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EFFECTS OF ADDING ORGANIC MATTER TO A RED-YELLOW LATOSOL IN THE SORPTION AND DESORPTION OF TEBUTHIURON

Efeitos da Adição de Matéria Orgânica em Um Latossolo Vermelho-Amarelo na Sorção e Dessorção do Tebuthiuron

ABSTRACT - Tebuthiuron is one of the most widely used herbicides in the sugarcane culture and its characteristic is the long persistence in soil. When used without knowing its interactions with soil attributes, it can reduce the sustainability of cropping systems and contaminate surface and groundwaters. In this research, by using a high-performance liquid chromatography, the effects of adding organic matter in a Red-Yellow Latosol were evaluated, as for the sorption and desorption of tebuthiuron. It was concluded that there is a direct relation between the sorption of tebuthiuron and the organic matter content in Red-Yellow Latosols and there is an inverse relation for desorption. The hysteresis index was lower in samples with high organic matter content.

Keywords: chromatography, hysteresis index, persistence.

RESUMO - O tebuthiuron é um dos herbicidas mais utilizados na cultura da cana-de-açúcar e tem como característica a longa persistência no solo. Quando utilizado sem o conhecimento de suas interações com os atributos dos solos, pode reduzir a sustentabilidade dos sistemas de cultivos e contaminar águas superficiais e subterrâneas. Nesta pesquisa, utilizando a Cromatografia Líquida de Alta Eficiência, foram avaliados os efeitos da adição de matéria orgânica em um Latossolo Vermelho-Amarelo sobre a sorção e dessorção do tebuthiuron. Conclui-se que existe relação direta entre a sorção do tebuthiuron e os teores de matéria orgânica no Latossolo Vermelho-Amarelo e relação inversa para a dessorção. O índice de histerese foi menor nas amostras com alto conteúdo de matéria orgânica.

Palavras-chave: cromatografia, índice de histerese, persistência.

INTRODUCTION

Among the problems found by technicians and farmers in the management of weeds in the sugarcane cultivation, greater spacing between planting lines is the main limitation to the use of control programs with the exclusive use of herbicides. In order to solve this problem, there are two options: the first one consists in the pre- or post-emergence application of herbicides that have a short residual effect on the soil. In this case, for crops with a long critical period to prevent interferences, producers will have to repeat the operation several times, due to new infestations that may compromise the development and growth of the culture. Another option is using herbicides that have a long

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persistence in the soil (Chirukuri and Atmakuru, 2015). In this case, with a single application it is possible guarantee weed control until the end of the crop, preventing further infestations of the area. This technology, being the cheapest, is more used by most producers (Silva et al., 2013). Among the most commonly used herbicides in the sugarcane culture there is tebuthiuron, which has a long residual effect on the soil and is efficient in controlling several monocot and dicot species when applied before weed emergence.

However, regardless of whether the herbicide is applied during weed pre-or post-emergence, its final destination is the soil, in which this herbicide will undergo a redistribution process; it may be retained by colloids or it may be available in the soil solution. This part, available in the soil solution, may be absorbed by plants and microorganisms and degraded, and the rest may be leached to deeper layers of the soil profile (Lapworth and Gooddy, 2006). Therefore, the main key factor of the herbicide behavior in the soil refers to its sorption and desorption capacity of mineral and organic colloids from the soil matrix (Cadková, 2013).

The energy for herbicide sorption to the soil is variable and depends on the nature of the herbicide-soil connection. These interactions may be Van der Waals, electrostatic and/or hydrogen bonding type (Low, 2001). When there is enough free energy to promote the return of the herbicides to the soil solution, the desorption process occurs (Rigi et al., 2015). This process is very important, since it will influence the availability of the herbicide over time, guaranteeing or not its efficiency in controlling weeds, that is, the residual effect of the herbicide (Sondhia, 2014).

