SORPTION OF OXADIAZON IN SOILS CULTIVATED IN THE BRAZILIAN CERRADO[1]

Sorção do Oxadiazon em Solos Cultivados no Cerrado Brasileiro

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ABSTRACT - The objective of this study was to evaluate oxadiazon sorption in different soils of the Brazilian Cerrado, highlighting the correlations of lethal doses of this herbicide capable of inhibiting 50% of the dry matter accumulation of the bio-indicator (LD50) among the chemical characteristics of the soil and its direct and indirect effects. The experiment was carried out in a greenhouse in a randomized block design and four repetitions. Each experimental unit consisted of a pot with increasing rates of oxadiazon and oat (*Avena sativa*), as the bio-indicator species. For sorption evaluation, washed sand and 22 soils (substrates) from Cerrado Brazilian's Alliaceae cultivated areas were used. LD50 and sorption ratio (SR) = [(LD50soil - LD50sand)/LD50sand] to the substrates were determined. Pearson correlation analysis was performed between the chemical characteristics of the substrates and the LD50 of oxadiazon. A path analysis was quantified, to deploy only the significant correlations estimated in direct and indirect effects of the characters on LD50, which is a basic variable. A more pronounced LD50 (528.09 g ha^{-1}) for the Cerrado soil sample resulted in higher SR (> 53.00), while in the washed sand substrate, LD50 corresponded only to 9.74 g ha^{-1} of the oxadiazon (available in soil). It was concluded that oxadiazon sorption is influenced by the chemical characteristics of the soils, highlighting the correlation with pH ($CaCl_2$), magnesium content, aluminum, organic matter, organic carbon, and aluminum saturation.

Keywords: bioassay, neutral herbicide, organic matter.

*RESUMO - Objetivou-se neste estudo avaliar a sorção do oxadiazon em diferentes solos do Cerrado Brasileiro, destacando as correlações da dose letal do herbicida capaz de inibir 50% do acúmulo da massa seca do bioindicador (DL50) entre as características químicas do solo e seus efeitos diretos e indiretos. O experimento foi realizado em casa de vegetação, com delineamento em blocos casualizados com quatro repetições. Cada unidade experimental foi constituída de um vaso com doses crescentes do oxadiazon; utilizou-se a aveia (**Avena sativa**) como espécie bioindicadora. Na avaliação da sorção, foram utilizados areia lavada e 22 solos (substratos) provenientes de áreas cultivadas com Alliaceae no cerrado Brasileiro. Foram determinadas a DL50 e a relação de sorção (RS) = [(DL50solo – DL50areia)/DL50areia], para os substratos. Posteriormente, análise de correlação de Pearson foi realizada entre as características químicas dos substratos e a DL50 do oxadiazon. Foi quantificada ainda a análise de trilha, a fim de desdobrar somente as correlações significativas estimadas em efeitos diretos e indiretos de caracteres sobre a DL50, que é uma variável básica. A DL50 mais expressiva (528,09 g ha^{-1}) para uma das amostras de solo de cerrado resultou em maior RS (> 53,00). Já no substrato de areia lavada, a DL50 foi de apenas 9,74 g ha^{-1} do oxadiazon (disponível no solo). Conclui-se que a sorção do oxadiazon é influenciada pelas características químicas dos solos, ressaltando a correlação com o pH ($CaCl_2$), teor de magnésio, alumínio, matéria orgânica, carbono orgânico e a saturação por alumínio.*

Palavras-chave: bioensaio, herbicida neutro, matéria orgânica.

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INTRODUCTION

The sorption process controls the transport, persistence, bioavailability and fate of herbicides in the soil (Tao & Tang, 2004). This process comprises passing solute (herbicide) of the aqueous phase to the surface of a solid substance (soil), by means of physical or chemical interactions (Estévez et al., 2008). From the kinetic point of view, the sorption of herbicides presents a rapid initial step, responsible for much of the overall sorption, followed by a slower phase, tending to final equilibrium between the sorbed phase and the remaining in solution (Oliveira et al., 2005; Estévez et al., 2008).

The sorption varies with soil properties, such as content of clay, organic matter, Ca^{2+}, cation exchange capacity and surface area (Burns et al., 2006). The highest content of organic matter in the soil promotes increased sorption herbicide; therefore, the herbicidal activity decreases with increasing content of soil organic carbon (Ben-Hur et al., 2003). There is an increasing application of agroindustrial wastes rich in organic matter in agricultural soils, due to the low cost or infeasibility of alternatives, such as green manure or animal manure (Delgado-Moreno & Peña, 2008). Strong positive correlation has been reported between the organic carbon content of the soil and the sorption of herbicides (Albarrán et al., 2003; Ahangar et al., 2008), in which leaching of these molecules could be reduced by application of organic compounds.

Although the increase of the amount of organic matter in the soil generally increasing absorption of herbicides and reducing leaching, it may also, in parallel, increase the persistence of the herbicide, and therefore increase the risk of water contamination over time (Cabrera et al., 2008). Moreover, the efficiency of the interaction of the soil organic matter with herbicides is influenced by its molecular configuration, polarity and size, as well as by its chemical characteristics and the nature of the soil (Celis et al., 1998).

The sorption of neutral or nonionic compounds such as oxadiazon has been extensively studied and appears to be dependent on the molecular nature of the organic matter contained in the soil (Estévez et al., 2008).

