PLANTA DANINHA

SBCPD
SOCIEDADE BRASILEIRA DA
CIÊNCIA DAS PLANTAS DANINHAS
<http://www.sbcpd.org>

ISSN 0100-8358 (print)
1806-9681 (online)

Article

Sorption and Desorption of Tembotrione and its Metabolite AE 1417268 in Soils with Different Attributes

Sorção e Dessorção do Tembotrione e do Seu Metabólito AE 1417268 em Solos com Diferentes Atributos

FARIA, A.T.[1]
FIALHO, C.A.[1]
SOUZA, M.F.[2]*
FREITAS, N.M.[3]
SILVA, A.A.[1]

ABSTRACT - Tembotrione is registered in Brazil for maize and is used in large areas of the country in each harvest. In recent years, producers have reported carryover effects of this herbicide in succeeding crops to maize. This fact can be attributed to tembotrione recommendations without knowing their interactions with tropical soils colloids. In this study, using high-performance liquid chromatography, it was possible to evaluate the influence of chemical and physical attributes on the sorption and desorption of tembotrione, as well as its metabolite AE 1417268, on seven soils from different regions of Brazil. The coefficients referring to sorption and desorption, as well as the hysteresis index (Kf, 1/n and H) of tembotrione and its metabolite were influenced by pH, clay content and organic matter. In soil samples with low levels of clay and organic matter, values of sorption coefficients were reduced as pH increased. The desorption of tembotrione and its metabolite in all soils were low, mainly in the clayey ones and in soils with higher organic matter content. The sorption of tembotrione and its metabolites varies with the attributes of soil, presenting a direct relation with clay and organic matter contents and an inverse one with soil pH. The desorption of tembotrione and its metabolite decreased with the increase in clay and organic matter contents in the evaluated soils.

Keywords: herbicide, sorption coefficient (K_f), hysteresis, environmental impact.

RESUMO - O tembotrione é registrado no Brasil para a cultura do milho, sendo aplicado em extensas áreas do país em cada safra agrícola. Nos últimos anos, produtores relataram efeitos carryover desse herbicida em culturas sucessivas ao milho. Esse fato pode ser atribuído a recomendações do tembotrione sem o conhecimento de suas interações com os coloides dos solos tropicais. Nesta pesquisa, utilizando a cromatografia líquida de alta eficiência, foi avaliada a influência dos atributos químicos e físicos na sorção e dessorção do tembotrione, bem como do seu metabólito AE 1417268, em sete solos de diferentes regiões do Brasil. Os coeficientes referentes à sorção e dessorção, além do índice de histerese (Kf, 1/n e H) do tembotrione e do seu metabólito, foram influenciados pelo pH, teor de argila e matéria orgânica. Em solos com baixos teores de argila e matéria orgânica, os valores dos coeficientes de sorção foram reduzidos com o aumento do pH. A dessorção do tembotrione e do metabólito em todos os solos foi baixa, principalmente naqueles argilosos e com maiores teores de matéria orgânica. A sorção do tembotrione e seu metabólito varia com os atributos dos solos, apresentando relação direta com os teores de argila e de matéria orgânica e inversa com o pH dos solos. A dessorção do tembotrione e do seu metabólito reduziu com o aumento dos teores de argila e matéria orgânica dos solos avaliados.

Palavras-chave: herbicida, coeficiente de sorção (K_f), histerese, impacto ambiental.

*** Corresponding author:**
<freitasouza@yahoo.com.br>

Received: September 5, 2016
Approved: June 28, 2017

Planta Daninha 2019; v37:e019168791

[1] Universidade Federal de Viçosa, Viçosa-MG, Brasil; [2] Universidade Federal Rural do Semi-Árido, Mossoró-RN, Brasil; [3] Universidade Estadual de Maringá, Maringá-PR, Brasil.

Doi: 10.1590/S0100-83582019370100096

INTRODUCTION

Approximately 70% of all pesticides applied in agricultural areas have soil as their final destination (Law, 2001), and they can follow different routes, such as volatilization, drainage and/or leaching (Rojas et al., 2015). In the soil, agrochemicals can migrate to different compartments of the environment, becoming a source of contamination for both air and water, and this risk of environmental contamination by some pesticide depends on its time of permanence and mobility in the soil (El Bakouri et al., 2010).

Agrochemicals can be retained by the organic and/or mineral fraction of soil, and degraded (photochemically, chemically or biologically), volatilized or leached to deeper layers. These factors determine the amount of herbicide present in the soil solution that can be absorbed by plants or degraded by the soil microbiota (Ahmad et al., 2011), affecting the persistence of these compounds.

Tembotrione 2-[2-chloro-4-methylsulfonyl-3-(2,2,2-trifluoroethoxymethyl) benzoyl] - cyclohexane-1,3-dione (Figure 1) was launched in 2008 in Brazil for post- emergence use on maize (Tarara et al., 2009). In the soil, this herbicide can be absorbed by the roots of the plants and translocated via xylem and phloem. It presents water solubility of 28 g L^{-1} at pH = 7 and pK_a = 3.2 (Barchanska et al., 2016). It is an herbicide from the triketone group and its mechanism of action is the inhibition of the enzyme 4-hydroxyphenyl-pyruvate-dioxygenase; it inhibits the formation of carotenoids, which are responsible for the protection against the excessive energy generated by the absorption of light into the leaf. This excessive energy destroys cell membranes, leading sensitive plants to death (Silva et al., 2007).