For herbicides with basic or non-ionic characteristics, the soil organic matter content and quality are the most important attributes in the retention (sorption) of this compound by the soil matrix (Pereira Júnior, 2015). However, for acidic herbicides, other soil attributes, such as pH and the physical and chemical characteristics of mineral colloids, may be of greater importance. The sorption intensity is quantified by the partition coefficient (K_d), which refers to the ratio of the product sorbed by the colloids and that free part in the soil solution (Piwowarczyk and Holden, 2013). However, when intending to use mathematical models to infer the herbicide leaching capacity in the soil profile, such as the ERI (Environmental Risk Index), Koc or K_{foc} are used; they represent K_d or K_f values normalized by the soil organic carbon (Oliver et al., 2016).

In Brazil, there are large areas of Red-Yellow Latosol used to cultivate sugarcane, and in these areas one of the mostly used herbicides is tebuthiuron. In addition, studies about tebuthiuron behavior in tropical soils are scarce. It is believed that the obtained results may be very important to make safe recommendations about tebuthiuron, both from the agronomical and environmental point of view.

The goal of this research was to quantify the sorption and desorption of tebuthiuron in samples of a Red-Yellow Latosol enriched with different organic carbon contents, using the High-Performance Liquid Chromatography.

MATERIAL AND METHODS

In samples of a Red-Yellow Latosol, collected at a 0-20 cm depth, air-dried and sieved in 4 mm mesh, different volumes of bovine manure were incorporated (Substrate 1: 0.0 kg OM/kg; Substrate 2: 0.250 kg OM/kg soil; Substrate 3: 0.500 kg OM/kg soil; Substrate 4: 0.750 kg OM/kg soil; Substrate 5: 1.00 kg OM/kg), increasing the organic matter content in the samples to 1.55, 2.84, 3.97, 6.35 and 7.28 dag kg^{-1} , respectively (Table 1). The mixture of soil and bovine manure was made in a homogenous way and incubated for 30 days in 100 L plastic boxes. After that period, samples were collected and characterized chemically and physically (Tables 1 and 2). In order to determine tebuthiuron quantitatively, the high-performance liquid chromatography (HPLC) technique was used, according to the adjusted methodology described by Calvayrac et al. (2013).

The quantification of tebuthiuron in soils was determined by a high-performance liquid chromatography with a Shimadzu LC 20AT model equipment, equipped with UV-Vis detector (Shimadzu SPD 20A) and C_{18} stainless steel column (Shimadzu VP-ODS Shim-pack 250 Mm x 4.6 mm d.i.). All used solvents were HPLC grade, and the other reagents were of analytical grade.

Table 1 - Data from the chemical analyses of each substrate

Substrate*	pH	P	K	Ca	Mg	Al	H+ Al	SB	(t)	(T)	OM
	(H ₂ O)	(mg dm ⁻³)		(cmol _c dm ⁻³)							(%)
1	5.40	1.2	30	0.3	0.30	0.0	3.1	3.14	0.68	17.64	1.55
2	5.73	1.9	44	0.8	1.80	0.0	4.0	5.80	15.80	19.80	2.84
3	5.14	2.8	42	0.8	1.99	0.0	3.9	6.52	16.52	20.32	3.97
4	4.78	2.6	43	0.7	2.30	0.0	4.7	6.22	15.22	22.82	6.35
5	5.65	2.6	48	0.9	2.45	0.0	4.3	7.74	14.74	25.04	7.28

* Substrates obtained after the incubation of a Red-Yellow Latosol with increasing doses of bovine manure. 1- Red-Yellow Latosol with 1.55% of organic matter; 2- Red-Yellow Latosol with 2.84% of organic matter; 3- Red-Yellow Latosol with 3.97% of organic matter; 4- Red-Yellow Latosol with 6.35% of organic matter; 5- Red-Yellow Latosol with 7.28% of organic matter.

Table 2 - Data from the physical analyses of each substrate

Substrate*	Clay (%)	Silt (%)	Sand (%)	Textural class
1	39	12	49	Clayey
2	41	13	46	Clayey
3	41	12	47	Clayey
4	43	15	42	Clayey
5	45	15	40	Clayey

* Substrates obtained after the incubation of a Red-Yellow Latosol with increasing doses of bovine manure. 1- Red-Yellow Latosol with 1.55% of organic matter; 2- Red-Yellow Latosol with 2.84% of organic matter; 3- Red-Yellow Latosol with 3.97% of organic matter; 4- Red-Yellow Latosol with 6.35% of organic matter; 5- Red-Yellow Latosol with 7.28% of organic matter.