Oxadiazon is oxidase protoporphyrinogen inhibitor (PROTOX), which operates in the accumulation of protoporphyrinogen in the chloroplast, diffusing into the cytosol, the oxidation occurring at protoporphyrin IX (precursors of chlorophyll), which is a photodynamic pigment. Oxadiazon applied in cotyledons of *Cucumis sativus* promoted disruption of cell membranes after one hour of exposure to light (Duke et al., 1989), rapidly dehydrating and disintegrating the organelles cells.

The evaluation of sorption of herbicides have been assessed by different methods, such as the bioassay (Freitas et al., 1998; Firmino et al., 2008), which is simple, rapid and low-cost. Alternatively, test plants (bio-indicator) are used, which exhibit high sensitivity to the herbicide of interest (Eliason et al., 2004; Szmigielski et al., 2009). This technique is more affordable than the chromatographic quantitative methods. In view of the above, studies involving the interaction between herbicides and soil components (Celano et al., 2008; Moure et al., 2009; Sun et al., 2012) were conducted, aimed mainly to know the possible behavior of herbicides in soil.

Information about sorption of oxadiazon in soil contribute to better understand their behavior and fate in the environment, since the sorption affects mobility and degradation and hence the potential for contamination of surface and groundwater.

There is a lack of studies concerning the effects of soil chemical properties on the sorption of oxadiazon in tropical soils. Considering the above, the aim of this work was to evaluate the sorption capacity of oxadiazon and the effects of 17 chemical characteristics in 23 soils cultivated with Alliaceae.

MATERIALS AND METHODS

For the experiment, were collected 22 soil samples from the plow layer (0.00 0.20 m), marked with Global Positioning System (GPS) in different areas cultivated with Alliaceae – garlic and onion (Figure 1), with soils classified as dystrophic red latosol (oxisol), clayey texture, besides the washed sand substrate, considered as inert material.

The soil and sand washed were sieved through a 2.0 mm mesh. The process of washing sand previously incubated with diluted HCl solution in water at 6.0% for 24 hours, followed by new incubation with NaOH solution in the same proportion for 24 hours; and, as a result, it was washed with running water until reaching a pH near 7.0.

Subsequently, the sand and soil samples were air-dried, and 100 g of substrate were put in plastic pots with a capacity of 0.1 L. Chemical analyzes of each soil sample were conducted (Table 1).

The experiment was conducted in a design with randomized blocks with four replications and the treatments consisted of the substrates and increasing rates of oxadiazon. The experimental unit consisted of a pot with two plants of the species bio-indicator (*Avena sativa*), sensitive to oxadiazon (Fourie, 1992).

A single application was conducted (0.01 L) of balanced nutrient solution at 10 days after emergence (DAE), containing 4% of N, 14% of P_2O_5 and 8% of K_2O, with primary macronutrients and micronutrients (Green Root 1.25 g L^{-1}), diluting 0.005 L of the solution in 1 L of water. At 21 DAE, the aerial part was collected and taken to forced ventilation oven at 72 °C for 48 h.

The 10 oxadiazon increasing rates were applied in pre-emergence (0.00; 0.49; 0.98; 1.95; 3.91; 7.81; 15.63; 31.25; 62.50; and 125.00 g ha^{-1}) under all the pots containing the soils substrates and 20 rates (0.00; 0.06; 0.09; 0.12; 0.18; 0.24; 0.37; 0.49; 0.73; 0.98; 1.46; 1.95; 2.93; 3.91; 5.86; 7.81; 11.72; 15.63; 31.25; and 62.50 g ha^{-1}) in the washed sand, to prepare