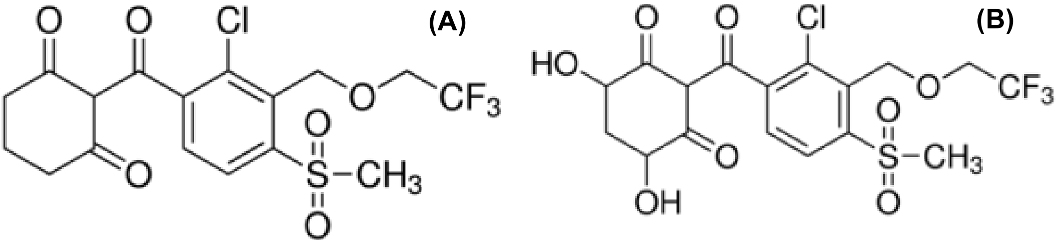

Figure 1 - Structural Formula of Tembotrione (A) and its Metabolite AE 1417268 (B).

When tembotrione reaches the soil, it presents high longitudinal mobility (PMRA, 2012) and variable persistence (mean half-life of 127 days) in the environment, which is influenced by the organic matter content, soil texture and pH (Rojas et al., 2015). Thus, under conditions of greater persistence of this herbicide, the risk of contamination of groundwater and surface water is increased. In addition, maize cultivation areas in the Brazilian cerrado have reports of the carryover effect of this herbicide, especially on some vegetables. Thus, it is important to know the sorption, desorption, half-way and leaching of tembotrione in tropical soils, especially in Brazil, so that this product is recommended in a safe way. Another important factor is the formation of metabolites with herbicidal properties, such as AE 1417268 (Figure 1).

Metabolite AE 1417268 (2-{2-chloro-4-mesyl-3-[(2,2,2-trifluoroethoxy) methyl] benzoyl}-4,6-dihydroxycyclohexane-1,3-dione), with a pKa value of 2.49 and molecular formula ($C_{17}H_{16}ClF_3O_8S$) (Faria, 2016), has an herbicidal action and is poorly studied in the environment.

The objective of this work was to evaluate the influence of chemical and physical attributes on the sorption and desorption of tembotrione, as well as its metabolite AE 1417268, in seven soils from different regions of Brazil.

MATERIAL AND METHODS

Evaluated soils: collection and sample preparation

Samples from different soils were collected at depths from 0 to 20 cm: Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais (LVAV), Red-Yellow Latosol from the city of Rio Paranaíba - Minas Gerais (LVAR), Yellow Latosol from Sooretama - Espirito Santo (LA), Red-Yellow

Latosol from the municipality of Gurupi -Tocantins (LVAG) and Organosol (OR) from the municipality of Venda Nova do Imigrante - Espirito Santo. The samples of Red-Yellow Latosol from the municipalities of Viçosa and Gurupi were divided in two; part of the soil was maintained in the original condition, and on the other part, liming with $CaCO_3$ was performed using an acid neutralization curve. This resulted in two more samples, totaling seven soils.

Determination of tembotrione and metabolite AE 1417268

The determination of tembotrione and metabolite AE 1417268 (2-{2-chloro-4-mesyl-3-[(2,2,2-trifluoroethoxy)methyl] benzoyl}-4,6-dihydroxycyclohexane-dione), obtained from a stock solution of 1,000 mg L^{-1} of tembotrione and its metabolite (99.8% purity, provided by Sigma-Aldrich), in methanol in the different soil samples was done by high efficiency liquid chromatography. The used equipment was a Shimadzu LC 20AT chromatograph, with a DAD detector (Shimadzu SPD 20A) and stainless steel column (Shimadzu VP-ODS Shim-pack 280 mm x 4.6 mm d.i. x 5 µm particle diameter). The chromatographic conditions for the analysis were: mobile phase composed of water and acetonitrile in the ratio of 40:60 (v/v), flow of 1.4 mL min^{-1}, injection volume of 20 µL and wavelength of 190 nm. The retention time of tembotrione under these conditions was approximately 5.9 min, and that of metabolite AE 1417268, 5.4 min. The concentration was estimated by the external calibration method. The identification was made by comparing the retention times of the peaks of the analytical standards of tembotrione and its metabolite with the peaks found in the chromatograms of the samples.

Determination of the equilibrium time

The determination of the time required for the equilibrium of the herbicide concentration between soil and soil solution, besides the sorption and desorption analyses for tembotrione and its metabolite, were performed according to OECD recommendations (2000).

A $CaCl_2$ solution of 0.01 mol L^{-1} containing 10 mg L^{-1} of tembotrione and/or metabolite was prepared as stock solution. From this solution, 10.0 mL were added into polypropylene tubes containing 2.00 g of soil. These tubes were then placed under vertical stirring, at different times, at the rate of 80 rpm (0.5, 1.0, 2.0, 3.0, 4.0, 8.0, 12, 16, 24, and 30 h), at the temperature of 27 ± 2 °C. After stirring, the samples were centrifuged at 2,260 *g* for seven minutes. Subsequently, 2 mL of the supernatant were filtered in a Milipore filter with a 0.45 µm PTFE membrane, for later analysis by high performance liquid chromatography (HPLC). The equilibrium time was the one starting from which the concentration of the solution remained constant.

Sorption kinetics

The sorption of tembotrione and its metabolite was evaluated from working solutions at concentrations of: 0.5; 1.0; 1.5; 2.0; 2.5; and 3.0 mg L^{-1} in 0.01 mol L^{-1} $CaCl_2$. Ten ml of these solutions were added into polypropylene tubes containing 2.00 g of soil. These tubes were placed under stirring at a temperature of 27 ± 2 °C, for the previously determined equilibrium time. After stirring, the samples were centrifuged at 2,260 x *g* for seven minutes. The supernatant was removed and filtered in a 0.45 µm Milipore filter for further chromatographic analysis.

Concentrations of the herbicide and/or metabolite sorbed to the soil (Cs), in mg kg^{-1}, were calculated by the difference between the concentration in the standard solution that had been initially added to the soil and the amount found in the equilibrium solution (Ce). With these values, graphs were constructed, relating Cs versus Ce, adjusting to the Freundlich equation (Cs = Kf Ce 1/n) in order to obtain the sorption coefficients, where Kf and 1/n are empirical constants that represent the capacity and sorption intensity, respectively (Peruchi et al., 2015).