Calcium chloride was supplied by Vetec, Brazil. Tebuthiuron (4-amino-3,5,6-trichloropyridine-2-carboxylic acid, 99.6%) (Table 3) was obtained from Sigma-Aldrich, Germany. The stock solution of tebuthiuron was prepared using a 99.0% purity standard at the concentration of 1,000 mg L⁻¹.

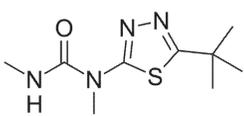
The chromatographic conditions for the analyses consisted in a mobile phase composed of a mixture of water and methanol in a 20:80 (v/v) ratio, with a 1.0 mL min⁻¹ flow and a 20 µL injection volume. The column temperature was 40 °C, and the wavelength used for the reading was 254 nm. The areas obtained in the chromatograms were quantified and compared by through the external calibration method, and this methodology was satisfactory for all method validation parameters.

The equilibrium time required for tebuthiuron sorption was determined by the batch equilibrium method. The method consists in weighing inside polypropylene Falcon tubes 2.00 g of soil sample and, afterwards, adding 10 mL of herbicide solution with a concentration equal to 1.00 mg L⁻¹ in 0.01 mol L⁻¹ CaCl₂. The tubes were agitated vertically for different time intervals (0.5, 1, 2, 4, 12, 16, 20, 24 and 30 h) at a temperature of 27 ± 2 °C and centrifuged for 4 minutes at 3,000 rpm. A portion of the supernatant was filtered in a 0.45 µm MCE membrane for further chromatographic analysis.

Tebuthiuron sorption in the soil samples was evaluated using working solutions prepared from the stock solution, at the concentrations of 0.50; 1.0; 1.5; 2.0; 2.5 and 3.0 mg L⁻¹, in 0.01 mol L⁻¹ CaCl₂. From these solutions, 10 mL were transferred to polypropylene Falcon tubes containing 2.00 g of soils. These tubes were then agitated vertically for the equilibrium time determined in the previous tests and centrifuged for four minutes at 3,000 rpm; the supernatant was filtered on a 0.45 µm MCE membrane for further chromatographic analysis. All analyses were performed in triplicate, and the obtained data were submitted to regression analysis in order to interpret the results.

After analyzing the data, the amount of herbicide sorbed to the soil (C_s) in mg kg⁻¹ was determined by the difference between the amount of standard solution initially added to the soil (C_p) in mg L⁻¹ and the quantity found in the equilibrium solution (C_e), in mg L⁻¹. With the encountered C_e and C_s values, the sorption constants were determined, where K_f and 1/n are empirical constants representing the sorption capacity and intensity, respectively.

Table 3 - Characteristics and structural formula of tebuthiuron

Structural formula	Characteristic
	Molecular Formula: C ₉ H ₁₆ N ₄ OS
	Molar Mass (g mol ⁻¹): 228.31
	pKa: non-dissociated
	Water solubility (mg L ⁻¹): 2,500

Available at: <http://sitem.herts.ac.uk/aeru/iupac/Reports/614.htm>.

The study about desorption was conducted by removing the supernatant from all tubes containing the soils after the sorption test, and adding to them 10 mL of the herbicide-free solution of CaCl₂ 0.01 mol L⁻¹. In order to homogenize soil and solution, the tubes were shaken manually for 10 seconds. Subsequently, they were subjected to vertical agitation for the same time as the sorption tests and then centrifuged. The supernatant was filtered on a 0.45 µm MCE membrane for further chromatographic analysis.

In the desorption tests, calculations were also made to determine K_f and $1/n$ and, with this, to estimate the desorption capacity of the herbicide through soils with different organic matter contents. The hysteresis index was also calculated by dividing $1/n$ desorption values by the sorption ones (Silva et al., 2007).

The analyses were performed in triplicate, and data were submitted to regression analysis to interpret the results; the coefficients of the equations tested by t test were at 5% significance.