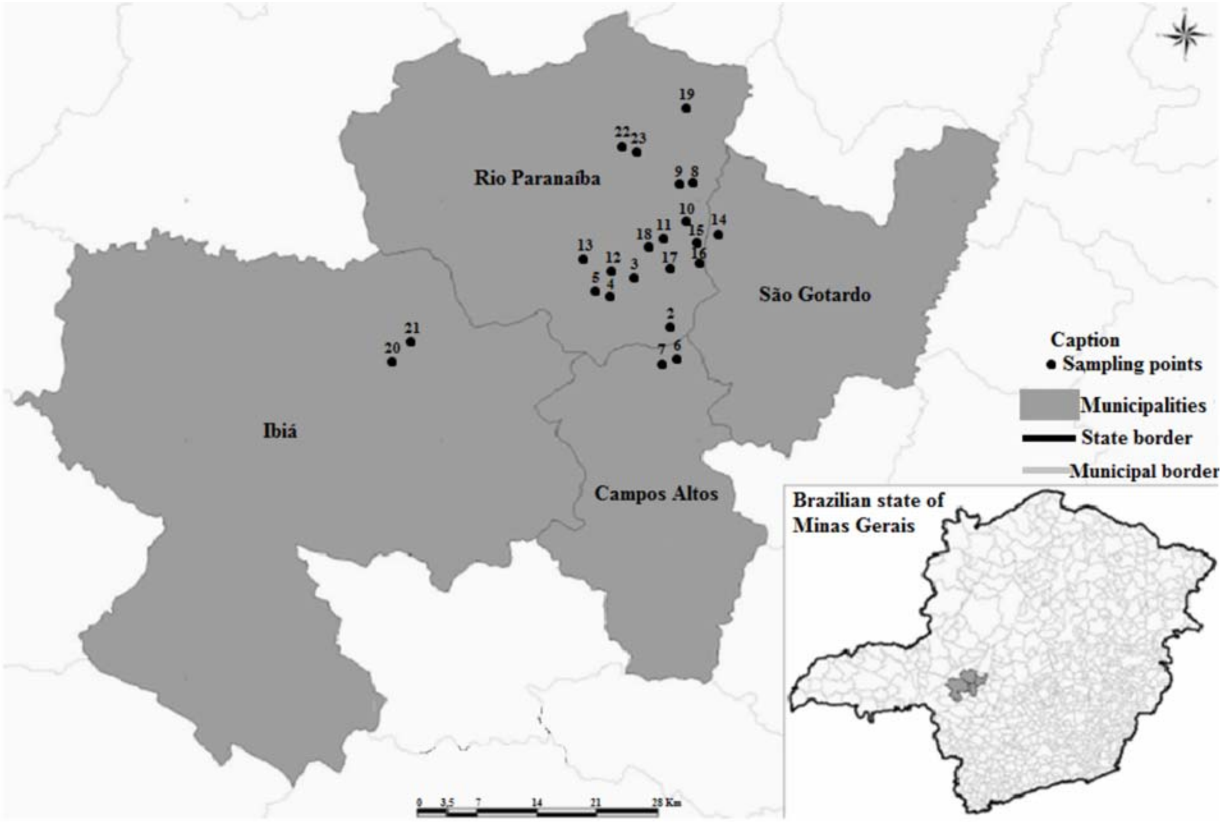


Figure 1 - Location of the sampling points in cultivated soils of the cerrado in the Brazilian state of Minas Gerais (except washed sand – sample 1), used in the bioassay of sorption of oxadiazon. Rio Paranaíba, MG, 2012.

Table 1 - Substrate chemical characteristics of soils used in the experiment. Rio Paranaíba, MG, 2012

Sample[1/]	pH		P(res)	P(melh)	P(rem)	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H + Al	OM	OC	SB	t	T	V	m
	(H_2O)	($CaCl_2$)	mg dm^{-3} (ppm)			($cmol_c$ dm^{-3})					(g dm^{-3})		($cmol_c$ dm^{-3})			(%)	
1	7.00	7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	5.30	4.20	12.00	7.00	10.50	0.33	1.50	1.20	0.15	4.08	52.00	30.20	3.03	3.18	7.11	42.60	4.70
3	6.00	5.30	266.00	93.70	13.70	0.37	4.00	0.80	0.00	4.13	34.00	19.70	5.17	5.17	9.30	55.60	0.00
4	6.20	5.30	320.00	96.10	14.70	0.30	4.30	1.00	0.00	2.13	33.00	19.10	5.60	5.60	7.73	72.40	0.00
5	5.60	5.10	116.00	63.50	8.20	0.21	2.70	0.60	0.00	4.63	35.00	20.30	3.51	3.51	8.14	43.10	0.00
6	6.20	5.50	294.00	96.50	17.60	0.37	4.80	1.10	0.00	2.20	38.00	22.00	6.27	6.27	8.47	74.00	0.00
7	6.30	5.40	217.00	91.40	18.30	0.54	3.80	1.20	0.00	3.53	39.00	22.60	5.54	5.54	9.07	61.10	0.00
8	6.00	5.30	219.00	89.60	18.50	0.26	3.20	1.20	0.00	4.13	34.00	19.70	4.66	4.66	8.79	53.00	0.00
9	5.80	4.70	121.00	62.80	13.10	0.58	2.20	1.10	0.00	3.92	36.00	20.90	3.88	3.88	7.80	49.70	0.00
10	6.50	5.80	160.00	68.20	10.90	0.41	4.40	1.00	0.00	2.68	35.00	20.30	5.81	5.81	8.49	68.40	0.00
11	5.80	5.10	112.00	50.90	12.20	0.50	3.70	1.40	0.00	2.92	39.00	22.60	5.60	5.60	8.52	65.70	0.00
12	6.90	6.10	290.00	90.30	9.50	0.14	4.90	1.70	0.00	2.13	37.00	21.50	6.74	6.74	8.87	76.00	0.00
13	6.20	5.10	122.00	53.20	11.00	0.63	3.30	1.40	0.00	2.83	39.00	22.60	5.33	5.33	8.16	65.30	0.00
14	6.40	5.70	167.00	49.10	8.40	0.41	3.70	1.10	0.00	3.04	35.00	20.30	5.21	5.21	8.25	63.20	0.00
15	6.20	5.30	187.00	81.90	14.20	0.45	3.40	1.00	0.00	2.47	35.00	20.30	4.85	4.85	7.32	66.30	0.00
16	6.30	5.60	233.00	96.50	15.70	0.34	3.80	1.10	0.00	3.45	37.00	21.50	5.24	5.24	8.69	60.30	0.00
17	5.80	5.20	182.00	85.30	18.30	0.64	3.20	0.70	0.00	2.92	35.00	20.30	4.54	4.54	7.46	60.90	0.00
18	6.50	5.80	296.00	95.70	17.90	0.46	4.40	1.30	0.00	2.86	35.00	20.30	6.16	6.16	9.02	68.30	0.00
19	6.70	5.90	200.00	70.60	4.90	0.44	5.80	1.70	0.00	1.73	37.00	21.50	7.94	7.94	9.67	82.10	0.00
20	6.10	5.40	150.00	60.00	13.10	0.78	3.80	1.10	0.00	3.04	31.00	18.00	5.68	5.68	8.72	65.10	0.00
21	6.20	5.40	127.00	56.00	12.40	0.67	3.50	1.10	0.00	2.27	29.00	16.80	5.27	5.27	7.54	69.90	0.00
22	6.00	5.70	98.00	50.20	12.80	0.32	5.00	1.40	0.00	1.80	43.00	24.90	6.72	6.72	8.52	78.90	0.00
23	7.20	6.30	250.00	96.50	14.90	1.37	5.90	2.30	0.00	1.74	49.00	28.40	9.57	9.57	11.31	84.60	0.00
Average	6.23	5.49	179.96	69.78	12.64	0.46	3.71	1.15	0.01	2.81	35.52	20.60	5.32	5.32	8.13	62.02	0.20
Standard deviation	0.45	0.55	86.28	27.28	4.53	0.27	1.31	0.44	0.03	1.04	9.28	5.38	1.80	1.79	1.98	17.45	0.98

