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Article

Sorption and Desorption of Diuron, Hexazinone and Mix (Diuron + Hexazinone) in Soils With Different Attributes

Sorção e Dessorção do Diuron, Hexazinone e da Mistura (Diuron + Hexazinone) em Solos com Diferentes Atributos Submetidos a Adição de Esterco

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ABSTRACT **-** In Brazil, sugarcane is grown in large areas. Weed control in sugarcane fields is done by chemical method, since it is more efficient and less expensive. In this method, herbicides that persist in the environment for long periods are used, among which there are hexazinone and diuron, which are applied in mixtures marketed by the industry. This research evaluated the sorption and desorption of hexazinone and diuron applied alone and in mixture, in two samples of Red-Yellow Latosols (LVAG and LVAV) and a Organosol (OR), with and without manure. Sorption isotherms were built using the batch equilibrium method and the identification and quantification of herbicides was obtained through a high-performance liquid chromatography (HPLC) with UV-Vis detector. There were high diuron sorption coefficients (K_f) in the soils. The hexazinone K_f values found were low in LVAG and LVAV soils, and they were high ground only in OR. In all soils, diuron and hexazinone showed higher K_f values when mixed. There was a direct relation between the addition of manure to the substrate and the K_f values . Higher desorption values (K_{fd}) in relation to those of sorption in LVAG and LVAV soils indicate gradual release of these herbicides in the soil solution when using organic fertilizer, showing increased sorption and desorption of these molecules; this is accentuated when they are mixed. In the Organosol, desorption was very low, and cannot be quantitated by the used method. It is possible to conclude that the incubation of LVAG and LVAV soil with manure helps both the process of sorption and desorption of herbicides. However, sorption and desorption in the Organosol is high indicating very low agrochemicals such strong bonds with soil colloids.

Keywords: herbicide, behavior in soil, environmental impact

RESUMO - No Brasil, a cana-de-açúcar é cultivada em extensas áreas. O controle das plantas daninhas nos canaviais é feito pelo método químico, pois é mais eficiente e de menor custo. Neste método são utilizados herbicidas que persistem no ambiente por longos períodos. Dos produtos recomendados para a cultura, os mais utilizados são o diuron e o hexazinone, aplicados isoladamente ou mistura comercializada pela indústria. Nesse sentido, o objetivo deste estudo foi avaliar a sorção e dessorção do hexazinone e do diuron, aplicados de forma isolada e em mistura, em duas amostras de Latossolo Vermelho-Amarelo (LVAG e LVAV), com e sem adição de esterco, e em um Organossolo (OR) sem adição de esterco. Primeiramente, foi determinado o tempo de equilíbrio dos herbicidas no solo pelo método batch equilibrium, e a identificação e quantificação dos herbicidas foram feitas por cromatografia líquida de alta eficiência (HPLC); em seguida, determinaram-se as

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isotermas de sorção e dessorção. Observaram-se elevados coeficientes de sorção (K_f) do diuron nos solos estudados. Os valores de K_f do hexazinone encontrados foram baixos nos solos LVAG e LVAV e elevados apenas no solo OR. Em todos os solos, o diuron e o hexazinone apresentaram valores de K_f maiores quando em mistura. Ocorreu relação direta entre a adição de esterco ao substrato e os valores do K_f. Maiores valores de dessorção (K_{fd}) em relação aos da sorção nos solos LVAG e LVAV indicam liberação gradual desses herbicidas na solução dos solos quando se fazem adubações orgânicas, indicando o aumento da sorção e dessorção dessas moléculas, acentuando-se quando em mistura. No Organosolo, a dessorção foi muito baixa e não pôde ser quantificada pelo método utilizado. Conclui-se que a aplicação da mistura diuron+hexazinone aumenta a sorção desses herbicidas ao solo. A recomendação do hexazinone isolado deve levar em consideração o teor de matéria orgânica do solo (MOS). O diuron em aplicação isolada apresenta alta sorção no solo. A dessorção apresenta alta magnitude em relação à sorção nos solos com baixo teor de MOS. No OR, a dessorção é baixa e por isso não pôde ser quantificada. Existe relação direta entre a adição de esterco ao substrato e a sorção nos solos. A incubação dos solos de baixo teor de MOS com esterco favorece tanto o processo de sorção quanto o de dessorção dos herbicidas.

Palavras-chave: herbicida, comportamento no solo, impacto ambiental.

INTRODUCTION

In Brazil, weed management in sugarcane cultures has been frequently carried out with herbicides that persist in the soil for a long period (Carbonari et al., 2010). The incorrect and indiscriminate use of these agrochemicals has caused environmental problems, such as the contamination of soil (making crop rotation unviable), groundwater and surface water (Santos et al., 2015). This occurs due to the scarce information about the dynamics of herbicides in the different Brazilian soils, resulting in single recommendations for different growing conditions.

In Brazil, there are 40 herbicide molecules registered for the control of weeds in sugarcane (Brasil, 2016). Among these products, it is possible to highlight the commercial mixture diuron + hexazinone, which has been studied in different works involving the management of weeds in sugarcane plantations (Dantas et al., 2009; Santos et al., 2009; Ferreira et al., 2010; Botelho et al., 2011). The application of the formulated mixture of these herbicides aims at a broader spectrum of weed species control (Queiroz et al., 2009).

Diuron (N-(3,4-dichlorophenyl)-N,N-dimethylurea) is a non-ionic molecule belonging to the chemical group of the broad spectrum substituted ureas used in pre- and post-emergence control of monocots and dicots in sugarcane cultures (ANVISA, 2016). It acts by inhibiting the photosynthesis process, and it is normally used in mixtures with other herbicides (hexazinone, MSMA and paraquat) (Procópio et al., 2014). The inhibitors of photosystem II, such as triazines, ureas and uracils, block the electron transport in the photosystem, and generate chlorophyll molecules that are more energetically charged, creating a chain reaction and forming free radicals, which peroxide membrane lipids, thus leading plants to death (Silva et al., 2012).

Hexazinone (3-cyclo-hexyl-6-dimethylamino-1-methyl-1,3,5-triazin-2,4(*1H, 3H*)-dione) belongs to the triazinone chemical group. In Brazil, it is registered for pre- and post-emergence weed control (ANVISA, 2016). This molecule is derived from a weak base and belongs to the C1 group of the photosystem II inhibitors (Oliveira Jr and Regitano, 2009).

Studies about the behavior of herbicides in the soil aim at knowing the interactions between soil attributes and herbicides that directly or indirectly affect the efficiency of weed control by these compounds, and also the possible negative effects they can cause to the environment (Silva et al., 2012).

The distribution of a chemical substance between soil and aqueous phase is a complex process, and it is a result of the interactions between various factors, such as the chemical nature of the substance, the characteristics of soil and the climatic factors (precipitation, temperature, sunlight and wind). Remaining in the soil, herbicides are subject to sorption, leaching and/or degradation processes by physical, chemical and biological processes. Sorption refers to a general process, without any distinction among the specific processes of adsorption, absorption and precipitation (Silva et al., 2012).

When sorbed, the molecule of an herbicide can return to the soil solution by the desorption process (Lavorenti et al., 2003; Pereira et al., 2016). The reversibility of the sorption process is related to the desorption intensity. Sorption can be completely reversible or, in other cases, only a part of the sorbed herbicide returns to the soil solution - a phenomenon called hysteresis (Oliveira Jr. and Regitano, 2009).

Desorption evaluation aims at quantifying the reversibility rate of the sorbed herbicide to the soil solution. This information has great relevance, since the desorption process also plays an important role, both agronomically and environmentally, in the behavior of a substance in the soil,. However, when applied in a mixture, herbicides may have different behaviors in the environment. The competition for soil adsorption sites or a possible interaction between them may influence the availability of their molecules in the soil solution (Arsego, 2009; Alves, 2012). Thus, they affect their mobility and, consequently, their destination in the environment (Passos et al., 2015).

Several independent studies about the sorption and desorption of different herbicides have already been conducted on several types of Brazilian soils (Queiroz et al., 2009; Rocha et al., 2013). However, there is little information about the behavior of herbicides when they are applied in mixtures and with changes in organic matter contents.

The objective of this study was to evaluate the sorption and desorption of hexazinone and diuron, applied alone and in a mixture, in samples of different soils subjected to the addition of organic fertilizers, through a high performance liquid chromatography.

MATERIAL AND METHODS

The experiments were conducted in the Laboratório de Análises de Solo Viçosa. All used solvents were HPLC grade, and the other reagents were of analytical grade at least. Calcium chloride was supplied by Vetec, Brazil. Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and hexazinone (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazin-2,4 (*1H, 3H*)-dione) were obtained from Sigma-Aldrich, Germany. Starting from the dilution of a standard stock solution of 1,000 mg L^{-1} of diuron and hexazinone in methanol, the working solutions were made in a $CaCl_2$ 0.01 mol L^{-1}solution.

Three soil samples: Red-Yellow Latosol from the Municipality of Gurupi - Tocantins state (LVAG), Red-Yellow Latosol from Viçosa - Minas Gerais state (LVAV) and Organosol from Venda Nova do Imigrante - Espirito Santo state (OR) were collected at the 0 to 20 cm depth. These samples were air dried and sieved in a 2 mm mesh. Before this, part of the LVAG and LVAV soil samples were incubated with fresh cattle manure for 30 days, in five volume/volume ratios. Table 1 shows the evaluated treatments and, in Table 2, there are the results of the physical-chemical analysis of the soil samples.

