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Sorption-desorption isotherms of diuron alone and in a mixture in soils with different physico-chemical properties

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Herbicide mixture is a widely used weed control practice in many agricultural areas. However, interactions between the herbicide mixture and soil may alter the soil dynamics. This research evaluated the effect of the physicochemical properties of the soils in the application of diuron alone and in a mixture with hexazinone, by means of sorption-desorption Freundlich isotherms. ^{14}C-diuron sorption (isolated and mixed) was evaluated by batch equilibration at five concentrations of diuron (0.14, 0.16, 0.19, 0.26 and 0.39 µg mL^{-1}) and hexazinone (0.03, 0.06, 0.13, 0.19 and 0.26 µg mL^{-1}), corresponding to the recommended field dose (D) of D/4, D/2, D, 2×D and 4×D, respectively, in five soils cultivated with sugarcane. The sorption of the diuron applied separately and in mixture presented Freundlich sorption coefficient (K_f) values in the range of 1.47 to 5.08 and 0.59 to 3.77 µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}, respectively. The lowest desorption values were found for Clay-1 soil (72.5% clay), with 6.01 and 5.87% for diuron isolated and blended, respectively. Diuron sorption was slightly higher when applied alone rather than in the herbicide mixture, and this sorption correlated positively with the clay content of the soils, regardless of the application form. The disponibility of diuron improved in mixture of hexazinone in soil, which can increase its absorption and control efficiency; on the other hand, the transport of herbicide can rise. Future researches about the transport, runoff or leaching are required for complete information of the behavior of this mixture of herbicides in soil.

Key words: Retention process, sorption kinetics, hysteresis, commercial mixture.

INTRODUCTION

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is a non-ionic, phenylurea herbicide, moderately persistent ($t_{1/2}$ = 75.5 days) and with low water solubility (42 mg L^{-1} at 25°C) (Giacomazzi and Cochet, 2004; PPDB, 2018). It is

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recommended for the control of eudicotyledons and dicotyledons in pre- and post-emergence of weeds, with registration for pineapple, cotton, coffee, sugarcane and citrus crops (Rodrigues and Almeida, 2011). As a non-ionic herbicide, diuron remains in its molecular formula in soil solution (Rocha et al., 2013). When applied in isolation, its sorption is influenced by the organic carbon (OC) content of the soil, being moderately hydrophobic (Alva and Singh, 1990; Ahangar et al., 2008). However, when the soil has higher OC than clay contents, the contributions of the mineral surfaces in the sorption of the diuron can be masked, because the herbicide has a relatively greater sorption affinity for the organic fraction than the mineral fractions in the sorption (Green and Karickhoff, 1990).

The retention of herbicides in the soil is a process influenced by the physicochemical properties of the herbicide and the soil, such as texture, pH, cation exchange capacity (CEC), OC content, among others. The sorption of the herbicide molecules present in the soil solution to the active parts of the soil particles is one of the most important processes of the herbicide behavior in the soil, as it limits the transport by leaching and volatilization (Cáceres-Jensen et al., 2013). However, the herbicide-soil interaction may interfere with the microbial biodegradation processes and the bioavailability of herbicides to be absorbed by plants (Smernik and Kookana, 2015).

The sorption process depends on the accessible surface of the soil particle and the sorption characteristics, which involve chemical and physical bonding of the herbicide molecule to the surface of the soil colloids (Cáceres-Jensen et al., 2013). For a better understanding of this process, several sorption studies have been performed with diuron applied alone. For example, Wang and Keller (2009) found that clay fractions K_f (Freundlich sorption coefficient) and K_{foc} (organic-C normalized K_f value) were, respectively, 18.0 and 6.9 times higher for diuron, in relation to sand fractions, as clay content increased in the soils studied, due to the increased K_f values in clayey soils. Rocha et al. (2013) observed high correlations of diuron sorption with OC and soil CEC, where K_f values varied by 8.53 times more for the soil with the higher versus lower OC contents. Inoue et al. (2008) found low mobility for the isolated diuron (precipitation up to 40 mm), which was associated with the highest clay content (56%) and low OC (1.6%). However, the application of diuron in a mixture may exhibit distinct behavior in the soil when compared with the isolated molecule (Sousa et al., 2018).

When in mixture, the herbicides can present competitive sorption (Martins and Mermoud, 1998; Pateiro-Moure et al., 2010); it is possible to have effective additivity, synergism and antagonism (Bonfleur et al., 2015) or behavior in soil similar to when herbicides are applied alone (Mendes et al., 2016a). This information is incomplete in literature, because of the complex interactions of herbicides in soil. So, many studies are realized with the herbicides alone. However, few studies have considered the interaction of the diuron mixture with other herbicides and their influence on soil sorption. The current research evaluates the effect of the physicochemical properties of soils and the application of diuron (isolated and in a mixture with hexazinone) on the sorption-desorption Freundlich isotherms.