Source: Fertilab – Laboratório de Análises de Solo e Foliar. São Gotardo, MG.

[1/] P(res) = resin phosphorus; P(melh) = Mehlich phosphorus; P(rem) = remaining phosphorus; OM = organic matter (calorimetric method); OC = organic carbon; t = effective cation exchange capacity; T = cation exchange capacity at pH 7.0; V = saturation by bases; m = saturation by aluminum.

the standard curve of sorption (Firmino et al., 2008).

In the applications of oxadiazon a pressurized coast sprayer was used with CO_2 at 200 kPa, equipped with a bar of 0.5 m composed of two flat spray tips (“range” type) 110.02, with a volume of syrup equivalent to 200 L ha^{-1}. The application of oxadiazon was made with the humidity of the environment of 30%, soil moisture of 42%, atmospheric air temperature of 29 °C and wind speed of 3.5 km h^{-1}.

For the interpretation of the results, the values were compared to the treatment with the herbicide (zero rate). The LD50 (lethal rate able to inhibit 50% of the dry matter accumulation of the bio-indicator) and the confidence interval of 95% were determined by Probit analysis (Goss et al., 2009). From the data obtained from LD50 on substrates of soil and sand, the RS equation was used = [(LD50soil – LD50sand)/LD50sand] (Souza et al., 1996), to express the relation of sorption (RS) of the soil compared to the response obtained in sand by means of bioassay as an indirect method for quantitation of waste (Szmigielska et al., 1998). It is considered that the higher values of RS indicate higher sorption capacity of the herbicide studied into the soil and, therefore, a lower potential for leaching of the herbicide into the soil profile.

Pearson correlation analysis was performed among the chemical characteristics of the soils assessed, and the LD50 of the oxadiazon by the t test ($p < 0.01$ and 0.05).

Linear regression analysis was also performed among the LD50 values of the oxadiazon and the organic matter content in the soil (except washed sand), by the F test ($p < 0.01$). Path analysis, which unfolds the correlations estimated in direct and indirect effects of characters on one basic variable (LD50) was quantified only for the significant correlations. All statistical analysis were performed in the Genes program (Cruz, 2006).

RESULTS AND DISCUSSION

In the washed sand substrate (sample 1), the rate of 9.74 g ha^{-1} of the oxadiazon (available in the soil) was sufficient to reduce 50% of the dry mass of the aerial part of the oats bio-indicator (*Avena sativa*) (Table 2). This result confirms the high sensitivity of oats to oxadiazon, evidencing the use as bio-indicator for this herbicide.

Table 2 - Lethal rate able to inhibit 50% of the dry mass accumulation of the aerial part of the bio-indicator (LD50), confidence interval at 95%, and the sorption relation (RS) for substrates of washed sand and cultivated soils of the cerrado in Minas Gerais. Rio Paranaíba, MG, 2012

Sample[1/]	LD50	Confidence interval at 95%		RS
	(g ha^{-1})	Minimum	Maximum	
1	9.7411	8.4869	11.2437	-
2	528.0912	492.3435	578.1634	53.2127
3	154.1518	132.8271	180.9461	14.8249
4	127.1026	105.6993	153.7940	12.0481
5	309.1174	260.2181	380.5146	30.7333
6	139.6343	109.2719	184.9395	13.3346
7	306.2613	207.5654	550.3201	30.4401
8	93.9248	74.4852	118.9231	8.6421
9	133.5501	111.9682	161.5546	12.7100
10	83.2561	68.7964	100.1738	7.5469
11	188.3500	135.7106	290.9707	18.3356
12	138.9968	112.6058	175.8252	13.2691
13	416.9082	326.2873	568.7160	41.7989
14	69.3272	50.8447	96.4899	6.1170
15	19.5972	1.5660	44.3907	1.0118
16	88.3191	61.8567	126.0854	8.0666
17	109.4462	83.8019	147.2100	10.2355
18	246.9210	187.7159	352.8427	24.3484
19	138.5987	111.7322	176.4142	13.2282
20	94.1549	78.2459	113.5733	8.6657
21	110.4422	95.6372	127.1088	10.3378
22	280.1504	178.5379	298.2964	27.7596
23	321.2256	298.3574	353.7457	31.9763

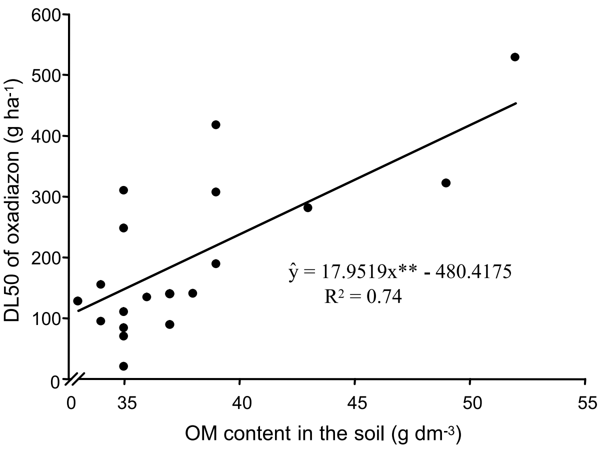
[1/] Substrate of washed sand and samples of soil cultivated of the cerrado in Minas Gerais.