Determining the required time for sorption equilibrium and the evaluation of the sorption and desorption of diuron and hexazinone in soils were carried out according to OECD recommendations (2000). At first, the equilibrium time of sorption was determined, from which the concentration of the analyzed solution remains constant. For this, a solution of $CaCl_2$ 0.01 mol L^{-1} containing 0.5 mg L^{-1} of herbicide was used in the tests with diuron and hexazinone alone, and a solution containing 0.22 mg L^{-1} of hexazinone and 0.78 mg L^{-1} of diuron was used for the tests with the mixture; this ratio corresponds to the recommendation of the commercial product insert.

Then, 10 mL of these solutions were added into polypropylene tubes containing 2.00 g of

Table 1 **-** Incubation of LVAG and LVAV soils with different soil/cattle manure ratios

Treatment	Soil	Soil/manure ratio vol./vol.	Treatment
1	LVAG[(1)]	1.00/0.00	LVAG 1.0
2	LVAG	1.00/0.25	LVAG 1.1
3	LVAG	1.00/0.50	LVAG 1.2
4	LVAG	1.00/0.75	LVAG 1.3
5	LVAG	1.00/1.00	LVAG 1.4
6	LVAV[(2)]	1.00/0.00	LVAV 1.0
7	LVAV	1.00/0.25	LVAV 1.1
8	LVAV	1.00/0.50	LVAV 1.2
9	LVAV	1.00/0.75	LVAV 1.3
10	LVAV	1.00/1.00	LVAV 1.4

(1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state; (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state.

Table 2 **-** Results of chemical and physical analyses of the evaluated soil samples

Soil	pH	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	CTC (t)	V	m	OM
	(H_2O)	(mg dm^{-3})		(cmol$_c$ dm^{-3})					(%)		(dag kg^{-1})
LVAG 1.0(1)a	5.5	2.0	168	1.0	0.8	0.0	4.13	2.23	35	0	2.75
LVAG 1.1(1)b	5.7	7.9	470	1.7	1.5	0.0	3.14	4.40	58	0	3.35
LVAG 1.2(1)c	6.0	15.2	780	2.3	1.7	0.0	2.48	5.99	71	0	4.54
LVAG 1.3(1)d	6.3	29.6	1170	2.6	2.7	0.0	2.15	8.29	79	0	4.82
LVAG 1.4(1)e	6.5	64.0	1530	3.1	3.0	0.0	1.16	10.0	90	0	5.90
LVAV 1.0(2)a	5.1	5.2	29	1.8	0.6	0.1	3.47	2.47	42	4	1.76
LVAV 1.1(2)b	5.5	15.6	360	2.4	1.3	0.0	2.97	4.62	61	0	2.63
LVAV 1.2(2)c	5.9	31.8	670	3.3	1.7	0.0	2.15	6.71	76	0	3.60
LVAV 1.3(2)d	6.2	47.9	940	3.5	2.5	0.0	1.98	8.40	81	0	4.82
LVAV 1.4(2)e	6.6	61.6	1550	4.2	3.4	0.0	1.32	11.6	90	0	6.40
OR(3)	4.4	18.9	310	4.7	3.0	1.5	36.1	9.99	19	15	33.3
EB(4)	6.7	179	5300	4.9	7.9	0.0	2.15	26.4	92	0	20.4

Soil	Clay	Silt	Sand	Texture classification
	(%)			
LVAG 1.0	35	10	55	Loam-clay-sandy
LVAG 1.1	38	7	55	Loam-clay-sandy
LVAG 1.2	35	11	54	Loam-clay-sandy
LVAG 1.3	36	11	53	Loam-clay-sandy
LVAG 1.4	34	13	53	Loam-clay-sandy
LVAV 1.0	46	17	37	Clay
LVAV 1.1	46	18	36	Clay
LVAV 1.2	41	18	41	Clay
LVAV 1.3	41	23	36	Clay
LVAV 1.4	41	14	44	Clay
OR	8	15	77	Loam-sandy

Analyses carried out in the Laboratório de Análises de Solo Viçosa, according to the methodology of the Empresa Brasileira de Pesquisa Agropecuária – Embrapa (1997); CTC (t) - effective cation exchange capacity; V = base saturation index; m = saturation index by aluminum; OM = soil organic matter.

(1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (3) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state; (4) Cattle manure.

soil. The tubes were placed under stirring for different periods of time (0.5, 1.0, 2.0, 3.0, 4.0, 8.0, 12, 16, 24 and 30 hours) at the temperature of 27 ± 2 °C. After stirring, the samples were centrifuged at 4,000 rpm for four minutes. Subsequently, part of the supernatant was filtered in a Millipore filter with 0.45 μm PTFE membrane, for further analysis by high performance liquid chromatography (HPLC).

The sorption kinetics estimates were adjusted according to the equation describing the rate of a first-order reaction $[A] = [A_0]*(1-e^{-kt})$, where $[A_0]$ is the initial concentration of the herbicide, k is the rate constant, t is the time in hours, and [A] is the concentration at a given time.

In order to evaluate the sorption of the isolated herbicides, solutions of diuron and hexazinone were prepared at concentrations of 0.10; 0.50; 1.0; 1.5; 2.0; and 2.5 mg L^{-1} in 0.01 mol L^{-1} C_aCl_2. On the other hand, to evaluate the sorption of the mixture, hexazinone/diuron solutions were prepared at concentrations of 0.11/0.39; 0.22/0.78; 0.44/1.56; 0.66/2.34; 0.88/3.12; and 1.10/3.90 mg L^{-1} in $CaCl_2$ 0.01 mol L^{-1}.

After that, 10.0 mL of these solutions were added in polypropylene tubes containing 2.00 g of soil, which were stirred at 27 ± 2 °C for the determined equilibrium time. After stirring, the samples were centrifuged at 4,000 rpm for four minutes, and the supernatant was removed and filtered in a 0.45 μm Millipore filter for further chromatographic analysis.

Control samples containing diuron and hexazinone in a solution of $CaCl_2$ 0.01 M (without soil) were submitted to the same steps of the sorption tests, in order to verify the stability and degradation of the substances in the $CaCl_2$ solution and their possible adsorption on the surface of the test containers.

The amount of herbicide sorbed to the soil (C_s), as mg kg^{-1}, was calculated through the difference between the amount of standard solution initially added to the soil (C_p), as mg L^{-1}, and the amount found in the equilibrium solution (C_e) as mg L^{-1}. With the C_e and C_s values, the Freundlich equation ($C_s = K_f \, C_e^{1/n}$) was adjusted to obtain the sorption coefficients, where K_f and $1/n$ are empirical constants representing the capacity and intensity, respectively. All analyses were performed in triplicate, and data were submitted to regression analysis for the interpretation of the results.

In the desorption tests, the whole supernatant was removed from the tubes, leaving them at rest for eight hours. After that, 10.0 mL of an herbicide-free $CaCl_2$ 0.01 mol L^{-1} solution were added thereto. These tubes were re-stirred for the same time and at the same temperature at which sorption tests were conducted. After stirring, the samples were centrifuged at 4,000 rpm for four minutes, removing and filtering the supernatant in 0.45 µm Millipore filter, for further chromatographic analysis. From the results of the desorption isotherms, the hysteresis index was calculated, dividing the sorption 1/n by the desorption 1/n, according to Peruchi et al. (2015).

Diuron and hexazinone were quantified by high performance liquid chromatography (HPLC), using an LC 20AT, UV-Vis detector Shimadzu liquid chromatograph (Shimadzu SPD 20A) and a stainless steel column (Shimadzu VP-ODS Shim-pack 250 mm x 4.6 mm d.i.). The chromatographic conditions for the analysis were those described by Queiroz et al. (2009); the mobile phase was composed of water and methanol in the ratio of 30:70 (v/v), a 1.0 mL min^{-1} flow, an injection volume of 100 µL and a wavelength of 247 nm. The retention time of diuron and hexazinone under these conditions was determined, and quantification was performed comparing the areas obtained in the chromatograms for each test by the external calibration method. Identification was made by retention time, using an analytical standard of diuron and hexazinone.

A white sample comprising the soil system + an herbicide-free $CaCl_2$ 0.01 mol L^{-1} solution was analyzed under the same chromatographic conditions, in order to verify if there are interferents in the analytical method, as well as possible matrix effects caused by the soil.

RESULTS AND DISCUSSION

The sorption equilibrium time of both herbicides, isolated and in a mixture, was reached before eight hours of stirring for all soils. In order to standardize the time for the soils, to guarantee the reliability of the tests and for operational reasons, in the studies about sorption and desorption the 12 hours period was established (Figures 1, 2 and 3 and Table 3).

The sorption kinetics of diuron, both alone and in mixture, presented a rapid initial phase (up to four hours of stirring) and, after that interval, a slow phase (Table 3). Liu et al. (2010); Mirzaei et al. (2013) and Rocha et al. (2013) attributed this sorption kinetics to the fact that, at the beginning, there is a large number of sorption sites available in the soil, and at the next stage, vacant surface sites are difficult to occupy, due to the repulsion forces between solute molecules in the solid phase and the molecules in solution. Thus, the presence of hexazinone did not alter the sorption kinetics of this herbicide.

Estimates about the sorption kinetics of hexazinone alone and in mixture also showed a rapid initial phase, followed by a slow phase (Table 4). However, the rapid phase occurred at a slower rate than diuron. Therefore, the time this herbicide took to reach the sorption equilibrium was higher (Figures 4, 5 and 6).

The presence of diuron in the mixture altered the sorption kinetics of hexazinone (Table 4). In mixtures, the time needed to achieve equilibrium was greater. This can be explained by the fact that diuron molecules occupy soil sorption sites at a higher rate than hexazinone.