MATERIALS AND METHODS

Soil

The five soil types used in the experiments were collected in sugarcane fields in the region of Piracicaba, São Paulo, Brazil, at Iracema farms, from 0.00 to 0.10 m deep layer, with a pre-cleaning layer of vegetation covering the soil. The soil samples were air-dried, sieved on a 1.7-mm mesh and stored at room temperature in labeled plastic bags. The main physicochemical properties of the soils are shown in Table 1.

Herbicide

The radiolabeled diuron herbicide (phenyl-14-C(U)) (DuPont, Wilmington, DE, USA) showed a radiochemical purity of 98.7% and specific activity of 2.43 MBq mg^{-1}. For non-radiolabeled hexazinone herbicide (DuPont), the chemical purity was 99.5%.

Sorption-desorption studies

The method was established according to the OECD-106 standard 'adsorption-desorption using a batch equilibrium method' (OECD, 2000). Five concentrations of diuron (0.14, 0.16, 0.19, 0.26 and 0.39 μg mL^{-1}) and hexazinone (0.03, 0.06, 0.13, 0.19 and 0.26 μg mL^{-1}) were used, corresponding to a recommended dose (D) of field of D/4, D/2, D, 2×D and 4×D, respectively. Each experimental unit consisted of a 50 mL Teflon tube with a screw cap, in duplicates. Aliquots of 5 g soil were weighed in duplicate in the tubes and 10 mL of 0.01 mol L^{-1} $CaCl_2$ was added resulting in a soil-solution ratio of 1:2 (m v^{-1}). In the sorption studies, 120 μL aliquots of radiolabeled solutions containing ^{14}C-diuron isolated and with hexazinone non-radiolabeled (analytical standard) were transferred to separate vials containing 10 mL of the scintillation solution for the determination of the initial concentration, to be used later in the Teflon tubes. The initial concentration of ^{14}C-herbicides was determined after 15 min, by liquid scintillation counting (LSC) with a Tri-Carb 2910 TR LSA counter (LSA PerkinElmer, Waltham, MA, USA).

In duplicate, 10 mL of the radiolabeled concentrations of all solutions were added to the Teflon tubes containing 5 g of soil samples. The tubes were agitated in a horizontal tabletop shaker in a dark room (20 ± 2°C) for 24 h to achieve the equilibrium concentration (data not shown). At the equilibration concentration, the tubes were centrifuged (Hitachi CF16RXII centrifuge, Hitachi Koki Co., Ltd., Indaiatuba, SP, Brazil) at 755 *g* for 15 min, and 1 mL aliquots of the supernatant from each tube were transferred in duplicate, to scintillation vials containing 10 mL of the scintillation solution. LSC analysis was then performed to determine the concentration of the ^{14}C-herbicides solution, by counting the radioactivity. The amount of herbicide sorption was calculated, using the difference between the initial concentration and the concentration in the supernatant after equilibration (Mendes et al., 2017).

Desorption studies were performed immediately after sorption,

Table 1. Physicochemical properties and geographical coordinates of the sugarcane areas of soils used in the studies in Piracicaba, São Paulo, Brazil.

Property	Soil classification - symbols*				
	Clay-1	Clay-2	Loam-1	Loam-2	Sand
Texture	Clay	Clay	Loamy sand	Loamy sand	Sand loam
Sand (%)	18.2	12.2	58.2	56.1	88.6
Clay (%)	72.9	75.4	30.2	32.7	10.1
Silt (g %)	8.9	12.4	11.6	11.2	13.0
pH ($CaCl_2$)	5.09	4.45	5.93	5.11	4.96
P (mg dm^{-3})	60	24	19	6	20
S (mg dm^{-3})	19	79	7	11	4
K ($mmol_c$ dm^{-3})	6.4	3.1	1.4	2.2	0.4
Ca ($mmol_c$ dm^{-3})	32	28	78	23	16
Mg ($mmol_c$ dm^{-3})	28	26	60	14	6
Al ($mmol_c$ dm^{-3})	0.01	1	0.01	0.01	1
H+Al ($mmol_c$ dm^{-3})	38	71	9	23	22
SB ($mmol_c$ dm^{-3})	66.4	57.1	139.4	39.2	22.4
CEC ($mmol_c$ dm^{-3})	104.4	127.8	148.3	62.6	44.4
V (%)	64	45	94	63	50
OC (%)	1.8	1.0	1.2	1.6	2.0
Latitude (S)	22°34’58.8”	22°35’49.2”	22°42’15”	22°41’19.8”	22°14’21.6”
Longitude (W)	47°33’58.8”	47°35’15.6”	47°32’16.8”	47°31’57”	47°43’6”
Altitude (m)	623	601	533	521	860