RESULTS AND DISCUSSION

The equilibrium time of tebuthiuron (the concentration of the herbicide in the soil solution becomes constant) was 12 hours for all the used substrates (Figure 1); this differs from the 7 hour equilibrium time observed by Faria et al. (2013) in Brazilian Latosols. The sorption rate depends on the kinetics of the molecule in the soil solution and on the availability of sites that are susceptible to adsorbing the herbicide; soil organic matter is one of the most important herbicide sorption sites (Mirzaei et al., 2013).

Generally speaking, the sorption process occurs in two steps. Initially, the higher availability of adsorption sites on the surface of the aggregates and the high herbicide concentration in the soil solution promote the quick sorption of the molecule in the soil (Marco-Brown et al., 2014). In the second step, the sorption rate is lower, due to the lower diffusion and saturation of superficial sites. At this stage, the herbicide is adsorbed by the sites located in the micropores of the soil, but the herbicide molecules that are in the soil solution are repelled by the molecules adsorbed on the surface of the aggregate, reducing the contact between herbicide and micropore spaces. Moreover, the lower herbicide concentration in the soil solution reduces the diffusion of the molecule (Liu et al., 2010; Faria et al., 2013).

Tebuthiuron sorption was determined by an analytical curve constructed with growing herbicide concentrations. Linearity in the working range was determined at the concentration from 0.05 to 3.0 mg L⁻¹, with a correlation coefficient of 0.99 (Figure 2), indicating good linearity of the method response to tebuthiuron at the used concentration. Detection and quantification limits were 0.64 and 2.97 mg L⁻¹, respectively. In the chromatograms of the five substrates, no interferences were found as for the retention time of tebuthiuron; this indicates that the method is selective.

Tebuthiuron sorption was lower in the soil without the addition of organic matter (Figure 3). The sorption of herbicides in soil is associated with the presence of available sites that are capable of binding to the molecule (Kearns et al., 2014). Tebuthiuron is a non-ionic herbicide and it can bind with hydrophobic and hydrophilic groups that are present in both organic matter and clay colloids, through covalent hydrogen and Van der Waals bondings (Li et al., 2003; Kovaios et al., 2006). Moreover, sandy soils have a low capacity to adsorb herbicides, due to their lower electrostatic surface, when compared to clayey soils (Firmino et al., 2008). Thus, the low sorption of tebuthiuron in substrate 1 may be associated to low organic matter content and soil texture.