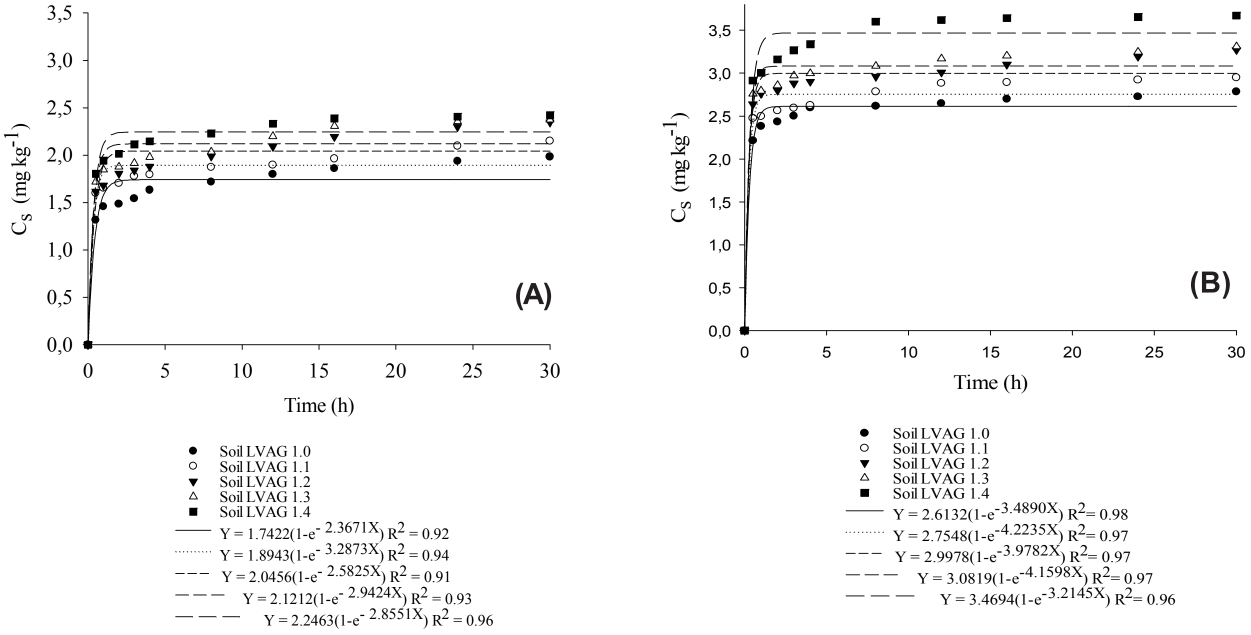

Figure 1 - Sorption kinetics of diuron alone (A) and diuron in mixture (B), in samples of a LVAG Red-Yellow Latosol from Gurupi - Tocantins state (1.0 - without manure; 1.1 - soil ratio: manure at 1: 0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1), according to time.

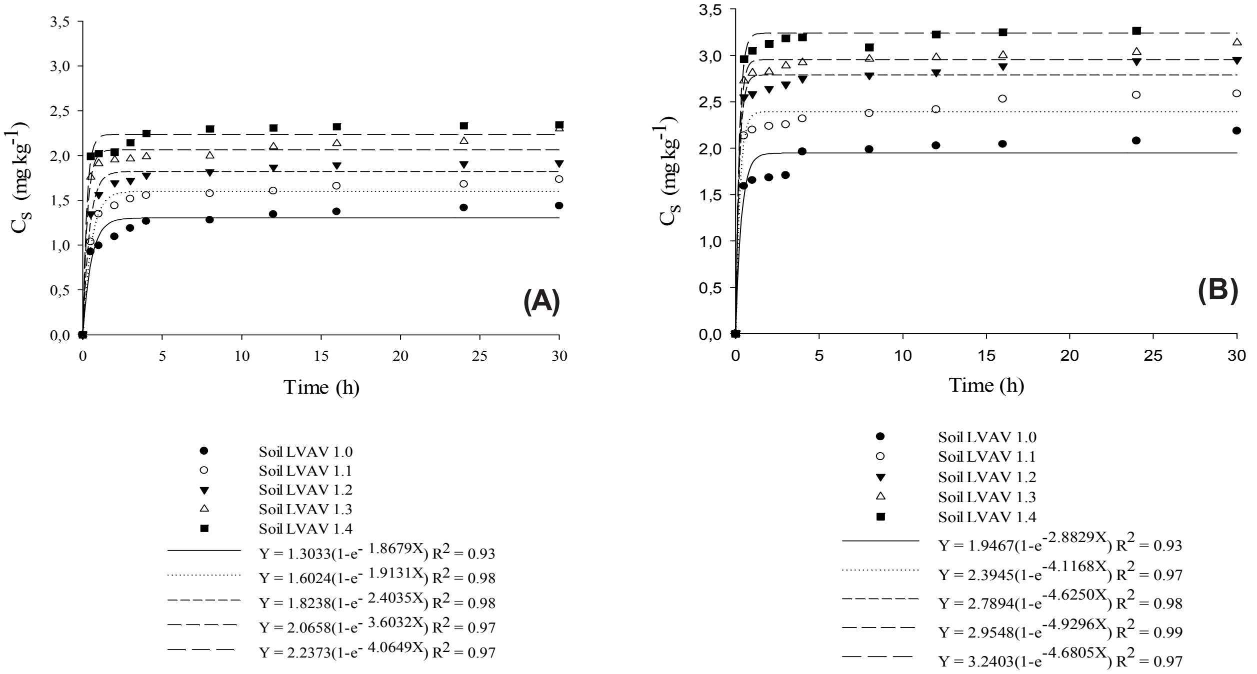

Figure 2 - Sorption kinetics of diuron alone (A) and diuron in mixture (B), in samples of a LVAV Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1: 0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1), according to time.

Control samples showed no differences between the initial concentrations and the final concentrations of the herbicides after 12 hours of stirring. Therefore, the herbicides are stable in the $CaCl_2$ solution and are not adsorbed to the surface of the test containers.

The sorption coefficients obtained from diuron alone and in mixture were higher in the OR soil (Figures 7, 8, 9 and Table 5), which has the highest organic matter content among all

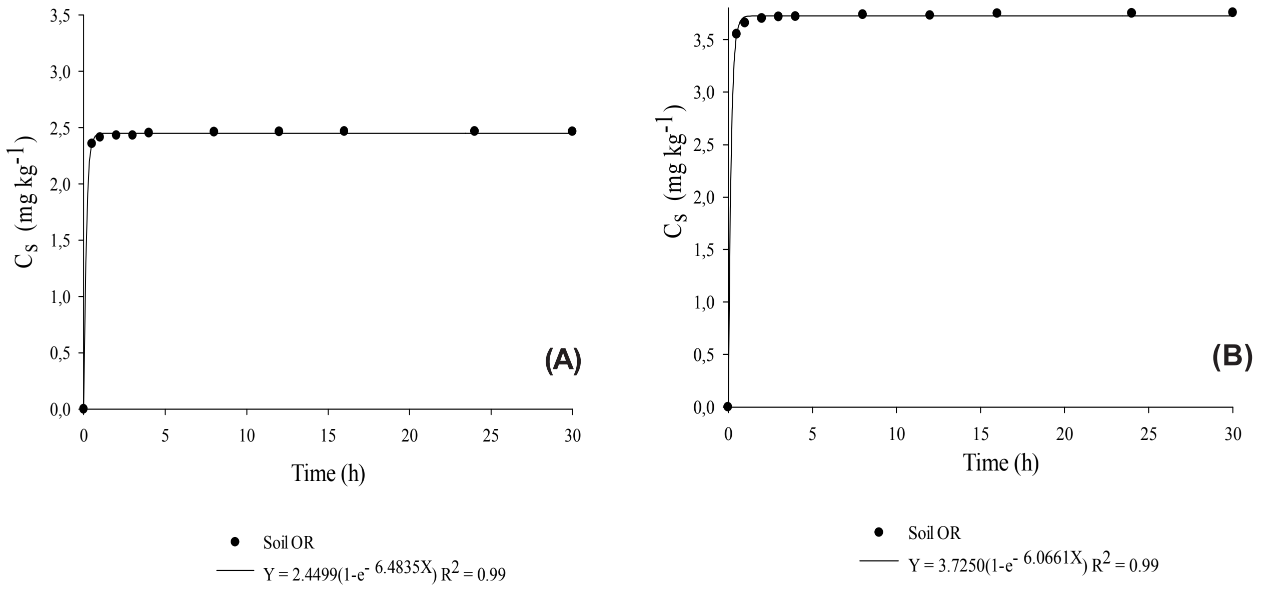

Figure 3 - Sorption kinetics of diuron alone (A) and diuron in mixture (B) in samples of an Organosol from Venda Nova do Imigrante - Espirito Santo state (OR), according to time.

Table 3 - Values of the kinetics estimates of the sorption of diuron alone and in mixture in the used soils

Soil	Diuron alone		Diuron mixture	
	$[A_0]$ (mg kg^{-1})	k	$[A_0]$ (mg kg^{-1})	k
LVAG 1.0$^{(1)}$a	1.74	2.37	2.61	3.49
LVAG 1.1$^{(1)}$b	1.89	3.29	2.75	4.22
LVAG 1.2$^{(1)}$c	2.05	2.58	2.99	3.98
LVAG 1.3$^{(1)}$d	2.12	2.94	3.08	3.08
LVAG 1.4$^{(1)}$e	2.25	2.85	3.47	3.47
LVAV 1.0$^{(2)}$a	1.30	1.87	1.95	2.88
LVAV 1.1$^{(2)}$b	1.60	1.91	2.39	4.12
LVAV 1.2$^{(2)}$c	1.82	2.40	2.79	4.63
LVAV 1.3$^{(2)}$d	2.07	3.60	2.95	4.93
LVAV 1.4$^{(2)}$e	2.24	4.06	3.24	4.68
OR$^{(3)}$	2.44	6.48	3.73	6.07

$[A_0]$ is the initial concentration of the herbicide and k is the rate constant. $^{(1)}$ Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); $^{(2)}$ Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); $^{(3)}$ Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

evaluated soils. There is a positive relationship between the organic carbon contents and sorption of this herbicide (Rocha et al., 2013). Diuron is a non-ionic molecule and has hydrophobic properties, as well as several compounds found in the organic fraction of soil. Therefore, mechanisms of hydrophobic partition and hydrogen bonding are favored among them and sorption becomes greater, as already observed in other non-ionic molecules, such as clomazone and diuron (Gunasekara et al., 2009; Cao et al., 2013; Umiljendic et al., 2013; Rocha et al., 2013).