*According to Soil Taxonomy and Brazilian Soil Science Society (EMBRAPA, 2013). Latossolo Vermelho eutrófico (Clay-1) [Oxisol Typic Hapludox], Latossolo Vermelho Amarelo distrófico (Clay-2) [Oxisol Typic Hapludox], Nitossolo Háplico eutrófico (Loam-1) [Nitosol Eutrophic], Argissolo Vermelho Amarelo eutrófico (Loam-2) [Udult soil] and Neossolo Quartzarenico órtico (Sand) [Typic Quartzipsaments]. BS: sum of bases; CEC: cation extend capacity; V: base saturation; OC: organic carbon.
Source: Department of Soil Science – ESALQ/USP, Piracicaba, SP, Brazil.

under the same conditions. Such that, $CaCl_2$ solution (10 mL, 0.01 mol L^{-1}) was added to the Teflon tubes containing the soil and the radiolabeled herbicide sorbed from the sorption experiment. The tubes were agitated in a horizontal tabletop shaker in a dark room (20 ± 2°C) for 24 h to reach the equilibrium concentration. After re-equilibration, the tubes were centrifuged. Then, 1 mL aliquots of the supernatant were pipetted in duplicate to scintillation vials containing 10 mL of the scintillation solution, before analysis by LSC. The desorbed amount was calculated as the difference between the radioactivity sorbed in the soil and the remaining supernatant (Mendes et al., 2017).

Sorption-desorption model

Sorption coefficients, K_f and 1/n, were calculated from the slope and intercept of the Freundlich equation: $C_s = K_f \times C_e^{1/n}$; where C_s is the concentration (mg g^{-1}) of herbicide sorbed onto the soil after equilibration; K_f is the Freundlich equilibrium constant ($\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1}); C_e is the herbicide concentration (mg L^{-1}) after equilibration, and 1/n is the degree of linearity of the isotherm. The equilibrium constant K_{foc} sorption standard for the OC content of the soil was adjusted by using the following equation: $K_{foc} = (K_f/(\%OC)) \times 100$. The desorption coefficients, K_f and 1/n, were determined in a similar way to the sorption coefficients, using a plot of the amount of the remaining chemical sorbed at desorption versus the equilibrium concentration. The hysteresis coefficient (H) for the sorption-desorption isotherms was calculated according to the following equation: $H = (1/n_{desorption})/(1/n_{sorption})$, where $1/n_{sorption}$ and $1/n_{desorption}$ are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively (Barriuso et al., 1994).

Statistical analysis

The non-linear regressions of sorption and desorption of diuron isolated and mixed were adjusted by the Freundlich models, as described previously. Pearson's correlations (*r*) were evaluated for the K_f values of the herbicide in both forms of application with the physical and chemical properties of the five soils, and only the clay content showed a significant correlation with the K_f when compared with the t test ($p < 0.01$, $n = 5$). Figures were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software, Inc., Point Richmond, CA, USA).

RESULTS AND DISCUSSION

Sorption isotherms of diuron alone and mixture

The Freundlich equation adequately described the sorption of diuron alone and when mixed with hexazinone ($R^2 \geq 0.94$). The K_f values of diuron ranged from 1.47 to 5.08 $\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1} when isolated and 0.59 to 3.77 $\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1} when in mixture with hexazinone, for the same soils (Table 2). The K_{foc} values were between 73.50 and 445.00 and 29.50 and 367.00 $\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for the diuron alone and in mixture with hexazinone, respectively. The sorption was increased in soils in 1.56 times for the diuron isolated and 1.64 times for the application of the diuron in mixture, concerning the

Table 2. Freundlich sorption parameters for the diuron alone and a mixture with hexazinone in the five soils with different physico-chemical properties.

