

3.5. *Microbial activity of soil contaminated with tebuthiuron*

Microbial activity in different soils, in the incubation period of 1, 7, 14, and 28 d, in the following three treatments: absence of tebuthiuron, use of the recommended dose (1200 g ha^{-1}) and 5-fold the recommended dose (6000 g ha^{-1}) are presented in Table 4.

According to the results, the microbiological activity in loamy sand was higher than in the soil, in the absence of herbicide was 2.87%, and 4.01% in the application of recommended dose of tebuthiuron, and 4.26% in the application of 5-fold the recommended dose at 1 d of incubation. After 28 d of incubation, a little decreased in microbiological activity was observed in both soils, this decrease may be related to higher sorption or formation of herbicide bound residue in soils, consequently will have a lower bioavailability of tebuthiuron in soil solution to microbial degradation.

Table 4
^{14}C-CO$_2$ derived from mineralization of ^{14}C-glucose (%) in relation to the total radioactivity initially applied and evaluated at 1,7,14, and 28 d after tebuthiuron (non-radiolabel) application.

Soil	Period of incubation (d)			
	1	7	14	28
	Control (no herbicide)			
Clay	18.63 ± 0.01[a]	17.71 ± 0.01	16.58 ± 0.42	16.04 ± 1.08
Loamy sand	21.50 ± 0.01	21.84 ± 0.01	19.80 ± 0.11	19.62 ± 0.29
	1200 g ha^{-1} of tebuthiuron			
Clay	17.87 ± 0.01	19.29 ± 0.01	17.47 ± 0.28	17.66 ± 0.14
Loamy sand	21.88 ± 0.01	23.53 ± 0.01	21.00 ± 0.21	20.56 ± 0.23
	6000 g ha^{-1} of tebuthiuron			
Clay	17.46 ± 0.01	16.30 ± 0.01	17.68 ± 0.62	18.39 ± 0.21
Loamy sand	21.72 ± 0.01	17.76 ± 0.01	18.30 ± 0.24	21.00 ± 0.41

[a] Mean followed by standard deviation (±SD) of the mean (n = 3).

After herbicide application, the microbiological activity of the soil changed little in both soils, so it is not possible to conclude that the herbicide affected the microbial community in soils.

4. Discussion

According to the study, K_f and K_d values of ^{14}C-tebuthiuron sorption were 30% and 35% higher in clay soil compared to loamy sand soil, respectively (Table 2). ^{14}C-tebuthiuron sorption was lower in loamy sand soil, as the clay and OC content are low (Table 1). Tebuthiuron sorption in the soil was dependent on the presence of available sites that are able to bind to the herbicide molecule (Kearns et al., 2014). OC and clay are the most important colloids of the charges formation in these sorption sites (Mirzaei et al., 2013). Tebuthiuron is a non-ionic herbicide and can bind to hydrophobic and hydrophilic groups that are present in both OC and clay colloids by covalent hydrogen bounds and Van der Waals (Kovaios et al., 2006). The energy for the rupture of these bounds is high, this promote the decrease of herbicide desorption (Trubetskaya et al., 2014; Okada et al., 2016). Similar results were found in this study, with low desorption of tebuthiuron in clay soil. The loamy sand soil had low capacity to sorb the tebuthiuron due to its smaller electrostatic surface compared to clay soil (Firmino et al., 2008). Studies conducted by Chang and Stritzke (1977) showed that tebuthiuron sorption was higher in soils with high OC and clay content, indicating that the soil with 0.3% of OC, 95% of sand and 2% of clay, sorbed ~11% of the herbicide, while another soil, with contents of 4.8% of OC, 14% of clay and 49% of sand, sorbed 71% of tebuthiuron.

The variability in the interaction dynamics of soil and herbicide attributes causes a differential sorption, which interferes with the different bioavailability of the herbicide in the soil solution, and can generate variation in weed control (Mohammadzamani, 2009). The application of tebuthiuron should consider the sorption capacity of each soil type. And then, using soil physicochemical attributes to interpolate sorption, desorption and bioavailability maps of herbicides applied in PRE of weeds, as well as studies of control efficiency is an important alternative to increase the accuracy in the recommendation of doses avoiding economic losses and environmental impacts (Mendes et al., 2021b). However, there are few studies with this approach to herbicides, including those frequently used in Brazil, such as tebuthiuron.