Soil organic matter (SOM) has a marked capacity for herbicide sorption (Benoit et al., 2008). This pronounced reactivity of SOM is mainly related to its high specific surface area and to the presence of several functional groups, such as carboxylates, hydroxyls and amines, and aliphatic and aromatic structures (Li et al., 2017). However, their role depends on their concentration in the soil; the chemical composition can vary significantly and thus influence the nature and extent of herbicide sorption (Đurovic et al., 2008).

Another feature of the soil that influences the sorption of non-ionizable herbicides, but which may have polarity, such as diuron, is the cation exchange capacity (CTC), which is associated with the minerals of the clay fraction (Silva et al., 2012). These minerals are formed by layers of silicon and aluminum oxides, capable of binding to the cations in the soil and to other polarized molecules with positive partial charges (Fontes et al., 2001). Thus, it is possible to explain the higher sorption of diuron in the clayey LVAV soil compared to the sandy LVAG soil. These results corroborate those of Oliveira Jr et al. (2009), which report, generally speaking, an increase in the sorption of herbicides to the soil with the increase of CTC.

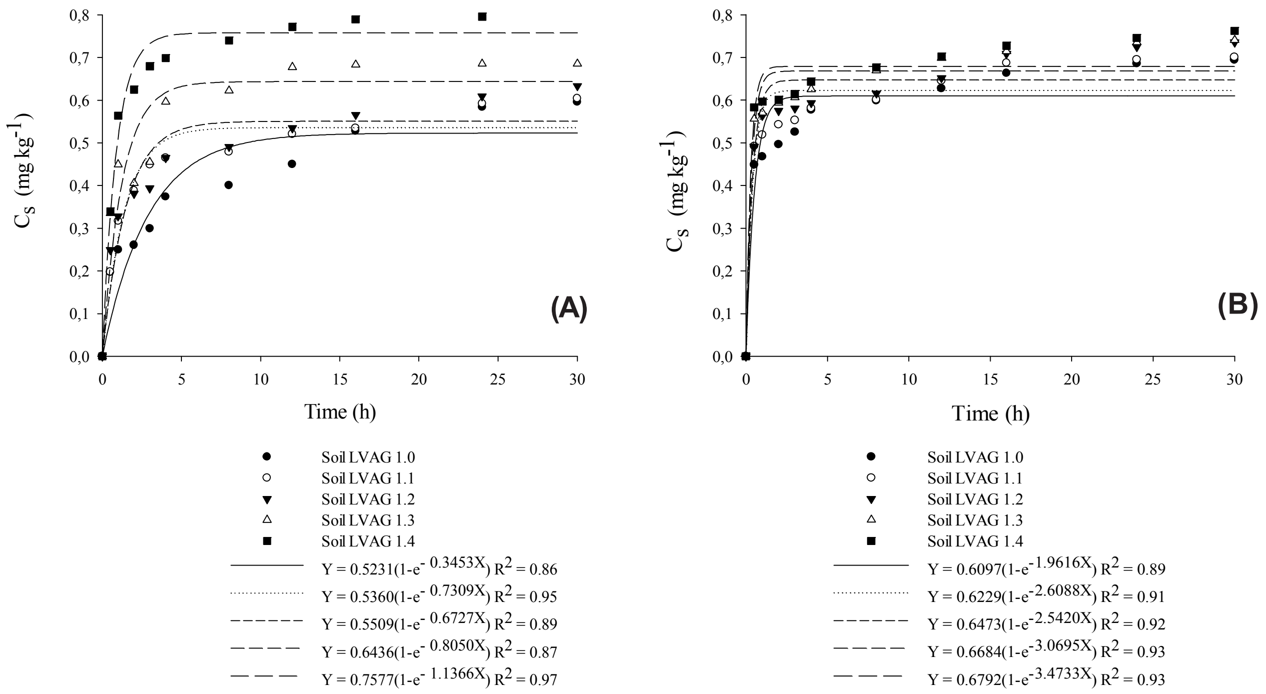

Figure 4 **-** Sorption kinetics of hexazinone alone (A) and hexazinone in mixture (B) in samples of a LVAG Red-Yellow Latosol from Gurupi - Tocantins state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1), according to time.

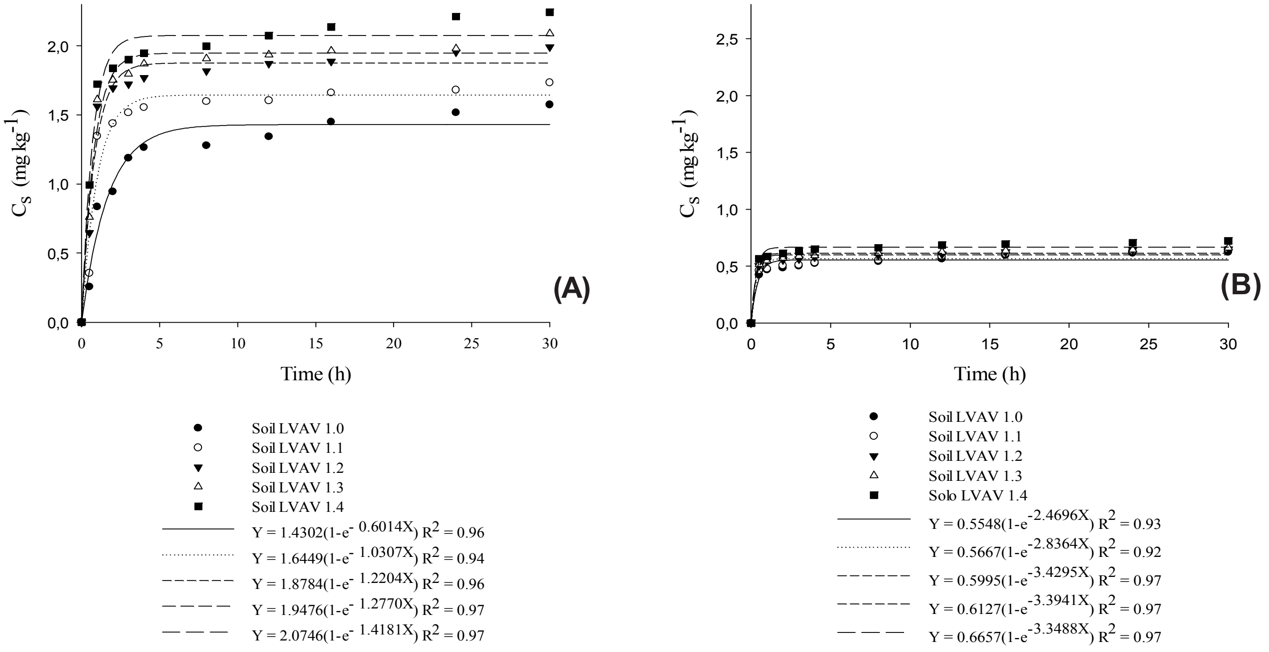

Figure 5 **-** Sorption kinetics of hexazinone alone (A) and hexazinone in mixture (B) in samples of a LVAL Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1), according to time.

In all evaluated soils, diuron in mixture showed, on an average, twice the values of sorption coefficients (K_f) in relation to their use alone (Table 5). This demonstrates that hexazinone does not compete with diuron for soil sorption sites; instead, it helps its sorption. As diuron and hexazinone have distinct properties, their sorption to the soil involves different mechanisms that occur simultaneously. Moreover, interactions between the already sorbed herbicides may

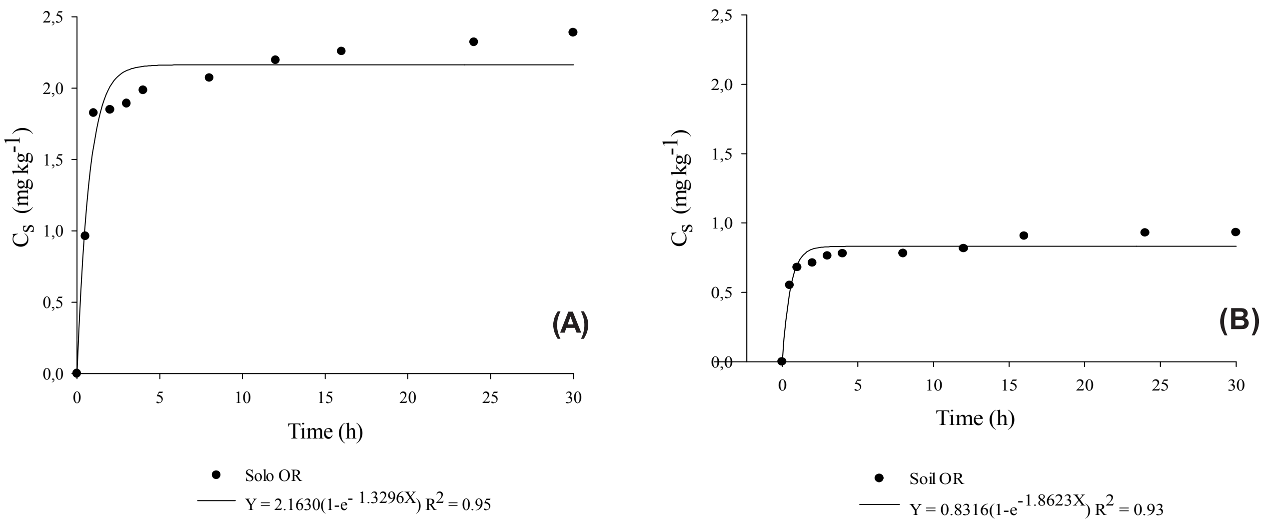

Figure 6 - Sorption kinetics for hexazinone alone (A) and for diuron in mixture (B) in samples of an Organosol from Venda Nova do Imigrante - Espirito Santo state (OR), according to time.