Herbicide	Soil[a]	$K_{f\ (sorption)}$	$K_{foc\ (sorption)}$	$1/n_{\ (sorption)}$	R^2	Sorption (%)
		($\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$)				
Diuron alone	Clay-1	5.08 (4.97-5.18)[b]	282.22 (276.11-287.78)	0.51 ± 0.01[c]	0.97	89.33
	Clay-2	4.45 (4.16-4.71)	445.00 (416.00-471.00)	0.49 ± 0.03	0.98	88.33
	Loam-1	3.00 (2.91-3.09)	250.00 (242.50-257.50)	0.47 ± 0.01	0.99	81.54
	Loam-2	2.74 (2.67-2.79)	171.25 (166.87-174.37)	0.48 ± 0.01	0.99	76.79
	Sand	1.47 (1.28-1.70)	73.50 (64.00-85.00)	0.50 ± 0.05	0.94	56.32
Diuron in a mixture	Clay-1	3.77 (3.72-3.82)	209.44 (206.67-212.22)	0.43 ± 0.01	0.99	88.65
	Clay-2	3.67 (3.58-3.74)	367.00 (358.00-374.00)	0.44 ± 0.01	0.99	87.35
	Loam-1	1.92 (1.90-1.93)	160.00 (158.33-160.83)	0.34 ± 0.01	0.96	79.95
	Loam-2	1.92 (1.85-1.99)	120.00 (115.62-124.37)	0.38 ± 0.02	0.95	75.75
	Sand	0.59 (0.58-0.60)	29.50 (29.00-30.00)	0.16 ± 0.01	0.96	53.99

[a] Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments. [b] Number in parentheses are confidence intervals of the mean, *n* = 2. [c] Mean 1/n value ± standard deviation of the mean.

increase of CO content in soils by 69%, a growing effort for sand soil for clay-1 (Table 1).

The closeness of the K_f values indicated similarity in the sorption between the forms of application of the herbicide diuron, isolated or in mixture with hexazinone, considering the conditions of the present study. In corroboration with this results, Mendes et al. (2016a) also did not find differences between the application modes (alone and in mixtures), for the mesotrione mixture with S-metolachlor + terbuthylazine. Correlating the retention of herbicides with soil leaching, Reis et al. (2017) noted the application mode of diuron (alone and in combination with sulfometuron-methyl + hexazinone) did not influence diuron mobility along the soil, proving the herbicide presented low mobility in the soils. Furthermore, the soil texture had no impact on diuron leaching. However, higher percentages of the diuron in mixture with hexazinone than diuron applied alone were found in the leachate in the clayey soil. On the other hands, when in combination with the same mixture (diuron in mixture with sulfometuron-methyl + hexazinone), Mendes et al. (2016b) noted negligible diuron in the leachate (0.19%), due to the higher affinity with OC present in the upper layers of the profile of a dystrophic “Argissolo Vermelho-Amarelo distrófico - PVAd” (Yellow Red Argisol-Oxisol) (0.52% OC and 81.6% clay).

The sorption of diuron applied isolated was 56.32% for soil with low clay content (10.1%) and reached 89.33% when in soil with high clay content (72.9%) (Table 2). For the mixed diuron, the results were similar but relatively slightly lower, presenting sorption of 53.99% for the sand and 88.65% for the Clay-1. These data are in agreement with the results found for the K_f values, described earlier. On the other hand, Sousa et al. (2018), studying the sorption of the diuron alone and in combination with the hexazinone, found that the mixture had on average twice the sorption with respect to the diuron alone. The same authors state that the sorption variations of these herbicides when mixed may be related to soil OC quality, so that being that material of origin, decomposition and structure of the organic matter of the soil can exert different influences on the sorption of herbicides. The addition of organic compounds to the soil in the research of Sousa et al. (2018) may increase the retention capacity of these herbicides when mixed, differing from the present study.

The $1/n_{sorption}$ values were lower than 0.51 and 0.44 for the application of diuron alone and mixture with hexazinone, respectively; this indicated an L-type isotherm (1/n < 1), with a non-linear and concave slope relative to the abscissa (Giles et al., 1960) as shown in Figure 1. Then, the sorption rate decreased with increasing herbicide concentration, where this increase in herbicide concentration in the soil solution reduced the availability of the sorption sites. Chaplain et al. (2008), Rocha et al. (2013) and Giori et al. (2014) also found a similar L sorption isotherm trend for the diuron applied alone, indicating the influence of soil sorption sites filling with diuron sorption.