The LD50 – lethal rate of the oxadiazon (528.09 g ha^{-1}) able to inhibit 50% of the dry mass of the aerial part of the bio-indicator – was more significant for the Cerrado soil substrate (sample 2), with confidence minimum and maximum interval at 95% of 492.34 and 578.16 g ha^{-1}, respectively, resulting in greater relative sorption – RS (53.2) compared with the other soils (Table 2). This fact is explained by this being a soil sample, among those studied, with higher organic matter content (52.00 g dm^{-3}) (Table 2). According to Freitas et al. (1998), the LD50 of diuron (100 a 900 g ha^{-1}) is also dependent on the organic matter content in the soil, where the addition of 0, 20, 40 and 60 m^3 ha^{-1} of pig slurry provided RS of 23.38, 25.32, 28.70, and 30.55 respectively; in the addition of 0, 30, 60 and 90 t ha^{-1} of organic compost produced from bagasse of sugarcane, the RS were 28.76, 32.75, 34.59, and 39.94 respectively.

In China, the sorption of ethametsulfuron-methyl ranged from 68.4 to 92.4% in soils without the addition of OM – organic matter (1.02% of OC – organic carbon) and adding (2.61% of OC), which was attributed to the high sorption capacity of the insoluble OM added to the soil in the presence of the herbicide (Si et al., 2006).

The weed control is also declining, especially in the presence of higher concentrations of OM in the soil, indicating less amount of the bioavailable herbicide in the soil solution. However, sample 21 of soil substrate had the lowest OM content (29.00 g dm^{-3}) in relation to other substrates and was not directly proportional to the RS.The lower RS (1.01) is represented in sample 15 with 35.00 g dm^{-3} of OM (Table 2). Thus, not only the level of OM in the soil influences the sorption potential of the oxadiazon, but due to other soil chemical characteristics, which should be studied.

The relationship between the OM content in the soil and the LD50 of the oxadiazon in the soils studied was linear; the addition of 1.00% of OM, corresponding to 10.00 g dm^{-3}, provides a LD50 of approximately 179.52 g ha^{-1} (Figure 2). As already reported by Hoque et al. (2007), the oxadiazon sorption by the soil is a rapid process and linearly related to the concentration, depending on the OC content and occurs within two hours.



** $p < 0.01$ by the F test.

Figure 2 - Relationship between the OM content in the soil and the LD50 of oxadiazon for substrates of cultivated soils of the cerrado in Minas Gerais (except washed sand – sample 1). Rio Paranaíba, MG, 2012.

The correlations of LD50 of oxadiazon with the chemical characteristics of the soils confirm the influence of the soil variability in the sorption processes of the herbicide (Table 3). The positive correlations, 0.63 ($p < 0.01$), of the OM and OC contents of the soil with the LD50 of the oxadiazon demonstrate the higher sorption capacity of the herbicide in soil with high levels of OM and OC. This behavior is extremely important from a practical point of view, because the efficiency of the oxadiazon in weed control can be reduced in soils rich in OM, because of the unavailability and/or degradation of the herbicide (Prata & Lavorenti, 2000).

The OM is the universal colloid of the soil, retaining most of the herbicides (Moure et al., 2009), with highly heterogeneous structures (Cornelissen et al., 2005; Chefetz & Xing, 2009). Due to its high specific surface area and the diversity of functional groups, the OM can interact with the organic molecules of different shapes. The possible mechanisms involved in the interaction among herbicides of low water solubility, such as oxadiazon (Garbi et al., 2006), with 0.57 mg L^{-1} (Footprint, 2013), and the OM are hydrogen bonding, Van der Waals forces, hydrophobic interactions and charge transfer, and they can operate concurrently in the sorption of the same molecule (Sheng et al., 2001). The molecular

Table 3 - Pearson correlations among the 23 lethal rates of oxadiazon able to inhibit 50% of the dry mass accumulation of the aerial part of the bio-indicator (LD50) and 17 chemical characteristics of cultivated soil samples of the cerrado of Minas Gerais. Rio Paranaíba, MG, 2012