Table 4 - Values of the sorption kinetics of hexazinone alone and in mixture in the evaluated soil samples

Soil	Hexazinone alone		Hexazinone in mixture	
	$[A_0]$ (mg kg^{-1})	k	$[A_0]$ (mg kg^{-1})	k
LVAG 1.0$^{(1)}$a	0.52	0.35	0.61	1.96
LVAG 1.1$^{(1)}$b	0.54	0.73	0.62	2.61
LVAG 1.2$^{(1)}$c	0.55	0.67	0.65	2.54
LVAG 1.3$^{(1)}$d	0.64	0.81	0.67	3.07
LVAG 1.4$^{(1)}$e	0.76	1.14	0.68	3.47
LVAV 1.0$^{(2)}$a	1.43	0.60	0.55	2.47
LVAV 1.1$^{(2)}$b	1.64	1.03	0.57	2.83
LVAV 1.2$^{(2)}$c	1.88	1.22	0.60	3.43
LVAV 1.3$^{(2)}$d	1.95	1.28	0.61	3.39
LVAV 1.4$^{(2)}$e	2.07	1.42	0.67	3.49
OR$^{(3)}$	2.16	1.33	0.83	1.86

$[A_0]$ is the initial concentration of the herbicide and k is the rate constant. $^{(1)}$ Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); $^{(2)}$ Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); $^{(3)}$ Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

occur, since no concentration reduction was observed in the control samples where the mixture was stirred without soil for the same time (Petter et al., 2016).

Sorption 1/n values in all soils were higher in the diuron mixture (Table 5). For Arsego (2009), this indicates a greater dependence of the sorption, due to the limited number of sorption sites; this becomes more evident with the increase of the herbicide concentration.

The incubation of the LVAG and LVAV soils with manure provided increased sorption of diuron alone and in mixture (Table 5). This occurs because this material increased the organic matter and CEC of soils (Table 2), and these attributes, as previously discussed, help the sorption of diuron. Moreover, a soil pH increase was observed in this treatment; however, due to the non-ionic characteristic of diuron, this attribute does not influence its sorption.

Organic matter deriving from manure has different properties than those present in the OR soil, and the source material and decomposition states are different. Therefore, even if OR has a higher content of organic matter, it is possible to observe greater sorption of diuron in the LVAV 1.4 soil.

According to the IBAMA classification (IBAMA, 1990), the sorption capacity of chemical agents in the soil indicates that the K_f values observed in diuron alone (119.8 to 873.1) and in mixture (336.7 to 1879.1) are considered from high to very high in the evaluated soil samples.

According to the classification proposed by IBAMA (1990), the K_f values determined for hexazinone alone (1.21 to 2.41) or in mixture (17.36 to 24.56) in LVAG and LVAV soils characterize low sorption (Figures 10, 11, 12 and Table 6), as observed by Sarmah et al. (2009). In the OR soil, it is considered high and very high for hexazinone alone (125.2) and in mixture (236.61),

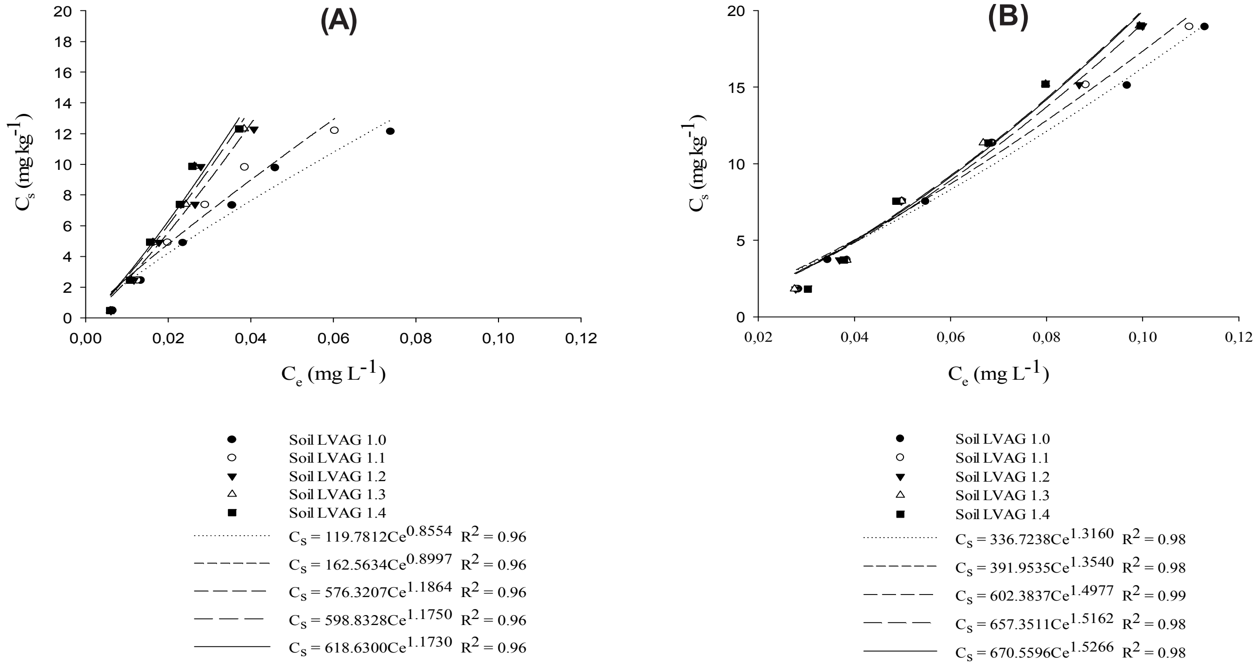

Figure 7 **-** Sorption of diuron alone (A) and in mixture (B) in a LVAG Red-Yellow Latosol from Gurupi - Tocantins state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1). C_s: Concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: Concentration of herbicide in the equilibrium solution as mg L^{-1}.

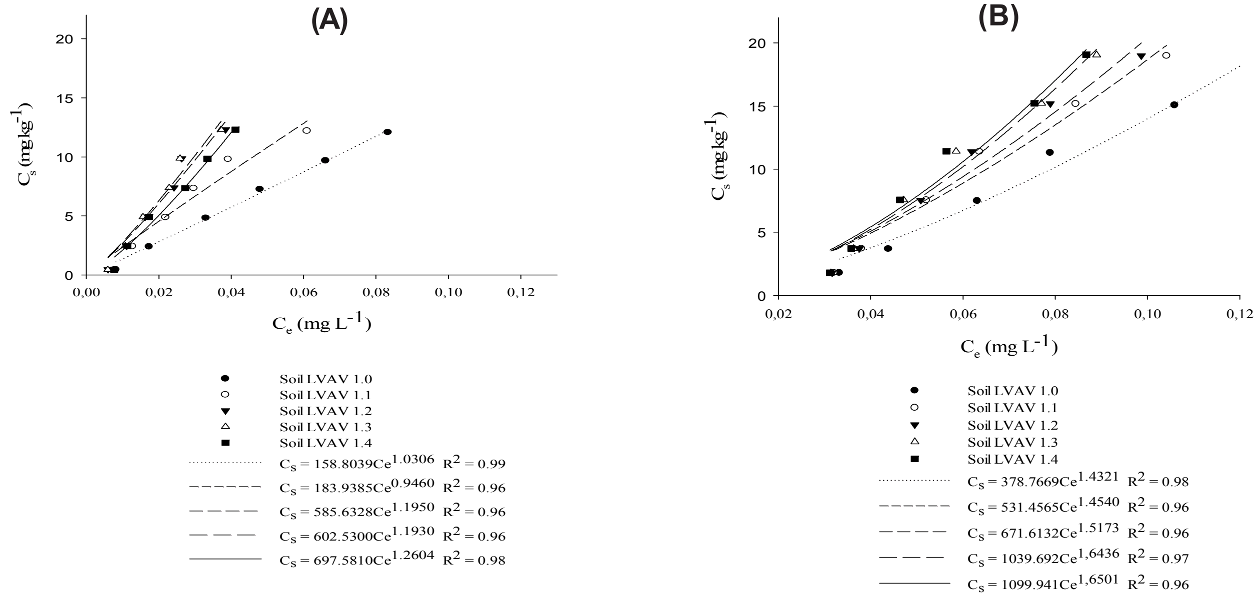

Figure 8 **-** Sorption of diuron alone (A) and in mixture (B) in a LVAV Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1). C_s: Concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: Concentration of herbicide in the equilibrium solution as mg L

respectively. The higher sorption of hexazinone in the OR soil is also due to its hydrophobic characteristics. This herbicide is classified as a weak base and presents pKa of 2.2 and, in the pH of the used soils, from 4.4 to 6.6, its molecules are deprotonated with no net charge. Thus, the mechanisms that were favored in the sorption are those occurring between the hydrophobic compounds of the organic matter of soil and the herbicide.