Desorption kinetics

Desorption was evaluated using the soil samples resulting from the sorption process. Two ml of the 0.01 mol L^{-1} $CaCl_2$ solution without the herbicide were added to the tubes used in the sorption quantification, completing the volume with 10 mL in each tube. These tubes were restirred for the same time and at the same temperature at which sorption tests were conducted. After stirring, the samples were centrifuged at 2,260 x *g* for seven minutes. From the supernatant, 2 mL were filtered in a 0.45 µm Milipore filter, for later chromatographic analysis and determination of the new concentration.

The amount of herbicide and soil-desorbed metabolite (Cd), as mg kg^{-1}, was calculated by the difference between the soil-sorbed amount, as mg kg^{-1}, and the amount that returned to the equilibrium solution (Ce), as mg L^{-1}. Data were used to adjust the Freundlich equation to the desorption (Cs = Kf Ce1/n), in order to obtain the desorption coefficients. The hysteresis index was also calculated, dividing the (1/n) of the sorption by the (1/n) of the desorption (Peruchi et al., 2015).

The relationship between soil attributes (organic matter, clay, sand, silt and soil pH) and sorption and desorption coefficients was established by the Pearson's correlation, using the STATISTICA 7® software.

RESULTS AND DISCUSSION

Equilibrium time

The equilibrium time for the sorption of tembotrione and the AE 1417268 metabolite was approximately five hours in all soils; however, a period of eight hours was adopted as a guarantee that equilibrium had occurred. Sorption kinetics was characterized in two distinct phases (Figure 2). In the first one, sorption happened quickly due to the greater number of available sites for the occurrence of binding on the surface of soil aggregates. As tembotrione molecules interacted with the soil binding sites, sorption became slower and more difficult. The competition between herbicide molecules and other tembotrione-like affinity compounds with soil sites may have reduced the adsorption rate of the herbicide to the soil (Mirzaei et al., 2013).

In addition, the saturation of the sites increased the repulsion force between the molecules found in the solid phase and in the solution (Khenifi et al., 2010; Liu et al., 2010; Rocha et al., 2013), making tembotrione sorption difficult. The difference in the sorption rate can also be attributed to adsorption processes on different surfaces: the first phase associated with the

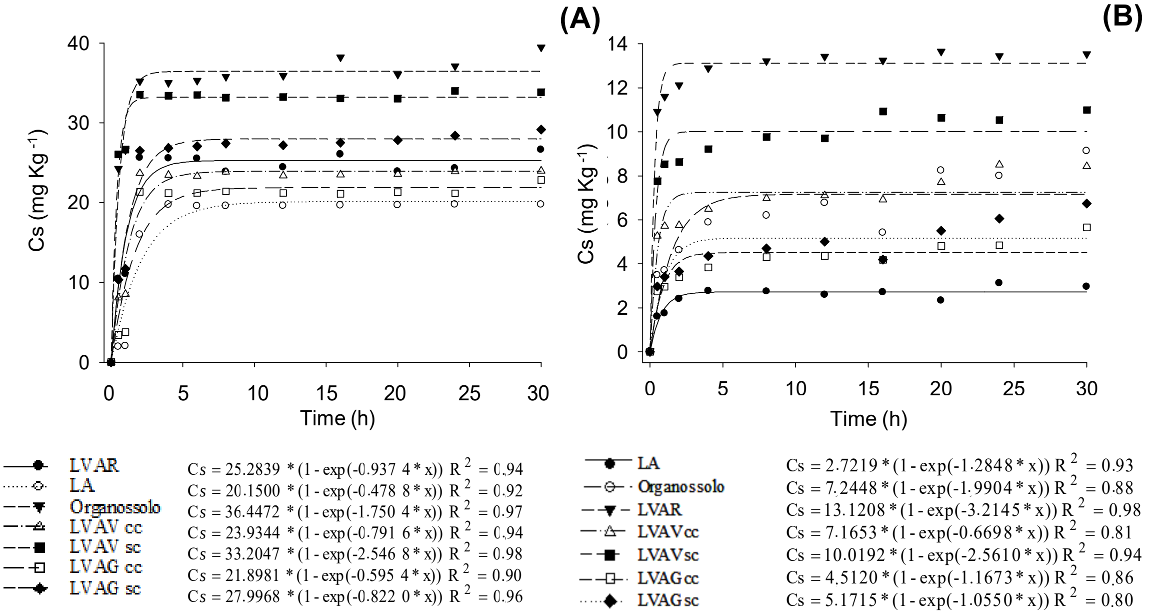

Figure 2 **-** Sorption kinetics for tembotrione (A) and metabolite AE 1417268 (B) in samples of a Yellow Latosol of Sooretama - Espirito Santo (LA), Red-Yellow Latosol of Rio Paranaíba - Minas Gerais (LVAR), Red-Yellow Latosol Viçosa - Minas Gerais (LVAV) with and without liming, Red-Yellow Latosol of Gurupi - Tocantins (LVAG) with and without liming, and Organosol of Venda Nova do Imigrante - Espirito Santo, according to time.

external surface, and the second one, the inner layers, being energetically disadvantaged (Marco-Brown et al., 2014). At high concentrations, sorption does not increase due to the saturation of the sites by the available elements, unlike what occurs in low concentrations (Khadivinia et al., 2014).

Tembotrione sorption

The sorption isotherms of tembotrione and its metabolite were adjusted using the Freundlich model and were characterized as type L (Figure 3). This means that the equilibrium between the compound in solution and the compound adsorbed to the particles does not occur instantly. Sorbate molecules occupy the sorption sites over time, reducing the amount of available sites for the herbicide molecules to bind to the soil (Rojas et al., 2015). Sorption is influenced by the mass transfer of the solute found in the soil solution to the surface of the colloid, by the diffusion of the film around the adsorbent particles and in the pores of the adsorbent, and by the adsorption on the solid surface and internal diffusion of solute (Kadous et al. al., 2010; Rojas et al., 2015). From the adjusted Freundlich equation, the sorbed amount increases as the concentration of pesticide in the solution rises. This means that sorption is non-linear (Rojas et al., 2015). The lack of linearity is due to the specific interactions between the polar groups of the pesticide and the organic matter of the substrate (De Wilde et al., 2009).