Characteristic[1/]	LD50	pH (H_2O)	pH ($CaCl_2$)	P(res)	P(melh)	P(rem)	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H + Al	OM	OC	SB	t	T	V	m
LD50	1.00	-0.32	-0.43*	-0.22	-0.20	0.09	0.23	0.01	0.38*	0.59**	0.32	0.63**	0.63**	0.14	0.14	0.29	0.09	0.59**
pH (H_2O)		1.00	0.90**	0.33	0.20	-0.27	0.18	0.37*	0.30	-0.45*	-0.71**	-0.32	-0.32	0.36*	0.36*	-0.04	0.16	-0.45*
pH ($CaCl_2$)			1.00	0.16	0.04	-0.38*	-0.05	0.20	0.01	-0.50**	-0.77**	-0.55**	-0.55**	0.14	0.14	-0.27	-0.06	-0.50**
P(res)				1.00	0.93**	0.57**	0.14	0.70**	0.37*	-0.42*	0.05	0.23	0.23	0.61**	0.61**	0.58**	0.60**	-0.42*
P(melh)					1.00	0.71**	0.25	0.68**	0.36*	-0.50**	0.20	0.31	0.31	0.61**	0.61**	0.67**	0.61**	-0.50**
P(rem)						1.00	0.36*	0.35	0.25	-0.10	0.42*	0.48*	0.48*	0.37*	0.37*	0.55**	0.45*	-0.10
K							1.00	0.41*	0.58**	-0.10	-0.01	0.43*	0.43*	0.58**	0.58**	0.53**	0.49**	-0.10
Ca^{2+}								1.00	0.74**	-0.37*	-0.12	0.52**	0.52**	0.97**	0.97**	0.81**	0.93**	-0.37*
Mg^{2+}									1.00	0.02	-0.04	0.72**	0.72**	0.87**	0.87**	0.77**	0.78**	0.02
Al^{3+}										1.00	0.26	0.39*	0.39*	-0.26	-0.26	-0.11	-0.24	1.00
H + Al											1.00	0.46*	0.46*	-0.10	-0.10	0.43*	-0.03	0.27
OM												1.00	1.00	0.62**	0.62**	0.81**	0.66**	0.39*
OC													1.00	0.62**	0.62**	0.81**	0.66**	0.39*
SB														1.00	1.00	0.85**	0.94**	-0.28
t															1.00	0.85**	0.94**	-0.27
T																1.00	0.83**	-0.11
V																	1.00	-0.24
m																		1.00

* and ** $p < 0.01$ and 0.05, by the t test, respectively. [1/] P(res) = resin phosphorus; P(melh) = Mehlich phosphorus; P(rem) = remaining phosphorus; OM = organic matter (calorimetric method); OC = organic carbon; t = effective cation exchange capacity; T = cation exchange capacity at pH 7.0; V = saturation by bases; m = saturation by aluminum.

nature of the OM of the soil has been shown to be the key to determine the sorption of nonionic herbicides (Correia & Langenbach, 2006). The molecular OM and its complex structure influence the behavior of fluridone and norflurazon, providing greater sorption (Sun et al., 2012). In China, the amount of sorption of butachlor in soils (1.50 a 4.78% de OM) was positively correlated with the OM content of the soil (Xu et al., 2005).

Oxadiazon sorption is related to the OC content of the soils (Comoretto et al., 2008). In addition, the sorption of the herbicide in the suspended sediments can reduce the degradation rates of oxadiazon in the soil (Lin et al., 2000; Ying & Williams, 2000), forming carboxylic acid, phenolic derivatives and polar dealkylated products, which were identified as the metabolites of degradation of oxadiazon in the soil (Ying & Williams, 1999).

The sorption in the soil of s-triazines – atrazine, terbuthylazine and simazine – was mainly related to the OC content, hydrophobicity and aromaticity of humic acid, implying a predominant role of weak links and dispersive forces (Celano et al., 2008). Studies developed by Martinazzo et al. (2011) also showed that atrazine sorption was enhanced by the functionalization of the aliphatic structures, such as non-polar sites in the composition of the OM of Latosols (9.5 to 38.3 g kg^{-1} of OC).

Usually, the sorption coefficient is calculated in the retention studies of herbicides, considering the interactions herbicide-soil, not only as a surface phenomenon, but as a phenomenon that occurs evenly on the entire volume of the soil (K_d) or of the organic matter (K_{oc}) (Gomes et al., 2002). Given the above, Ying & Williams (2000) reported that oxadiazon is highly sorbed in the soil, with high K_d, varying from 23.43 to 28.07 mL g^{-1}, and $K_{oc,}$ of 2.343 to 2.718 mL g^{-1}, in soils with pH 7.2, 45.5% of clay and 1.00% of OC and with pH 4.7, 3.0% of clay and 0.86% of OC, respectively; from these results, the authors claim that the sorption of oxadiazon is clearly not related to the clay content of the soil, but with the OC content. The highest values of this coefficient are indicative of better retention of the herbicide by the soil and, consequently, less leaching (Oliveira et al., 2004).

Positive correlation (0.59; p<0.01) was also noticed for the aluminum saturation (m) with the LD50 of the oxadiazon, highlighting sample 2, with high levels of OM (52 g dm^{-3}) and m (4.7%). The m refers to the percentage of negative charges of the soil that is occupied by the chargeable Al^{3+}, next do the pH 7.0 of the soil. As a result, the correlation with levels of Al^{3+} corroborate the result (Table 3), which are related to the higher retention capacity of oxadiazon, nonionic herbicide, in soils with high toxicity for aluminum. The data confront the ones from Albuquerque et al. (2001), where the oxides of Fe and Al in Purple Latosolic had no capacity to absorb atrazine, derived from a weak base.