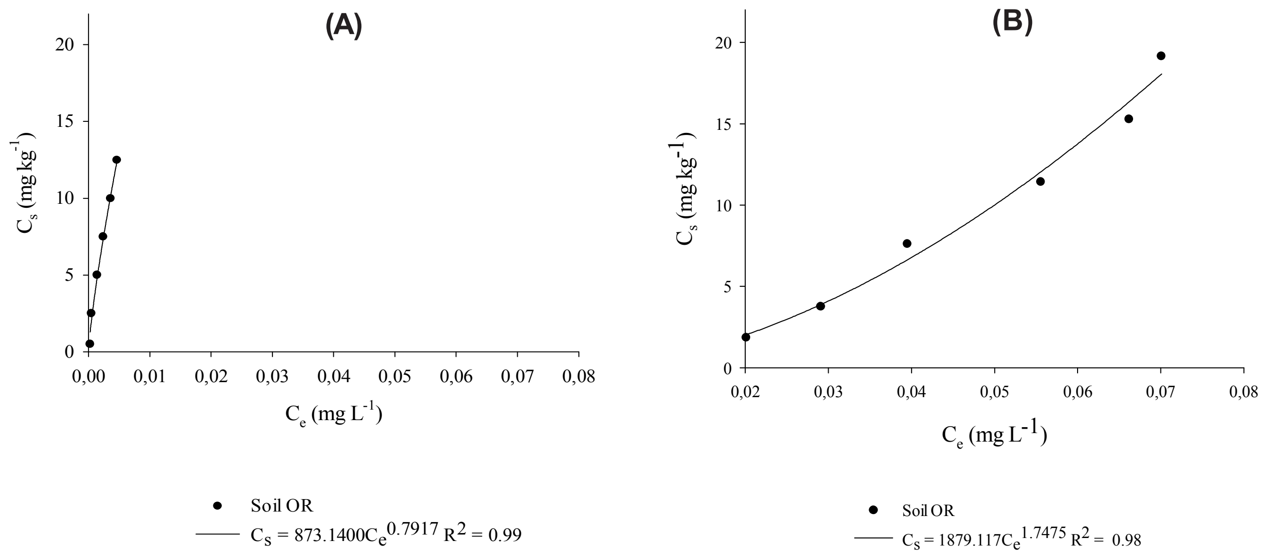

Figure 9 **-** Sorption of diuron alone (A) and diuron in mixture (B) in samples of an Organosol from Venda Nova do Imigrante - Espirito Santo state (OR). C_s: Concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: Concentration of herbicide in the equilibrium solution as mg L^{-1}.

Table 5 **-** Freundlich parameters for the sorption of pure and mixed diuron for samples of the evaluated soils

Soil	Diuron sorption			Mixed diuron sorption		
	K_f	1/n	R^2	K_f	1/n	R^2
LVAG 1.0$^{(1)}$a	119.78	0.86	0.96	336.72	1.32	0.98
LVAG 1.1$^{(1)}$b	162.56	0.90	0.96	391.95	1.35	0.98
LVAG 1.2$^{(1)}$c	576.32	1.19	0.96	602.38	1.50	0.99
LVAG 1.3$^{(1)}$d	598.83	1.18	0.96	657.35	1.52	0.98
LVAG 1.4$^{(1)}$e	618.63	1.17	0.96	670.56	1.53	0.98
LVAV 1.0$^{(2)}$a	158.80	1.03	0.99	378.77	1.43	0.98
LVAV 1.1$^{(2)}$b	183.94	0.95	0.96	531.46	1.45	0.96
LVAV 1.2$^{(2)}$c	585.63	1.20	0.96	671.61	1.52	0.96
LVAV 1.3$^{(2)}$d	602.53	1.19	0.96	1.039.69	1.64	0.97
LVAV 1.4$^{(2)}$e	697.58	1.26	0.98	1.099.94	1.65	0.96
OR$^{(3)}$	873.14	0.76	0.99	1.879.11	1.75	0.98

K_f, sorption coefficients; 1/n, exponent of the sorption equations. (1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (3) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

The K_f values of hexazinone alone were higher in the LVAG soil and, in mixture, in the LVAV soil (Table 6). Therefore, these results reinforce the secondary importance of clay in the sorption of this herbicide, and confirm that organic matter is the main attribute that governs sorption, as already proven by García-Valcárcel and Tadeo (1999), and Pang and Flintoft (2005). It is worth emphasizing that LVAG has a higher organic matter content and a lower clay content in relation to LVAV. On the other hand, when in mixture, the clay content of soil increases hexazinone sorption. This happens because interactions between the herbicide molecules may promote the formation of a positive partial charge on hexazinone molecules, increasing the interaction between the herbicide and the minerals of the clay fraction of soil (Petter et al., 2016).

In all soils, hexazinone in mixture is more sorbed, as is diuron. Alves (2012) also observed a similar behavior with the mixture of glyphosate and ametryn. When alone, glyphosate presented high sorption, and ametryn, however, presented low sorption; when in mixture, the sorption of both was higher.

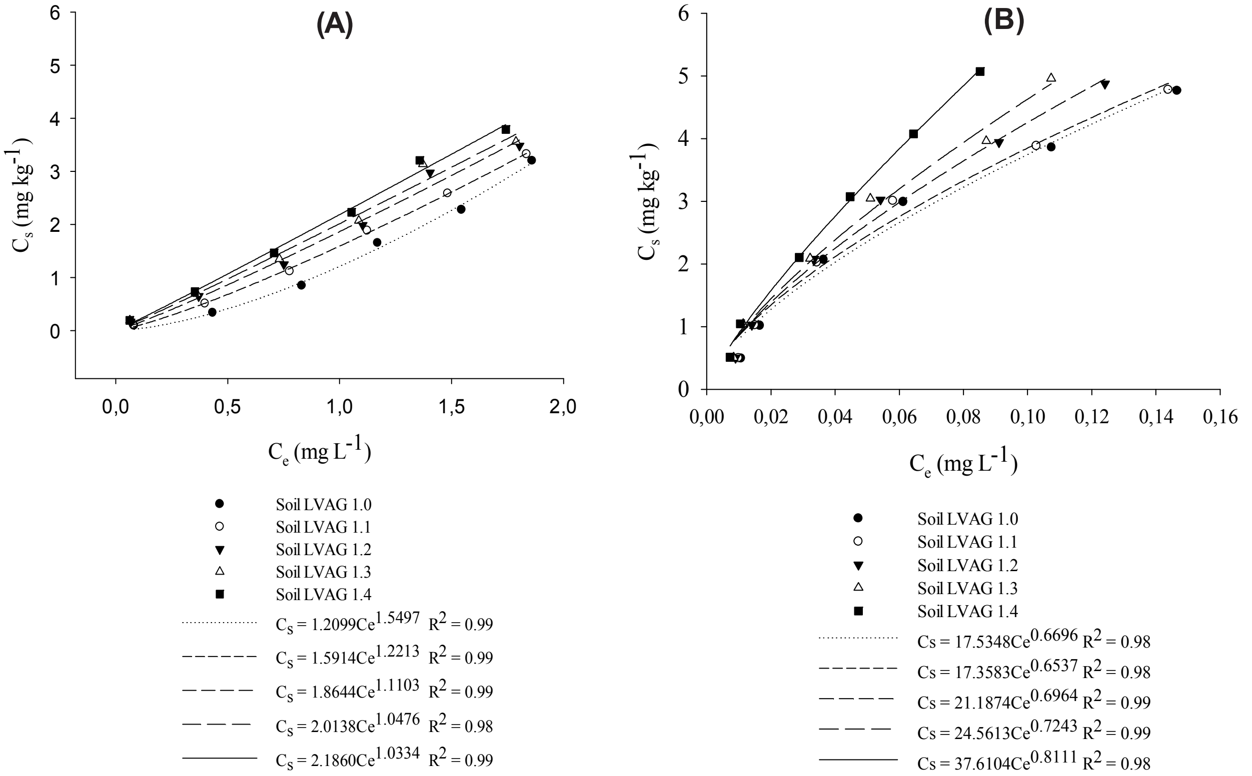

Figure 10 - Sorption of hexazinone alone (A) and hexazinone in mixture (B) in a LVAG Red-Yellow Latosol from Gurupi - Tocantins state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1). C_s: concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: concentration of herbicide in the equilibrium solution as mg L^{-1}.