Some management practices, such as liming, modify soil attributes and may affect herbicide sorption (Ouyang et al., 2016; Passos et al., 2019). Herbicides PSII inhibitors, such as tebuthiuron, decrease sorption when the soil pH becomes more alkaline. This increases the mobility of the herbicides and the potential to environmental contamination.

In soils with different physicochemical attributes, Toniêto et al. (2016) observed K_d values of tebuthiuron from 1.2 to 2.9 L kg^{-1}. Another study reported the low K_d values of tebuthiuron sorption, in which ranged from 0.7 to 2.6 L Kg^{-1} in Oxisols (Souza et al., 2001). Similar results were found in our study, with low K_d of the herbicide in clay soil (1.32 L Kg^{-1}) compared to loamy sand soil (0.85 L Kg^{-1}) (Table 2). These studies demonstrated the influence of herbicide attributes on sorption, in which tebuthiuron has a high S_w (2500 mg L^{-1} at 20 °C), and this influences the herbicide low sorption, high mobility and high leaching potential in soils (Toniêto et al., 2016).

The rain is an important factor that determines the environmental fate of herbicides, in the case of tebuthiuron, which has a high S_w. In addition, the water in the soil solution determines the bioavailability of the product, leaching capacity and runoff process. When relating the study of sorption, leaching, and mobility, with the physicochemical attributes of the soils, it was evident that the more retained the herbicide is in the soil, the lower the leaching capacity, and consequently greater is the transport by runoff. Higher CEC, OC, and clay content contribute to the herbicide remaining retained on the soil surface. Therefore, tebuthiuron tends to remain in higher amount in the surface layers of the soil. According to the sorption study, the herbicide in clay soil was more sorbed, which prevented greater mobility and leaching compared to loamy sand soil.

Tebuthiuron leaching in loamy sand soil occurred up to 25 cm depth, while in clay soil leaching was up to 5–10 cm (Fig. 3). In opposition, Emmerich (1985) found this herbicide movement up to 180 cm depth, in a soil with 92% of sand. However, Cerdeira et al. (2007), when evaluating tebuthiuron leaching in soils with different attributes, observed that after 240 d there was not detectable residue in the soil below 40 cm depth, even in soils with high sand contents. These authors observed that tebuthiuron shifted to a depth of 20–40 cm faster and deeper when applied to soil without sugarcane cover, possibly due to the fact that the cultivated plot would have greater evapotranspiration and, therefore, would slow the downward movement of water together herbicide. Results of Mattalo et al. (2003) coincided with our study, in which it found that tebuthiuron is weakly sorbed in soils, but with lower leaching potential in clay soils than in sandy soils.

The descending movement of the tebuthiuron in depth in the soil is due to the water retention capacity and the hydraulic conductivity, both influenced by the clay and OC content. Another study performed by Chang and Stritzke (1977) obtained different results, in which they observed that the mobility of tebuthiuron and fluometuron in soils are more related to sorption capacity than to the S_w of these herbicides. Once the R_f values of this herbicide were very similar (0.58 and 0.57) in clay soils, respectively, but the S_w is very different (2500 and 90 mg L^{-1}, for tebuthiuron and fluometuron, respectively). In sandy soils, the R_f was 0.98 for two herbicides. These studies demonstrated the need to know the physicochemical attributes of soils to understand in the environmental herbicides behavior.

Regarding tebuthiuron degradation, greater mineralization was observed at 126 d (3.22%) in loamy sand than in clay soil (2.55%) (Fig. 4). Low values of mineralized tebuthiuron may be related to the high amount of bound residues over the incubation time of tebuthiuron in soils. Studies conducted by Bicalho and Langenbach (2013), in a soil with a content of 40% of sand, 44% of clay; 3.6% of OC, it was observed that after 78 d of incubation, the mineralization of ^{14}C-tebutiuron was not higher than 0.9% of the amount initially applied. Low percentages of mineralized ^{14}C-tebuthiuron added to the absence of metabolites of this molecule suggests that this herbicide is not easily biodegradable, consequently it is highly persistent in the environment.