For Mg^{2+} content in the soils and oxadiazon sorption, the correlation was relatively low, but positive (0.38; p < 0.05), showing the highest sorption capacity of the herbicide in soils rich in Mg^{2+} (Table 3). The effect of reduction in the availability of flumioxazin, according to Lima et al. (1999), may be related to phenomena of interaction among the cations of the soil sorption complex and the electron rich centers of the herbicide molecule, where sorption may have occurred among the herbicide molecules and binding cations (calcium and/or magnesium) of the exchange complex and the clays and/or OM of the soil.

Low negative correlation (-0.43; p < 0.05) was found between the sorption relation of the oxadiazon and the pH ($CaCl_2$) of the soils studied (Table 3). These results demonstrated that for the soils studied the values of pH ($CaCl_2$) are inversely related with the oxadiazon sorption by the substrate. As for works developed by Araújo et al. (2012), even regarding diuron, nonionic herbicide, using only clay fraction minerals resulted in greater sorption capacity for the herbicide for oxides of Fe in pH 7.0 (constant of Freundlich – Kf = 1.47), followed by smectite in pH 7.0 and oxides of Fe in pH 3.5.

The data are consistent with those of Oliveira et al. (2005), who reported lower flazasulfuron sorption in soils with higher pH values, indicating a higher risk of leaching. The imazaquin sorption is higher in samples with lower pH values and higher levels of OM; therefore, the effect of the OM on retention of imazaquin is pH dependent (Oliveira et al., 2004). Conditions of soils with low pH values tend to increase the interaction between molecules of the herbicide and the colloids in the soil, especially by the OC (Berglof et al., 2003).

***Table 4* -** Estimates of direct and indirect effects of 23 rates of oxadiazon able to inhibit 50% of the dry mass accumulation of the aerial part of the bio-indicator (LD50) on 17 chemical characteristics of cultivated soils of the cerrado in Minas Gerais, obtained by the method of path analysis. Rio Paranaíba, MG, 2012

Characteristic			Estimate	Characteristic			Estimate	Characteristic			Estimate
LD50	ED(1) over	pH ($CaCl_2$)	-0.13765023	LD50	ED over	Mg^{2+}	0.18053865	LD50	ED over	Al^{3+}	-0.11388043
pH ($CaCl_2$)	EI(2)	pH (H_2O)	-0.17086834	Mg^{2+}	EI via	pH (H_2O)	-0.05695611	Al^{3+}	EI via	pH (H_2O)	0.08543417
pH ($CaCl_2$)	EI via	P(res)	0.07634655	Mg^{2+}	EI via	pH ($CaCl_2$)	-0.00137650	Al^{3+}	EI via	pH ($CaCl_2$)	0.06882512
pH ($CaCl_2$)	EI via	P(melh)	-0.02296625	Mg^{2+}	EI via	P(res)	0.17655141	Al^{3+}	EI via	P(res)	-0.20040970
pH ($CaCl_2$)	EI via	P(rem)	0.01707314	Mg^{2+}	EI via	P(melh)	-0.20669626	Al^{3+}	EI via	P(melh)	0.28707814
pH ($CaCl_2$)	EI via	K	-0.00788480	Mg^{2+}	EI via	P(rem)	-0.01123233	Al^{3+}	EI via	P(rem)	0.00449293
pH ($CaCl_2$)	EI via	Ca^{2+}	0.09167453	Mg^{2+}	EI via	K	0.09146373	Al^{3+}	EI via	K	-0.01576961
pH ($CaCl_2$)	EI via	Mg^{2+}	0.00180539	Mg^{2+}	EI via	Ca^{2+}	0.33919577	Al^{3+}	EI via	Ca^{2+}	-0.16959789
pH ($CaCl_2$)	EI via	Al^{3+}	0.05694022	Mg^{2+}	EI via	Al^{3+}	-0.00227761	Al^{3+}	EI via	Mg^{2+}	0.00361077
pH ($CaCl_2$)	EI via	H + Al	-0.42134791	Mg^{2+}	EI via	H + Al	-0.02188820	Al^{3+}	EI via	H + Al	0.14227332
pH ($CaCl_2$)	EI via	OM	-1.17207580	Mg^{2+}	EI via	OM	1.53435377	Al^{3+}	EI via	OM	0.83110829
pH ($CaCl_2$)	EI via	OC	0.34650000	Mg^{2+}	EI via	OC	-0.45360000	Al^{3+}	EI via	OC	-0.24570000
pH ($CaCl_2$)	EI via	SB	-0.14324934	Mg^{2+}	EI via	SB	-0.89019230	Al^{3+}	EI via	SB	0.26603448
pH ($CaCl_2$)	EI via	t	0.36252053	Mg^{2+}	EI via	t	2.25280612	Al^{3+}	EI via	t	-0.67325240
pH ($CaCl_2$)	EI via	T	0.49038612	Mg^{2+}	EI via	T	-1.39850857	Al^{3+}	EI via	T	0.19978694
pH ($CaCl_2$)	EI via	V	0.08827416	Mg^{2+}	EI via	V	-1.14756411	Al^{3+}	EI via	V	0.35309665
pH ($CaCl_2$)	EI via	m	0.11717411	Mg^{2+}	EI via	m	-0.00468696	Al^{3+}	EI via	m	-0.23434822
Total			-0.42734792	Total			0.37993050	Total			0.58878256
Characteristic			Estimate	Characteristic			Estimate	Characteristic			Estimate
LD50	ED over	OM	2.13104690	LD50	ED over	OC	-0.63000000	DLD50	ED over	m	-0.23434822
OM	EI via	pH (H_2O)	0.06075319	OC	EI via	pH (H_2O)	0.06075319	m	EI via	pH (H_2O)	0.08543417
OM	EI via	pH ($CaCl_2$)	0.07570763	OC	EI via	pH ($CaCl_2$)	0.07570763	m	EI via	pH ($CaCl_2$)	0.06882512
OM	EI via	P(res)	0.10974817	OC	EI via	P(res)	0.10974817	m	EI via	P(res)	-0.20040970
OM	EI via	P(melh)	-0.17798845	OC	EI via	P(melh)	-0.17798845	m	EI via	P(melh)	0.28707814
OM	EI via	P(rem)	-0.02156607	OC	EI via	P(rem)	-0.02156607	m	EI via	P(rem)	0.00449293
OM	EI via	K	0.06780931	OC	EI via	K	0.06780931	m	EI via	K	-0.01576961
OM	EI via	Ca^{2+}	0.23835379	OC	EI via	Ca^{2+}	0.23835379	m	EI via	Ca^{2+}	-0.16959789
OM	EI via	Mg^{2+}	0.12998783	OC	EI via	Mg^{2+}	0.12998783	m	EI via	Mg^{2+}	0.00361077
OM	EI via	Al^{3+}	-0.04441337	OC	EI via	Al^{3+}	-0.04441337	m	EI via	Al^{3+}	-0.11388043
OM	EI via	H + Al	0.25171434	OC	EI via	H + Al	0.25171434	m	EI via	H + Al	0.14774537
OM	EI via	OC	-0.63000000	OC	EI via	OM	2.13104690	m	EI via	OM	0.83110829
OM	EI via	SB	-0.63438992	OC	EI via	SB	-0.63438992	m	EI via	OC	-0.24570000
OM	EI via	t	1.60544804	OC	EI via	t	1.60544804	m	EI via	SB	0.28649867
OM	EI via	T	-1.47115837	OC	EI via	T	-1.47115837	m	EI via	t	-0.69914673
OM	EI via	V	-0.97101579	OC	EI via	V	-0.97101579	m	EI via	T	0.19978694
OM	EI via	m	-0.09139581	OC	EI via	m	-0.09139581	m	EI via	V	0.35309665
Total			0.62864142	Total			0.62864142	Total			0.58882447
Coefficient of determination (r^2)				0.71067160							
Effect of the residual variable (EVR)				0.53789255							