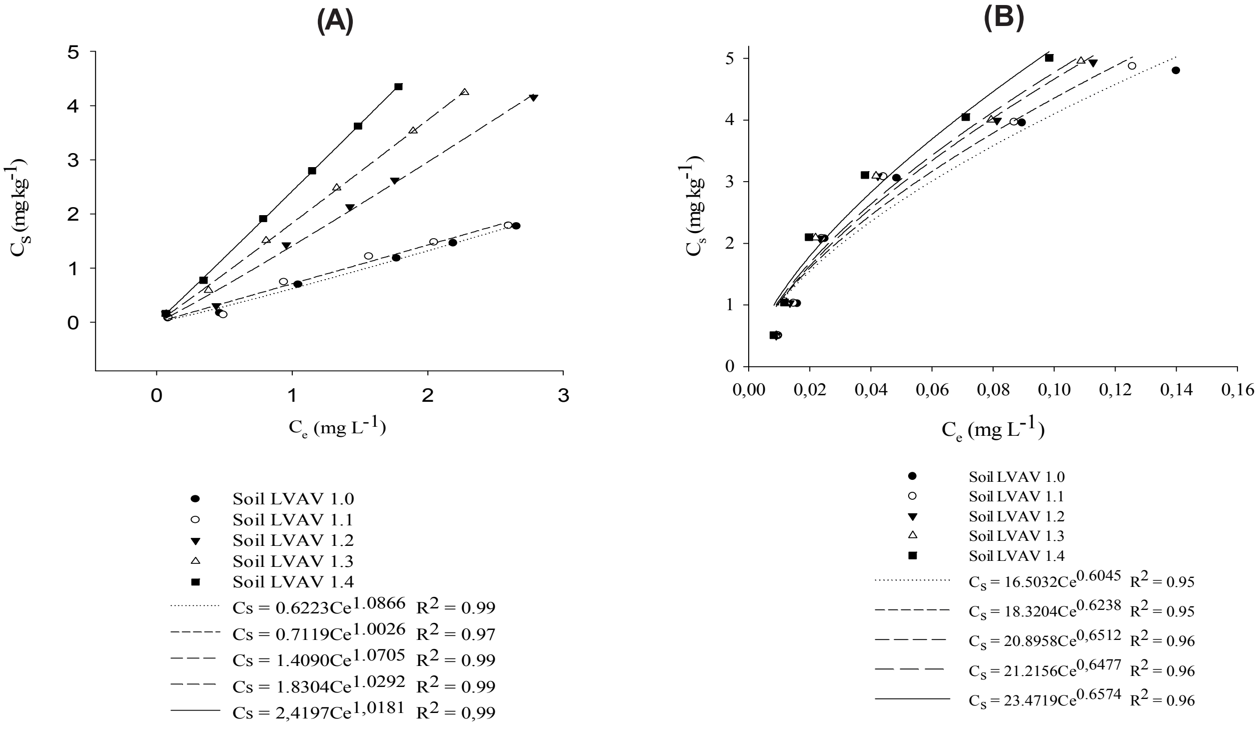

Figure 11 - Sorption of hexazinone alone (A) and hexazinone in mixture (B) in a LVAV Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1). C_s: concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: concentration of herbicide in the equilibrium solution as mg L^{-1}.

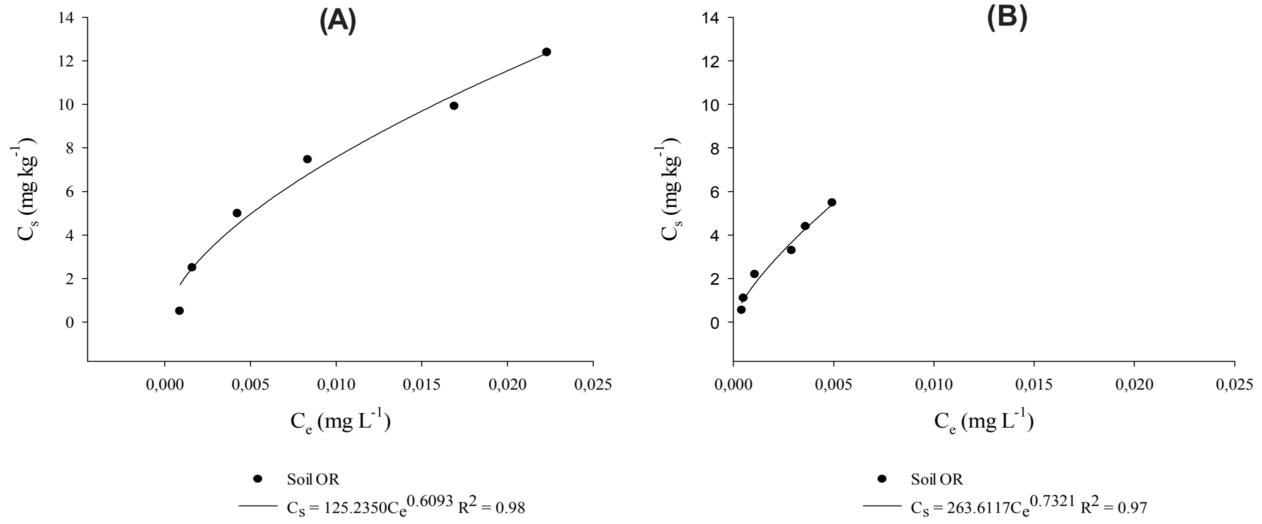

Figure 12 **-** Sorption of diuron isolated (A) and diuron in mixture (B) in samples of an Organosol from Venda Nova do Imigrante - Espirito Santo state (OR). C_s: concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: concentration of herbicide in the equilibrium solution as mg L^{-1}.

Table 6 **-** Freundlich parameters of the sorption of hexazinone, pure and in mixture, in the evaluated soils

Soil	Hexazinone sorption			Mixed hexazinone sorption		
	K_f	1/n	R^2	K_f	1/n	R^2
LVAG 1.0(1)a	1.21	1.55	0.99	17.53	0.67	0.98
LVAG 1.1(1)b	1.59	1.22	0.99	17.36	0.65	0.98
LVAG 1.2(1)c	1.86	1.11	0.99	21.19	0.70	0.99
LVAG 1.3(1)d	2.01	1.05	0.98	24.56	0.72	0.99
LVAG 1.4(1)e	2.19	1.03	0.99	37.61	0.81	0.98
LVAV 1.0(2)a	0.62	1.09	0.99	16.50	0.60	0.95
LVAV 1.1(2)b	0.71	1.00	0.97	18.32	0.62	0.95
LVAV 1.2(2)c	1.41	1.07	0.99	20.89	0.65	0.96
LVAV 1.3(2)d	1.83	1.03	0.99	21.22	0.65	0.96
LVAV 1.4(2)e	2.41	1.02	0.99	23.47	0.66	0.96
OR(3)	125.24	0.61	0.98	263.61	0.73	0.97

K_f, sorption coefficients; 1/n, exponent of the sorption equations. (1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: 1:0, b 1:0.25, c 1:0.5, d 1:0.75, and 1:1); (3) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

The desorption coefficients (Figures 13, 14 and Tables 7, 8) K_{fd} were higher than the sorption K_f of herbicides alone and in mixture, indicating that, in sorption-desorption equilibrium, the desorption process is favored in LVAG and LVAV soils (Tables 7 and 8). In the OR soil, sorption is favored. In this soil, it was not possible to quantify desorption, since the values found were lower than the quantification limit of the method.

The addition of cattle manure to the soils may be an alternative to avoid herbicide losses by draining or leaching due to the sorption increase, as already proven with the addition of organic compounds in the works done by Mendes et al. (2016), Gonçalves et al. (2012) and Briceño et al. (2008). However, most desorption experiments showed higher K_{fd} values with the increase of the manure incubated in LVAG and LVAV soils. Since in the OR soil desorption does not occur in a considerable way, it is believed that the quality of the organic matter also influences desorption. This is due to the fact that in soils where the organic matter is more stabilized, as in the OR, the mechanisms involving the sorption process are more intense.

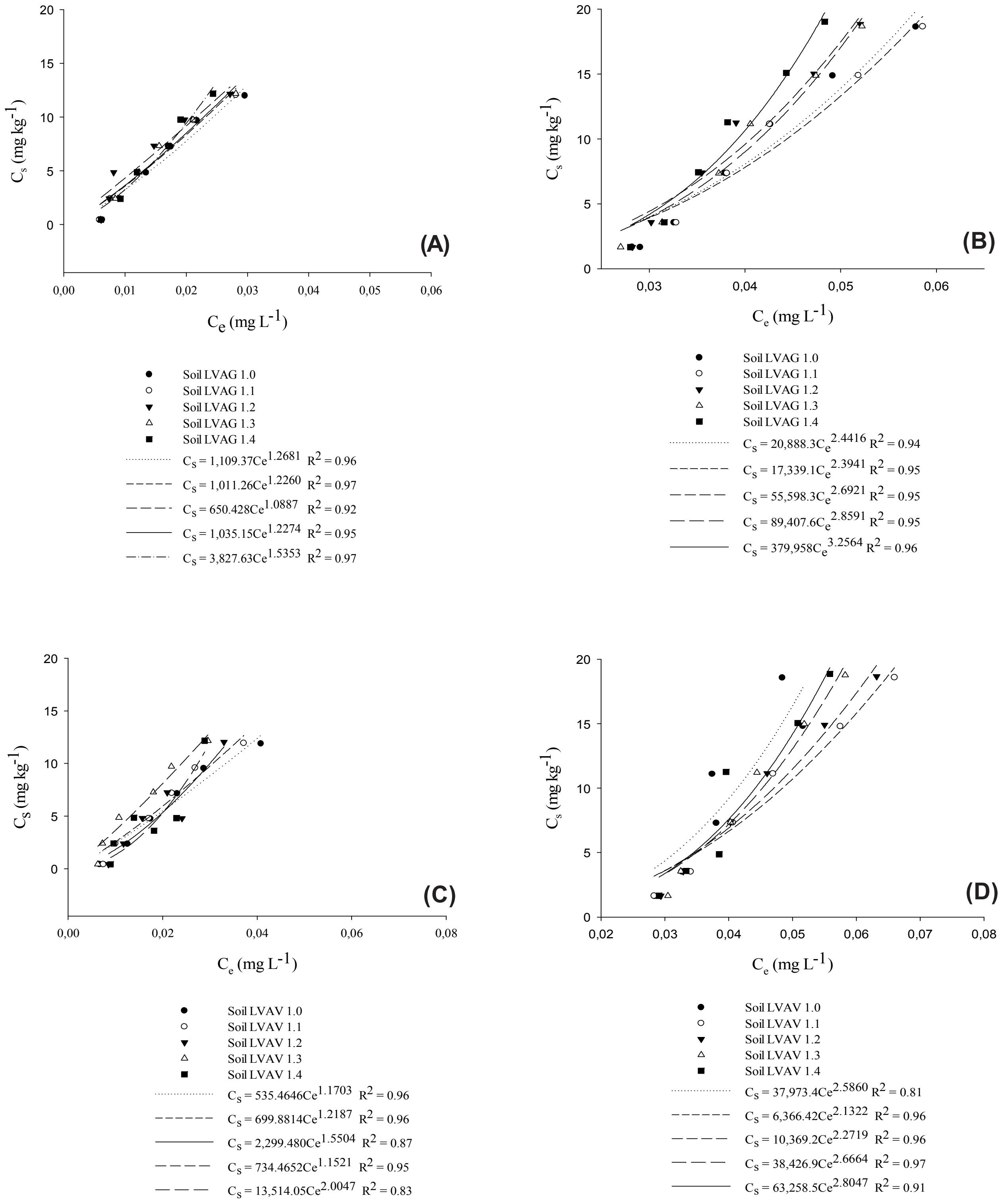

Figure 13 **-** Desorption of diuron alone (A and C) and diuron in mixture (B and D) in a LVAG Red-Yellow Latosol from Gurupi - Tocantins state and a LVAV Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1) C_s: concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: concentration of herbicide in the equilibrium solution as mg L^{-1}.