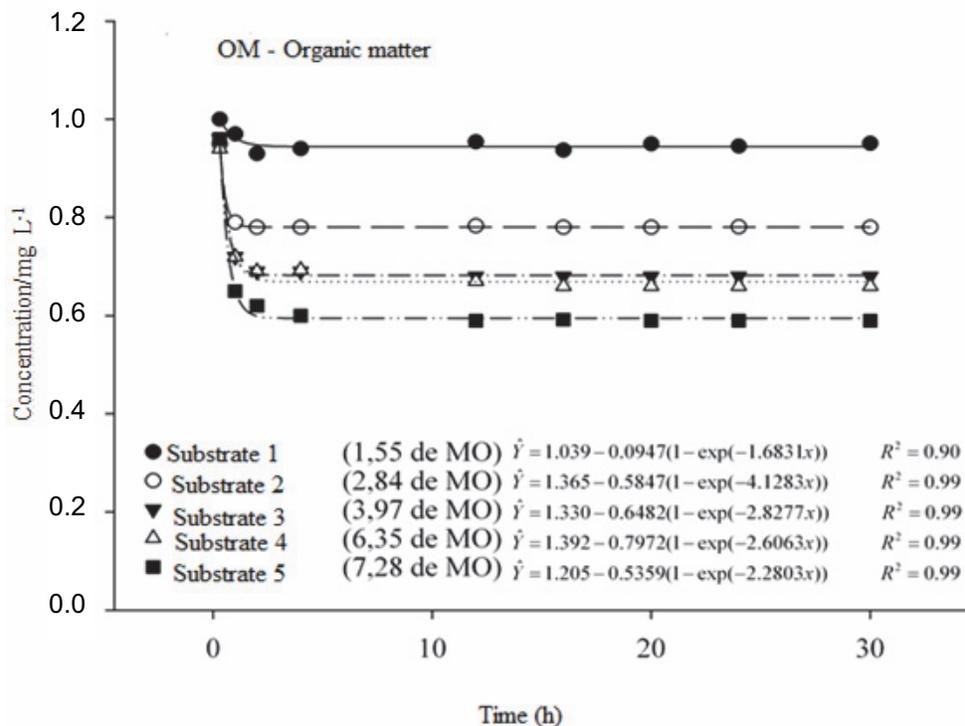


Figure 1 - Concentrations of tebuthiuron in soil solution, according to time, in Red-Yellow Latosol with different organic matter (OM) contents.

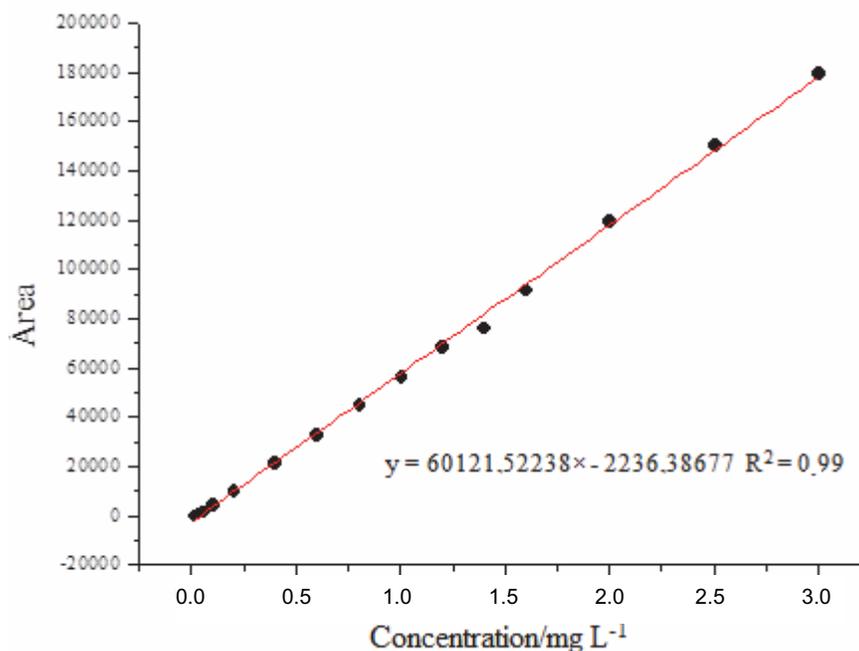


Figure 2 - Tebuthiuron calibration curve in CaCl_2 0.01 mol L⁻¹, obtained by high performance liquid chromatography.

Tebuthiuron sorption was increased with a growth in the soil organic matter content (Figure 3). The sorption process of an herbicide in the soil may change as the physical-chemical characteristics of the herbicide are altered (Ololade et al., 2015). The direct or conventional planting system and soil management practices, such as liming, adding gypsum and fertilization, can modify soil characteristics and affect the sorption of herbicides (Ouyang et al., 2016). Herbicides from the group of photosystem II inhibitors have their sorption reduced when the soil