A gradual increase in the formation of bound residues and a decrease in the amount of extractable residues was observed over 126 d incubation time (Fig. 4). Slightly higher values in the amount of extractable residues in loamy sand soil at 126 d compared to clay soil can be explained by the differences in OC and CEC content (Table 1). The low values of OC (0.12%) and CEC (42 $mmol_c$ dm^{-3}) were essential to increase the bioavailability of herbicide in the soil solution. However, these same soil attributes were not able to explain the difference observed in the formation of bound residues, being higher in loamy sand soil than in clay soil. Studies performed by Raman and Rao (1987) showed that there is a decrease in extractable tebuthiuron residue at initial incubation time up to about 40–80 d, followed by a gradual decrease in the extractable residue.

Bound residue consists of the herbicide strongly sorbed in the restricted sites in the soil and, unlike the extractable residue, cannot be desorbed by solvents (Raman and Rao, 1987). These authors showed that the degradation rate in extracted residue was 5-fold higher in sandy soils with percentages of 21.5% of clay, 59.8% of sand, and 0.672% of OC compared to clay soil with 62.5% of clay, 25.3% of sand, and 1.015% of OC. The bound residue and degradation tend to be higher for higher OC and clay content.

Tebuthiuron concentration in the form of extractable residue is always considered more important in the bioavailability of the herbicide, since the absorption by weed and the carryover potential. Studies conducted by Viti et al. (2021), demonstrated that herbicide bound residues can become bioavailable and mineralized, which can adversely affect subsequent crops and non-target organisms. Therefore, the remobilization of bound residues is important and should be considered in the assessment of environmental risks in the registration process.

According to the results, ^{14}C-tebuthiuron degradation was faster in clay soil than in loamy sand soil, with DT50 values of 103.45 and 121.60 d, respectively. Although the sandy soil is more bioavailable in the solution, microbiological activity is lower than in clay soil. An essential factor to microorganisms survival is the water content in the soil. According to Machado et al. (2008), soil water retention was influenced by soil texture and structure, OC content and clay type. Texture is the main factor because it defines the specific surface area (SSA) and pore size. The smaller the particle size, the larger the SSA, consequently, the greater is the volume of retained water. The larger the pore size, the lower the water retention force through the soil. Due to this, sandy soils have lower water retention capacity, lower microbiological activity, and consequently lower herbicide degradation over time. Similar results were obtained by Cerdeira et al. (2007), which found a DT50 of 128 d for tebuthiuron in sandy soils.

The DT90 values showed that tebuthiuron can persist for a long period in both soils. The long residual effect of tebuthiuron has caused injuries in sensitive crops cultivate after the use of this herbicide (carryover). Some examples are the injuries observed in soybean, peanut, and bean crops, when cultivated within 2 y after the application of this herbicide (Inoue et al., 2011). Studies conducted by Zanardo et al. (2019), analyzed five peanut cultivars planted 30 d after tebuthiuron application, the results concluded that the crop is highly sensitive to herbicide, with severe symptoms and plant death in all cultivars studied.

According to the study, microbial respiration in sandy soil was slightly higher than in clay soil. The absence and presence of soil tebuthiuron had little affect over microbial activity in soils. However, further studies are needed to identify the microbial community of these soils and the relationship with tebuthiuron.

5. Conclusion

Sorption-desorption process of ^{14}C-tebuthiuron was influenced by the physicochemical attributes of the soil. Sorption coefficient (K_f and K_d) was strongly related to the OC and clay content of the soils. The high solubility in water of this herbicide and the low sorption ($K_d = 1.32$ and 0.85 L Kg^{-1} in clay and loamy sand soil, respectively), explain the mobility of ^{14}C-tebuthiuron.

The ^{14}C-tebuthiuron had a long persistence in soils (DT90 of ~385 and 334 d) in loamy sand and clay soil, respectively. The long residual effect of tebuthiuron must be taken into account in the choice of crops in succession to sugarcane, in order to avoid the carryover process.

The tebuthiuron recommendation must be based on the physicochemical attributes of soils, with the objective of increase the weed control efficiency and it is essential to decrease the contamination potential of water resources.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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