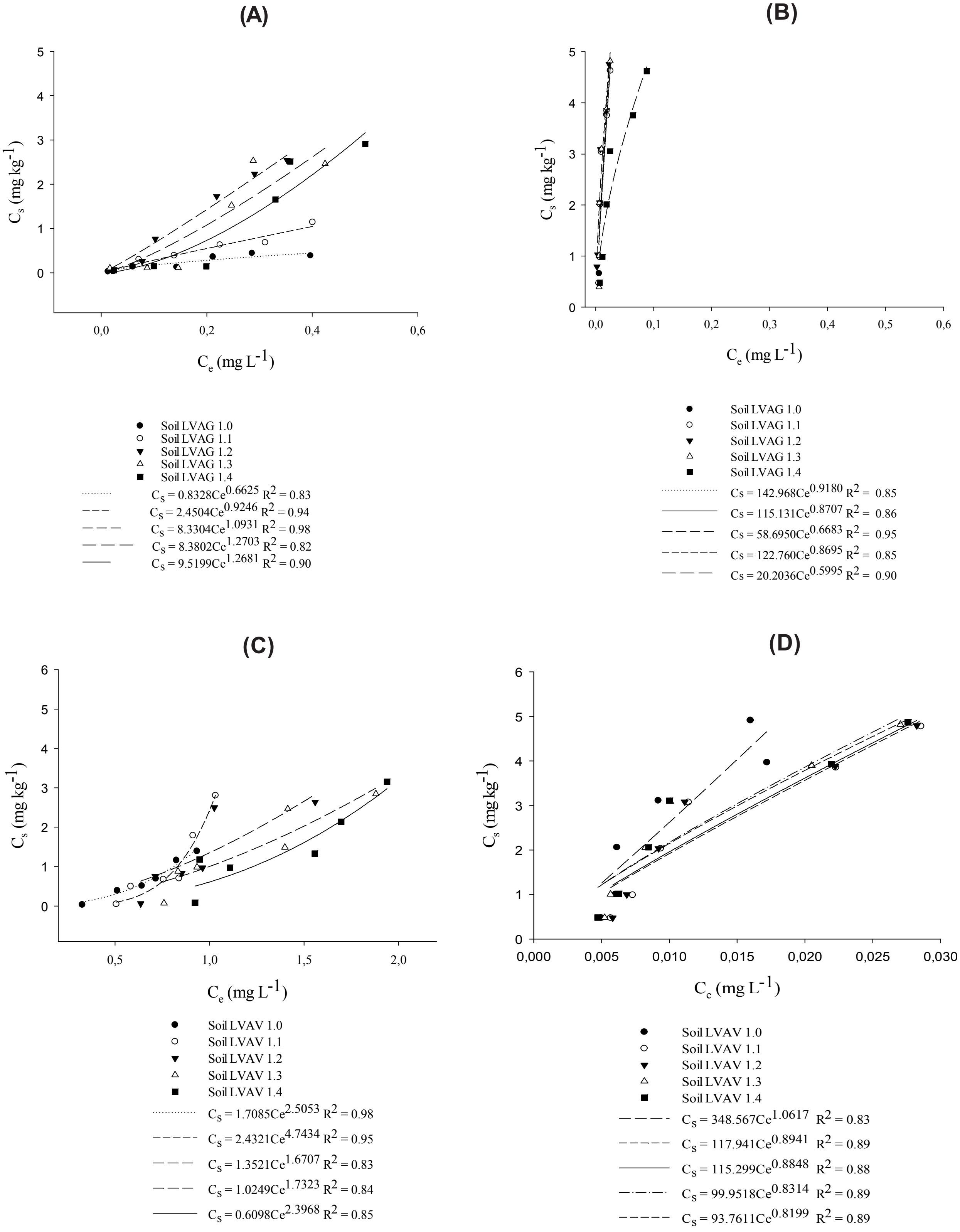

Figure 14 **-** Desorption of hexazinone alone (A and C) and hexazinone in mixture (B and D) in a LVAG Red-Yellow Latosol from Gurupi - Tocantins state and a LVAV Red-Yellow Latosol from Viçosa - Minas Gerais state (1.0 - without manure; 1.1 - soil ratio: manure at 1:0.25; 1.2 - soil ratio: manure at 1:0.5; 1.3 - soil ratio: manure at 1:0.75; 1.4 - soil ratio: manure at 1:1) C_s: concentration of herbicide sorbed in the soil as mg kg^{-1} and C_e: concentration of herbicide in the equilibrium solution as mg L^{-1}.

Table 7 **-** Freundlich parameters of desorption and hysteresis index of pure and mixed diuron for the used soils

Soil	Diuron desorption				Mixed diuron desorption			
	K_{fd}	1/n	R^2	H	K_{fd}	1/n	R^2	H
LVAG 1.0(1)a	1,109.37	1.27	0.96	0.67	20,888.3	2.44	0.94	0.57
LVAG 1.1(1)b	1,011.26	1.23	0.97	0.72	27,339.1	2.39	0.95	0.58
LVAG 1.2(1)c	650.43	1.09	0.92	0.99	55,598.3	2.69	0.95	0.50
LVAG 1.3(1)d	1,035.15	1.23	0.95	0.90	89,407.6	2.86	0.97	0.46
LVAG 1.4(1)e	3,827.64	1.54	0.97	0.76	379,958.6	3.26	0.96	0.41
LVAV 1.0(2)a	535.46	1.17	0.96	0.88	379,73.4	2.59	0.81	0.55
LVAV 1.1(2)b	699.88	1.22	0.96	0.82	6,366.4	2.13	0.96	0.64
LVAV 1.2(2)c	2,299.48	1.55	0.87	0.61	10,369.1	2.27	0.96	0.64
LVAV 1.3(2)d	734.47	1.15	0.95	1.08	38,426.8	2.67	0.97	0.59
LVAV 1.4(2)e	1,3514.5	2.00	0.83	0.57	63,258.4	2.80	0.91	0.71
OR(3)	ND	ND	ND	ND	ND	ND	ND	ND

K_{fd}. desorption coefficients; 1/n. exponent of the desorption equations; H. hystereses index; ND. not detected. (1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0. b 1:0.25. c 1:0.5. d 1:0.75. and 1:1); (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: 1:0. b 1:0.25. c 1:0.5. d 1:0.75. and 1:1); (3) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

Table 8 **-** Freundlich parameters of desorption and hysteresis index of pure and mixed hexazinone for the used soils

Soil	Hexazinone desorption				Mixed hexazinone desorption			
	K_{fd}	1/n	R^2	H	K_{fd}	1/n	R^2	H
LVAG 1.0(1)a	0.83	0.66	0.83	1.52	142.97	0.92	0.85	0.62
LVAG 1.1(1)b	2.45	0.92	0.94	0.98	115.13	0.87	0.86	0.67
LVAG 1.2(1)c	8.33	1.09	0.98	1.04	58.70	0.67	0.95	0.87
LVAG 1.3(1)d	8.38	1.27	0.82	0.99	122.76	0.87	0.85	0.78
LVAG 1.4(1)e	9.52	1.27	0.90	0.96	20.20	0.60	0.90	1.06
LVAV 1.0(2)a	1.79	2.51	0.98	0.43	348.57	1.06	0.83	0.61
LVAV 1.1(2)b	2.43	4.74	0.95	0.25	117.94	0.89	0.89	0.69
LVAV 1.2(2)c	1.35	1.67	0.83	0.64	115.30	0.88	0.88	0.69
LVAV 1.3(2)d	1.02	1.73	0.84	0.59	99.95	0.83	0.89	0.73
LVAV 1.4(2)e	0.61	2.40	0.85	0.42	93.76	0.82	0.89	0.74
OR(3)	ND	ND	ND	ND	ND	ND	ND	ND

K_{fd}. desorption coefficients; 1/n. exponent of the desorption equations; H. hystereses index; ND. not detected; (1) Red-Yellow Latosol from the municipality of Gurupi - Tocantins state (soil ratio: manure at 1:0. b 1:0.25. c 1:0.5. d 1:0.75. and 1:1); (2) Red-Yellow Latosol from the municipality of Viçosa - Minas Gerais state (soil ratio: 1:0. b 1:0.25. c 1:0.5. d 1:0.75. and 1:1); (3) Organosol from the municipality of Venda Nova do Imigrante - Espirito Santo state.

It is possible to conclude that the application of the diuron + hexazinone mixture increases the sorption of these herbicides to the soil. The recommendation of hexazinone alone should take into account the organic matter content (OMC) of soil. Diuron applied alone presents high soil sorption. Desorption presents high magnitude in relation to sorption in soils with low content of SOM. In the OR, desorption is low and, therefore, could not be quantified. There is a direct relation between the addition of manure to the substrate and sorption in soils. The incubation of soils with low SOM content with manure helps both the sorption and desorption processes of the herbicides.

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