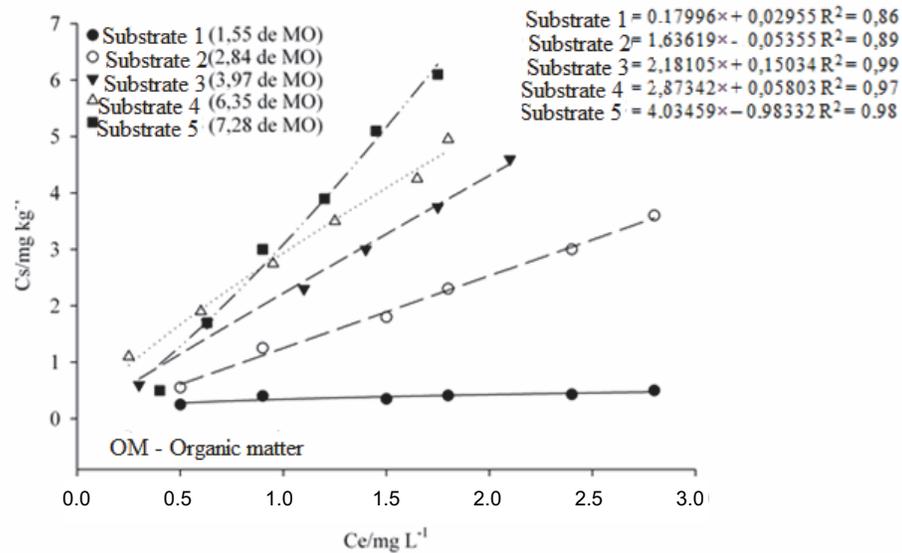


Figure 3 - Estimates of Freundlich sorption isotherms for tebuthiuron in Red-Yellow Latosol with different organic matter contents.

pH becomes more alkaline. This increases the motility of the molecule and increases the contamination potential of groundwater and springs by the herbicide (Refatti et al., 2014). In this case, when incubating with increasing amounts of bovine manure, the organic matter contents of the Red-Yellow Latosol increased, and so did the hydrophobic, carboxylic and hydroxylic sites capable of adsorbing the herbicide. Consequently, the sorption of tebuthiuron was increased.

As in the study about sorption, for the desorption of tebuthiuron, the parameters K_F , $1/n$ and R^2 for the isotherm were calculated and the hysteresis index for the five substrates was obtained. The substrates with higher contents of organic matter had lower hysteresis values (Table 4). The energy needed for the sorption and desorption of herbicides may be different and depends on the interaction force between soil and molecule. Low hysteresis indicates a greater difficulty for the previously sorbed herbicide to be desorbed (Koskinen et al., 2006), that is, the energy to promote the desorption of the herbicide is higher than the one required for the sorption process (Koskinen et al., 2006). The organic matter of the soil usually presents great group diversity (Velten et al., 2011; Armanious et al., 2014). Thus, herbicide molecules and organic matter in the soil establish distinct connections, and the covalents associated to secondary connections, such as hydrogen and Van der Waals bondings (Armanious et al., 2014). The strength of the covalent bonding between components is high and, when other interactions occur simultaneously, the energy for the disruption of these bondings is high; this can reduce herbicide desorption (Benoit et al., 2008; Trubetskaya et al., 2014; Okada et al., 2016).

It is possible to conclude that the tebuthiuron sorption is directly proportional to the organic matter content, and the desorption is inversely proportional to the sorption. Based on this, it is

Table 4 - Values of K_F , $1/n$ and R^2 for Freundlich isotherms and hysteresis index in Red-Yellow Latosol with different levels of organic matter for each substrate

Organic matter content	Freundlich parameters - Sorption			Freundlich parameters - Desorption			Hysteresis (H)
	K_F	$1/n$	R^2	K_F	$1/n$	R^2	
⁽¹⁾ Substrate 1	0.180	1.070	0.883	0.267	1.026	0.889	1.486
⁽²⁾ Substrate 2	1.636	0.883	0.915	0.334	1.017	0.903	0.204
⁽³⁾ Substrate 3	2.181	1.413	0.995	0.248	0.927	0.854	0.114
⁽⁴⁾ Substrate 4	2.873	1.142	0.984	0.297	1.063	0.832	0.103
⁽⁵⁾ Substrate 5	4.034	0.103	0.991	0.406	0.742	0.942	0.100

⁽¹⁾ Red-Yellow Latosol with 1.55% of organic matter; ⁽²⁾ 2.84% of organic matter; ⁽³⁾ 3.97% of organic matter; ⁽⁴⁾ 6.35% organic matter; ⁽⁵⁾ 7.28% of organic matter.

possible to state that knowing the organic matter content in the soil, before recommending tebuthiuron, is an essential condition to recommend the application of doses, seeking agronomic efficiency and reducing the environmental risks deriving from the use of this herbicide.

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