1/ Direct effect. 2/ Indirect effect.

The unfolding of the significant correlations of the chemical characteristics of the soils in their direct and indirect effects was conducted to assess the degree of importance of each explanatory variable with the LD50 of oxadiazon in the different soils evaluated (Table 4). The coefficient of determination (r^2) of the path analysis was 0.71, and the effect of the residual variable was 0.53 (Table 4), indicating a good adjustment of the model to explain the sorption effect related to the variable under consideration.

It was found that the direct effect of the LD50 on the OM was high, being representative in greater proportion by the indirect effect of the effective cation exchange capacity (t) present in the the soils, as measured by the amount of cations that the soil can absorb to its pH (Table 4), especially, according to Ciotta et al. (2003), the increase in the values of t with the accumulation of OM in the soil surface. However, the direct effect on the OC was negatively unrepresentative, highlighting the high magnitude of the indirect effect of the OM, because the OC is a major component of the OM of the soil and its stock is influenced by the management system adopted (Steiner et al., 2011), where it is assumed that the OM of the soil contains 58% of OC (Segnini et al., 2008).

It is noteworthy that the OC content of the soil is determined by the balance of the inputs, such as the incorporation of plant residues and the application of organic compounds, and the exits through the oxidation and decomposition of the OM of the soil (Leite et al., 2003).

The LD50 of the oxadiazon applied in pre-emergence in the soils has a direct effect in small magnitude and negative on the aluminum saturation (m) and the content of exchangeable Al^{3+}, being opposite to the sum of the direct and indirect effects (Table 4). The most representative features in this variable in the indirect effects are the content of OM and saturation by bases (V). Therefore, the indirect effects observed were responsible for the average correlation between the LD50 with the m and the content of Al^{3+}.

The direct effect on the content of Mg^{2+} was unremarkable, with representative indirect effects via OM and m (Table 4). The direct effect of the LD50 on the pH ($CaCl_2$) was low, being expressive its indirect effect via OH and content of H + Al (potential acidity), present in the colloids of the soil (Table 4). This also explains why only the Pearson correlation study would not be efficient in selecting chemical characteristics of the soil during the sorption process of oxadiazon, reinforcing the most detailed study of the relations obtained by path analysis.

The apparent discrepancy is due to the analytical approach; however, while the simple correlation identifies the mutual associations among the characteristics, the path analysis allows the determination of the relative magnitude of each effect (Cruz et al., 2011).

Thus, more attention should be given to monitoring of oxadiazon in soils cultivated with Alliaceae in the Brazilian Cerrado, in which these agricultural soils have high organic matter content, which predisposes them to greater sorption and possibility of increasing the residual effect of this herbicide, causing phytotoxicity on successor crops.

The sorption of the oxadiazon is influenced by the chemical characteristics of the soils cultivated of the Brazilian Cerrado, highlighting the hydrogen potential (pH in $CaCl_2$), magnesium and aluminum content, organic matter, organic carbon and aluminum saturation. Thus, it is necessary to know the chemical characteristics of the soil in order to obtain an efficient control of weeds and also to minimize the risk of environmental contamination with applications of oxadiazon.

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