The sorption of tembotrione and AE 1417268 metabolite was higher in the Organosol, being close to 12 mg kg^{-1} at the highest tested concentration, and lower in the Yellow Latosol, with Kf values of 46 and 0.6, respectively (Figure 3).

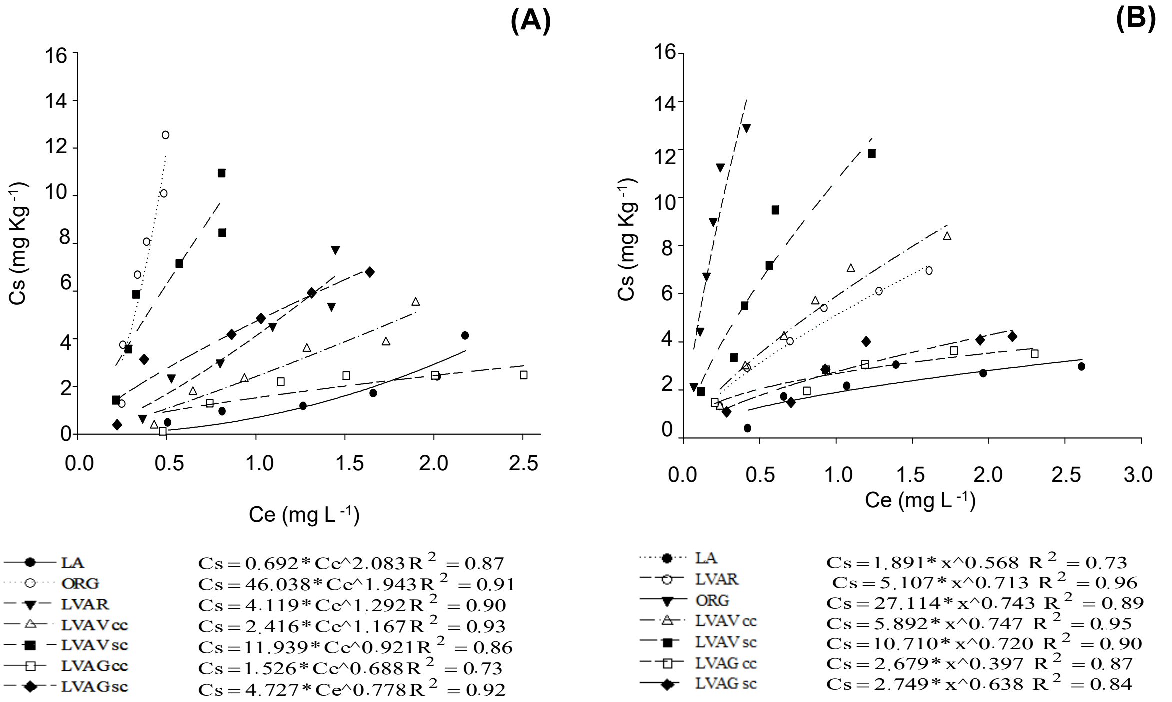

Figure 3 **-** Sorption of tembotrione (A) and metabolite AE 1417268 (B) in samples of a Yellow Latosol of Sooretama - Espirito Santo (LA), Red-Yellow Latosol of Rio Paranaíba - Minas Gerais (LVAR), Red-Yellow Latosol of Viçosa - Minas Gerais (LVAV) with and without liming, Red-Yellow Latosol of Gurupi - Tocantins (LVAG) with and without liming, and Organosolo of Venda Nova do Imigrante - Espirito Santo (amount of herbicide sorbed to soil - Cs and in equilibrium solution - Ce).

The higher sorption of tembotrione and the metabolite AE 1417268 in the Organosol can be explained by the higher amount of organic matter (Table 1), which elevates the hydrophobic interactions, as well as hydrogen bonds involving aromatic and aliphatic groups with the organic colloids of the soil (Sun et al., 2011; Zhang et al., 2011).

The sorption coefficient ($Kf_{(s)}$) correlated positively with the soil organic matter (Table 2). Organic matter is the most important factor for the sorption of pesticides with low water solubility,

Table 1 - Results of chemical and physical analysis of soils used in the research[(1)]

Soil	pH	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	(t)	V	m	OM
	(H_2O)	(mg dm^{-3})		(cmol$_c$ dm^{-3})					(%)		
LVAG[(2)]	5.70	0.80	79.00	0.99	0.52	0.00	4.70	1.71	26.70	0.00	3.00
LVAG cc[(3)]	6.50	0.80	79.00	1.30	0.70	0.00	4.50	2.30	33.50	0.00	3.00
LVAV[(4)]	5.10	0.60	9.00	0.04	0.06	1.60	5.30	1.66	2.90	90.70	2.07
LVAV cc[(5)]	6.50	0.60	9.00	0.34	0.15	0.00	2.52	0.79	60.00	0.00	2.07
LVAR[(6)]	6.50	2.60	39.00	1.20	0.40	0.00	2.64	1.70	39.00	0.00	2.18
LA[(7)]	6.30	9.60	110.00	2.90	1.00	0.00	1.32	4.18	76.00	0.00	2.20
Organosol[(8)]	5.00	18.10	185.00	5.10	3.00	0.60	26.64	9.17	25.00	31.00	20.20

	Coarse s.	Fine s.	Silt	Clay	Textural class
	(dag kg^{-1})				
LVAG	25.00	30.00	6.00	39.00	Clayey-sandy
LVAV	11.00	10.00	17.00	62.00	Very clayey
LVAR	10.00	33.00	16.00	41.00	Clayey
LA	60.00	19.00	1.00	20.00	Sandy loam
Organosol	14.00	20.00	30.00	36.00	Clayey loam

[(1)] Analyses carried out in the Laboratório de Análises de Solo Viçosa, according to the methodology of the Empresa Brasileira de Pesquisa Agropecuária - Embrapa (1997); (t) = effective cation exchange capacity; V = base saturation; m = saturation for Al^{+3}; OM = organic matter; [(2)] Red-Yellow Latosol from the municipality of Gurupi - Tocantins; [(3)] Red-Yellow Latosol from the municipality of Gurupi - Tocantins after liming; [(4)] Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais; [(5)] Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais after liming; [(6)] Red-Yellow Latosol from the municipality of Rio Paranaíba - Minas Gerais; [(7)] Yellow Latosol from the municipality of Sooretama - Espirito Santo; and [(8)] Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo.

due to the important absorbent surfaces of this layer (Cox et al., 2000). This was confirmed by the mobility reduction of some herbicides after the addition of organic matter to the soil (Martin et al., 2012; Fenoll et al., 2014) because of the greater specific surface area that elevates the available adsorption sites (Kearns et al., 2014; Rojas et al., 2015). The organic matter weathering stage may also influence tembotrione sorption (García-Jaramillo et al., 2014), due to differences in the physical-chemical properties of this soil component (Rojas et al., 2015).

The lower sorption of tembotrione and AE 1417268 metabolite in the Yellow Latosol is due to the lower clay content in these soils, as reported for a Cambisol from Germany (Bontempo et al., 2016). Generally speaking, the binding of a compound with soil colloids occurs by surface adsorption on the hydroxyl and carboxylic groups, either by hydrogen bonds and/or by Van der Waals interactions (Vivian et al., 2007). However, the clays found may be obstructed by amorphous compounds of Fe clusters and other metals that are holders for the oxidic minerals, reducing the cation exchange capacity (CTC) of soils (Stipicevic et al., 2014), as well as porosity and the specific surface of these adsorbents (Paul et al., 2010), reflecting in a lower sorption of tembotrione in soils. In sandy soils, this effect is more important due to the lower amount of clay.

In addition, sorption depends on the pKa and the hydrophobicity of the chemical product. This indicates that the tembotrione metabolite would be more polar than the original compound, and this explains the lower Kf values in most of the tested soils (Figure 3). The same fact was observed for indaziflam and its metabolite, highlighting that sorption, for both herbicides, depends on the soil pH (Trigo et al., 2014).

Tembotrione and the metabolite were more sorbed in soils without acidity correction (Red-Yellow Latosols from Viçosa and Gurupi), compared to soils with correction (Figure 3). In

Table 2 - Pearson correlation between the sorption and desorption coefficients of tembotrione and its metabolite and the physicochemical attributes of the studied soils

	pH	OM	Sand	Clay	Silt
$Kf_{(s)}$	-0.76*	0.97*	-0.34	0.82*	0.05
$Kf_{(d)}$	0.74*	-0.97*	0.33	-0.82*	-0.07
$Kf_{(sm)}$	-0.75*	0.93*	0.47	0.89*	0.08
$Kf_{(dm)}$	0.67**	-0.99*	-0.31	-0.82*	-0.11

* Significant correlation at $p<0.05$. ** Significant correlation at $p<0.06$. (t) = effective cation exchange capacity; OM = organic matter; $Kf_{(s)}$ = sorption coefficient; $Kf_{(d)}$ = desorption coefficient; $Kf_{(sm)}$ = sorption coefficient of the metabolite; $Kf_{(dm)}$ = sorption coefficient of the metabolite.

addition, soil pH had a negative correlation with $Kf_{(s)}$ values (Table 2). The higher sorption of tembotrione and AE 1417268 metabolite in soils with lower pH values (without liming) is due to the fact that in these soils there are more surfaces allowing hydrogen bonds with proton receptor groups (-N, -H, - O, -C=O) (Tian et al., 2010) and also proton donors (NH_2) (Eibisch et al., 2015). At low pH values, the formation of positive charges occurs due to the protonation of the -OH groups (Hu and Liu, 2003), with the attraction between soil and herbicide loads occurring, resulting in a greater sorption of tembotrione and its metabolite AE 1417268. The increase in soil pH reduced the number of cationic species (Trigo et al., 2014) and the sorption of tembotrione and its metabolite. On the other hand, the sorption of polar (basic) aromatic herbicides by electrostatic forces is higher, due to the hydrophilic sorption sites created by the deprotonation of the surfaces (Shi et al., 2015).

Tembotrione, as well as its metabolite, present the characteristics of a weak acid, being able to undergo repulsion by negative groups on the surface of soil; thus, only the part in the molecular form would be adsorbed (Trigo et al., 2014). Generally speaking, when the soil pH is lower than pKa, the herbicide will be mainly in the neutral form, and the hydroxyls on the surfaces of oxides and organic matter complexes will be positively charged at this pH range, thus providing binding sites for the herbicide (Muller et al., 2014). In soils with higher pH values, herbicides such as 2.4-D, also of acid nature, hydrophobic interactions with organic matter are more important (Muller et al., 2014). Metal ions may also influence the sorption of herbicides in the soil. As pH increases, there is the precipitation of these ions, also reducing the interaction of herbicides with these metals (Khadivinia et al., 2014). When available, metal cations electrostatically attract negatively charged compounds (Lafferty and Loeppert, 2005; Shimizu et al., 2010), forming a cationic bridge (Nagar et al., 2014), which can raise the sorption of herbicides with a residual negative charge. Thus, it is evident that, depending on the pH and besides the content and type of clay, sorption can be influenced by high percentages of Fe/Al hydroxides and also by the Ca/Mg content in the soil (Quazi et al., 2011).

Desorption of tembotrione and AE 1417268 metabolite

The desorption of tembotrione was low in all soils (observing hysteresis values, compared to other soils), but it was higher in the Yellow Red Latosol from Gurupi, with low hysteresis index, both with or without liming (Figure 4 and Table 3). A positive correlation between desorption coefficients ($Kf_{(d)}$, $Kf_{(dm)}$) and pH, and a negative one between $Kf_{(d)}$ and $Kf_{(dm)}$ and organic matter and clay were found in the evaluated soils (Table 2). This may be linked to the small portion of the herbicide strongly adsorbed to colloids (Stipicevic et al., 2014). A lower desorption of the compound in the soil is directly associated to higher levels of clay and organic matter, as reported for diuron, where an inverse correlation was observed between the organic matter content and the desorption of this herbicide in Latosols (Rocha et al., 2013). Generally, the sorption of an herbicide is determined without considering the desorption process, which is as important as the sorption process to predict the bioavailability of the pesticide in the soil solution (Rojas et al., 2015). Hysteresis (H) is a measure of the desorption degree. Low H values mean that desorption proceeds rapidly in the soil. High desorption for polar compounds can occur when there is dissolved organic matter in the solution (Zhang and He, 2013).

The desorption of the metabolite was low in all soils (observing the hysteresis values), but it was lower in the Yellow Latosol, with a higher hysteresis index (Figure 4 and Table 3).

The lower desorption of the tembotrione metabolite in the Yellow Latosol (Table 3) may be due to the clay types of this soil, which can retain herbicide molecules very strongly between the layers, making desorption difficult (Passos et al., 2013). The most active clays, such as montmorillonite, have a higher ability to suck herbicides, as well as high levels of organic matter (Prado et al., 2014). A high hysteresis means greater difficulty of the previously sorbed herbicide to be desorbed (Koskinen et al., 2006) and is related to the interactions between the soil particles surfaces and the herbicide, whether chemical or biological. Conditions of equilibrium, kinetics, effects and high energy binding in soils with higher sand contents help the desorption of the herbicide that was previously sorbed (Koskinen et al., 2006).

The sorption of tembotrione and metabolite AE 1417268 is directly proportional to the organic matter and clay content, and inversely proportional to soil pH. On the other hand, the desorption

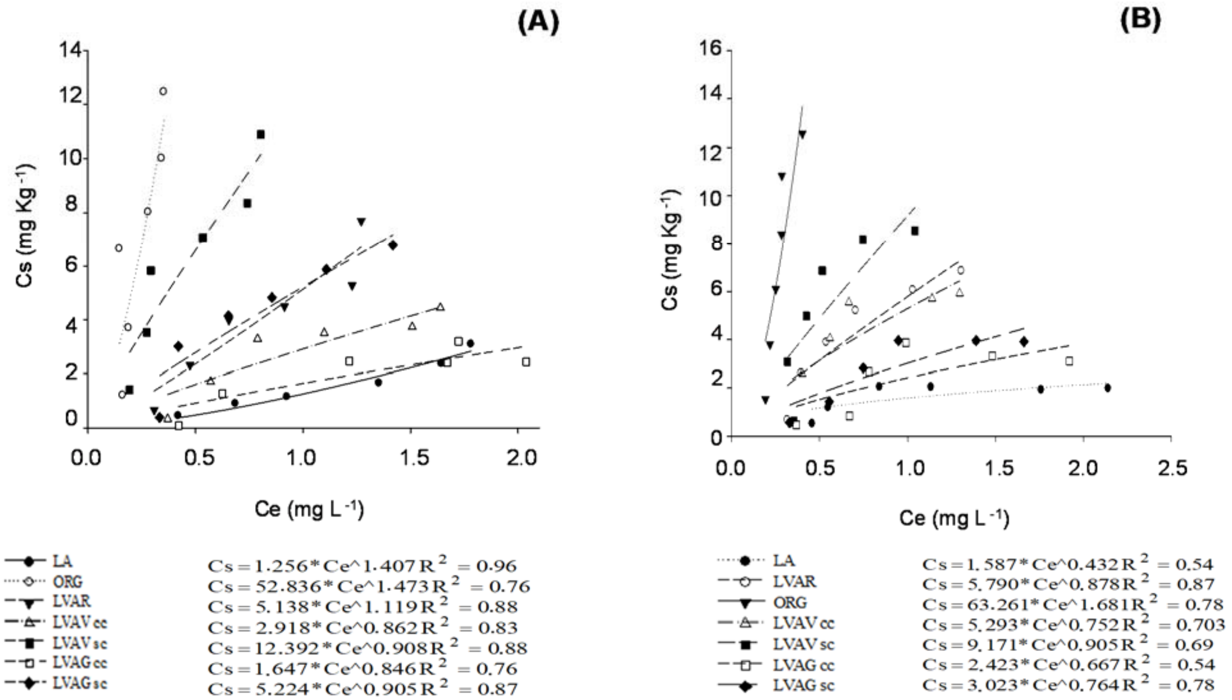

Figure 4 - Desorption of tembotrione (A) and metabolite AE 1417268 (B) in samples of a Yellow Latosol of Sooretama - Espirito Santo (LA), Red-Yellow Latosol of Rio Paranaíba - Minas Gerais (LVAR), Red-Yellow Latosol of Viçosa - Minas Gerais (LVAV) with and without liming, Red-Yellow Latosol of Gurupi - Tocantins (LVAG) with and without liming, and Organosolo of Venda Nova do Imigrante - Espirito Santo (amount of herbicide sorbed to soil - Cs and in equilibrium solution - Ce).

Table 3 - Adjusted Freundlich equation for sorption and desorption and hysteresis (H) index values of desorption for tembotrione

Soil	Sorption	Desorption	1/n S	1/n D	H
Tembotrione					
LA(1)	Cs= 0.692*Ce^2.083	Cs= 1.256*Ce^1.407	2.083	1.407	1.48
ORG(2)	Cs=46.038*Ce^1.943	Cs=52.836*Ce^1.473	1.943	1.473	1.32
LVAR(3)	Cs=4.119*Ce^1.292	Cs=5.138*Ce^1.119	1.292	1.119	1.15
LVAV cc(4)	Cs=2.416*Ce^1.167	Cs=2.918*Ce^0.862	1.167	0.862	1.35
LVAV sc(5)	Cs=11.939*Ce^0.921	Cs=12.392*Ce^0.908	0.921	0.908	1.01
LVAG cc(6)	Cs=1.526*Ce^0.688	Cs=1.647*Ce^0.846	0.688	0.846	0.81
LVAG sc(7)	Cs=4.724*Ce^0.778	Cs=5.224*Ce^0.905	0.778	0.905	0.86
AE 1417268 metabolite					
LA(1)	Cs= 1.891*Ce^0.568	Cs= 1.587*Ce^0.432	0.568	0.432	1.31
ORG(2)	Cs=27.114*Ce^0.743	Cs=63.261*Ce^1.681	0.743	1.681	0.44
LVAR(3)	Cs=5.107*Ce^0.713	Cs=5.790*Ce^0.878	0.713	0.878	0.81
LVAV cc(4)	Cs=5.892*Ce^0.747	Cs=5.293*Ce^0.752	0.747	0.752	0.99
LVAV sc(5)	Cs=10.710*Ce^0.720	Cs=9.171*Ce^0.905	0.720	0.905	0.79
LVAG cc(6)	Cs=2.679*Ce^0.387	Cs=2.423*Ce^0.667	0.387	0.667	0.58
LVAG sc(7)	Cs=2.749*Ce^0.638	Cs=3.023*Ce^0.764	0.638	0.764	0.83

1/nS, 1/nD /exponents of the sorption and desorption equations, respectively. H, hysteresis index. (1) Yellow Latosol from the municipality of Sooretama - Espirito Santo; (2) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo; (3) Red-Yellow Latosol from the municipality of Rio Paranaíba - Minas Gerais; (4) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais after liming; (5) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais; (6) Red-Yellow Latosol from the municipality of Gurupi - Tocantins after liming; and (7) Red-Yellow Latosol from the municipality of Gurupi - Tocantins.

of these compounds is directly proportional to the pH of soil and inversely proportional to the organic matter and clay content of soil. PH, organic matter and clay content are the main attributes that influence the sorption and desorption of tembotrione for the group of tested soils.

REFERENCES

Ahmad S, Rasul MG, Brown R, Hashib MA. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. J Environ Manage. 2011;92(3):311-30.

Barchanska H, Kluza A, Krajczewska K, Maj J. Degradation study of mesotrione and other triketone herbicides on soils and sediments. J Soils Sediments. 2016;16(1):125-33

Bontempo AF, Carneiro GD, Guimarães FA, Reis MR, Silva DV, Rocha BH, et al. Residual tembotrione and atrazine in carrot. J Env. Scie. Health B. 2016;51(7):465-8.

Cox L, Celis R, Hermosín MC, Cornejo J, Zsolnay A, Zeller K. Effect of organic amendments on herbicide sorption as related to the nature of the dissolved organic matter. Environ Sci Technol. 2000;34:4600-5.

De Wilde T, Spanoghe P, Ryckeboer J, Jaeken P, Springael D. Sorption characteristics of pesticides on matrix substrates used in biopurification systems. Chemosphere. 2009;75:100-8.

Eibisch N, Schroll R, Fuß R, Mikutta R, Helfrich M, Flessa H. Pyrochars and hydrochars differently alter the sorption of the herbicide isoproturon in an agricultural soil. Chemosphere. 2015;119:155-62.

El Bakouri H, Morillo J, Usero J, Vanderlinden E, Vidal H. Effectiveness of acid-treated agricultural stones used in biopurification systems to avoid pesticide contamination of water resources caused by direct losses: part I. Equilibrium experiments and kinetics. Bior Technol. 2010;101(14):5084-91.

Faria AT. Sorção, dessorção, meia-vida e lixiviação do tembotrione em solos com diferentes atributos [tese]. Viçosa, MG: Universidade Federal de Viçosa; 2016.

Fenoll J, Flores P, Hellín P, Hernández J, Navarro S. Minimization of methabenzthiazuron residues in leaching water using amended soils and photocatalytic treatment with TiO2 and ZnO. J Environ Sci. 2014;26:757-64.

García-Jaramillo M, Cox L, Cornejo J, Hermosín MC. Effect of soil organic amendments on the behavior of bentazone and tricyclazole. Sci Total Environ. 2014;467:906-13.

Hu Y, Liu X. Chemical composition and surface property of kaolins. Miner Eng. 2003;16:1279-84.

Kadous A, Didi MA, Villemin D. A new sorbent for uranium extraction: ethylenediamino tris (methylenephosphonic) acid grafted on polystyrene resin. J Radioanal Nucl Chem. 2010;284:431-8.

Kearns JP, Wellborn LS, Summers RS, Knappe DRU. 2,4-D adsorption to biochars: Effect of preparation conditions on equilibrium adsorption capacity and comparison with commercial activated carbon literature data. Water Res. 2014;62:20-8.

Khadivinia E, Sharafi H, Hadi F, Zahiri HS, Modiri S, Tohidi A, et al. Cadmium biosorption by a glyphosate-degrading bacterium, a novel biosorbent isolated from pesticide-contaminated agricultural soils. J Indian Eng Chem. 2014;20:4304-10.

Khenifi A, Derriche Z, Mousty C, Prévot V, Forano C. Adsorption of glyphosate and glufosinate by Ni2AlNO3 layered double hydroxide. Appl Clay Sci. 2010;47:362-71.

Koskinen WC, Calderón MJ, Rice PJ, Cornejo J. Sorption-desorption of flucarbazone, propoxycarbazone, and their benzenesulfonamide and triazolinone metabolites in two soils. Pest Manage Sci. 2006;62:598-602.

Lafferty BJ, Loeppert RH. Methyl arsenic adsorption and desorption behavior on iron oxides. Environ Sci Technol. 2005;39:2120-7.

Law SE. Agricultural electrostatic spray application: a review of significant research and development during de 20th century. J Electr. 2001;51:25-42.

Liu YH, Xu Z, Wu X, Gui W, Zhu G. Adsorption and desorption behavior of herbicide diuron on various Chinese cultivated soils. J Haz Mat. 2010;178:462-8.

Marco-Brown JL, Mar Areco M, Torres Sanchez RM, Afonso MS. Adsorption of picloram herbicide on montmorillonite: Kinetic andequilibrium studies. Colloid Surf A. 2014;449:121-8.

Martin SM, Kookana RS, Van Zwieten L, Krull E. Marked changes in herbicide sorption–desorption upon ageing of biochars in soil. J Agr Food Chem. 2012;231:70-8.

Mirzaei A, Ebadi A, Khajavi P. Kinetic and equilibrium modeling of single and binary adsorption of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) onto nano-perfluorooctyl alumina. Chem Eng J. 2013;231:550-60.

Muller K, Deurer M, Kawamoto K, Kuroda T, Subedi S, Hiradate S, et al. A new method to quantify how water repellency compromises soils' filtering function. Eur J Soil Sci. 2014;65:348-59.

Nagar R. Sarkar D, Makris KC, Datta R. Arsenic bioaccessibility and speciation in the soils amended with organoarsenicals and drinking-water treatment residuals based on a long-term greenhouse study. J Hydrol. 2014;518:477-85.

Passos ABRJ, Freitas MA, Torres LG, Silva AA, Queiroz ME, Lima CF. Sorption and desorption of sulfentrazone in Brazilian soils. J Environ Sci Health B. 2013;48:646-50.

Paul B. Yang D, Yang X, Ke X, Frost R, Zhu H. Adsorption of the herbicide simazine on moderately acid-activated beidellite. Appl Clay Sci. 2010;49:80-3.

Peruchi LM, Fostier AH, Rath S. Sorption of norfloxacin in soils: analytical method, kinetics and Freundlich isotherms. Chemosphere. 2015;119:310-7.

Pest Management Regulatory Agency – PMRA. Evaluation Report ERC2012-02, Tembotrione. Ottawa: Health Canada. [acessado em: 08 de fev. de 2016] Disponível em: http://www.hc-sc.gc.ca/cps-spc/pubs/pest/_decisions/erc2012-02/index-eng.php..

Prado B, Duwig C, Hidalgo C, Müller K, Mora L, Raymundo E, Etchevers JD. Transport, sorption and degradation of atrazine in two clay soils from Mexico: Andosol and Vertisol. Geoderma. 2014;232:628-39.

Quazi S, Sarkar D, Datta R. Changes in arsenic fractionation, bioaccessibility and speciation in organo-arsenical pesticide amended soils as a function of soil aging. Chemosphere. 2011;84:1563-71.

Rocha PRR Faria AT, Borges LGFC, Silva LOC, Silva AA, Ferreira EA. Sorção e dessorção do diuron em quatro Latossolos brasileiros. Planta Daninha. 2013;31:231-8.

Rojas R, Morillo J, Usero J, Vanderlinden E, El Bakouri H. Adsorption study of low-cost and locally available organic substances and a soil to remove pesticides from aqueous solutions. J Hydrol. 2015;520:461-72.

Shi K, Xie Y, Qiu Y. Natural oxidation of a temperature series of biochars: Opposite effect on the sorption of aromatic cationic herbicide. Ecotoxicol Environ Saf. 2015;114:102-8.

Shimizu M, Ginder-Vogel M, Parikh SJ, Sparks DL. Molecular scale assessment of methylarsenic sorption on aluminum oxide. Environ Sci Technol. 2010;44:612-7.

Silva AA, Silva JF, editores. Tópicos em manejo de plantas daninhas. Viçosa, MG: Universidade Federal de Viçosa; 2007. 367p.

Stipièeviæ S, Sekovaniæ L, Drevenkar V. Ability of natural, acid-activated, and surfactant-modified Terra Rossa soils to sorb triazine herbicides and their degradation products. Appl Clay Sci. 2014;89:56-62.

Sun K, Ro K, Guo M, Novak J, Mashayekhi H, Xing B. Sorption of bisphenol A, 17 a-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars. Bioresour Technol. 2011;102:5757-63.

Tarara G, Fliege R, Desmarteau D, Kley C, Peters B. Environmental fate of tembotrione. Bayer Crop Sci J. 2009;62:63-78.

Tian C, Wang M, Si Y. Influences of charcoal amendment on adsorption-desorption of isoproturon in soils. Agric Sci China. 2010;9:257-65.

Trigo C, Spokas KA, Cox L, Koskinen WC. Influence of soil biochar aging on sorption of the herbicides MCPA, nicosulfuron, terbuthylazine, indaziflam, and fluoroethyldiaminotriazine. J Agric Food Chem. 2014;62:10855-60.

Vivian R, Queiroz MELR, Jakelaitis A, Guimarães AA, Reis MR, Carneiro PM, Silva AA. Persistência e lixiviação de ametryn e trifloxysulfuron-sodium em solo cultivado com cana-de-açúcar. Planta Daninha. 2007;25:111-24.

Zhang G. Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. Environ Poll. 2011;159:2594-601.

Zhang J, He M. Effect of dissolved organic matter on sorption and desorption of phenanthrene onto black carbon. J Environ Sci. 2013;25:2378-83.