Correlation of diuron (isolated and in a mixture) sorption with soil physicochemical properties

Among the physicochemical properties of the studied soils, only the clay content was positively correlated with the K_f of diuron sorption in both forms of application (Figure 2). Thus, with a 10% increase in the clay content of the soil, the K_f values were increased by 1.67 $\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ for the diuron alone and by 0.77 $\mu mol^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ for the diuron in a mixture with hexazinone (Figure 2). The sorption values for the diuron alone were slightly

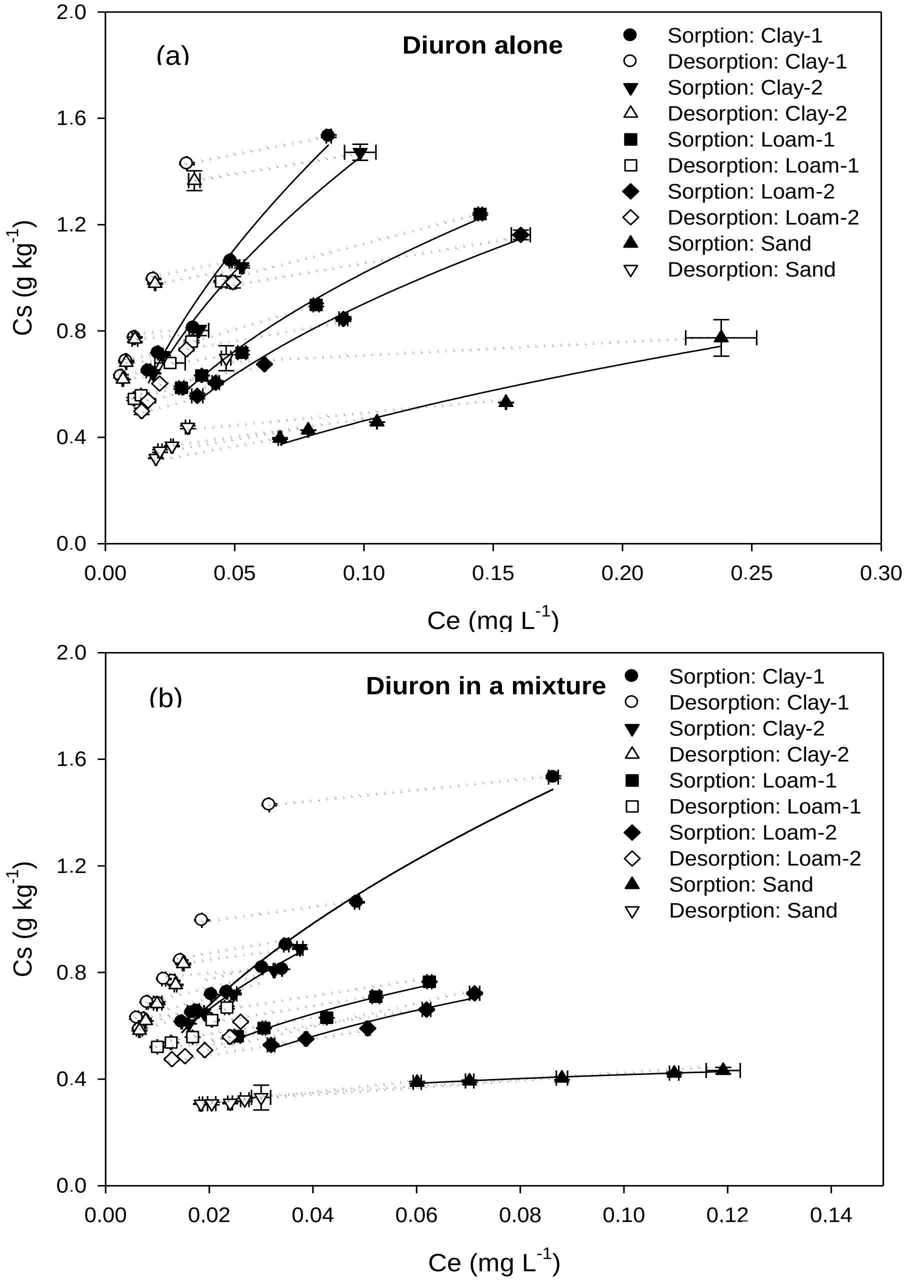

Figure 1. Freundlich sorption (●, ▼, ■, ♦, and ▲) and desorption (○, Δ, □, ◊, and ▽) isotherms of diuron alone (a) and in a mixture with hexazinone (b) in the five soils with different physico-chemical properties. Error bars represent standard error of the mean (*n* = 2) of Ce (equilibrium concentration) and Cs (soil concentration). Symbols may cover error bars. Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments.

higher than the mixture. This increase in clay content in the soil directly reflects more diuron sorption and may affect the availability of the herbicide in the soil solution. Namely, we believed there could be less herbicide bioavailable for biological degradation, and it be less absorbed by the target plants, reducing weed control efficiency and increasing the persistence of the product in more clayey soils.

The effect of clay content is more pronounced when diuron is applied alone. Fernández-Bayo et al. (2008) also found a positive correlation between the clay content and the specific surface area of the soils studied with diuron sorption. Sorption of diuron may be proportional to the number of active sites in the soil. This behavior may

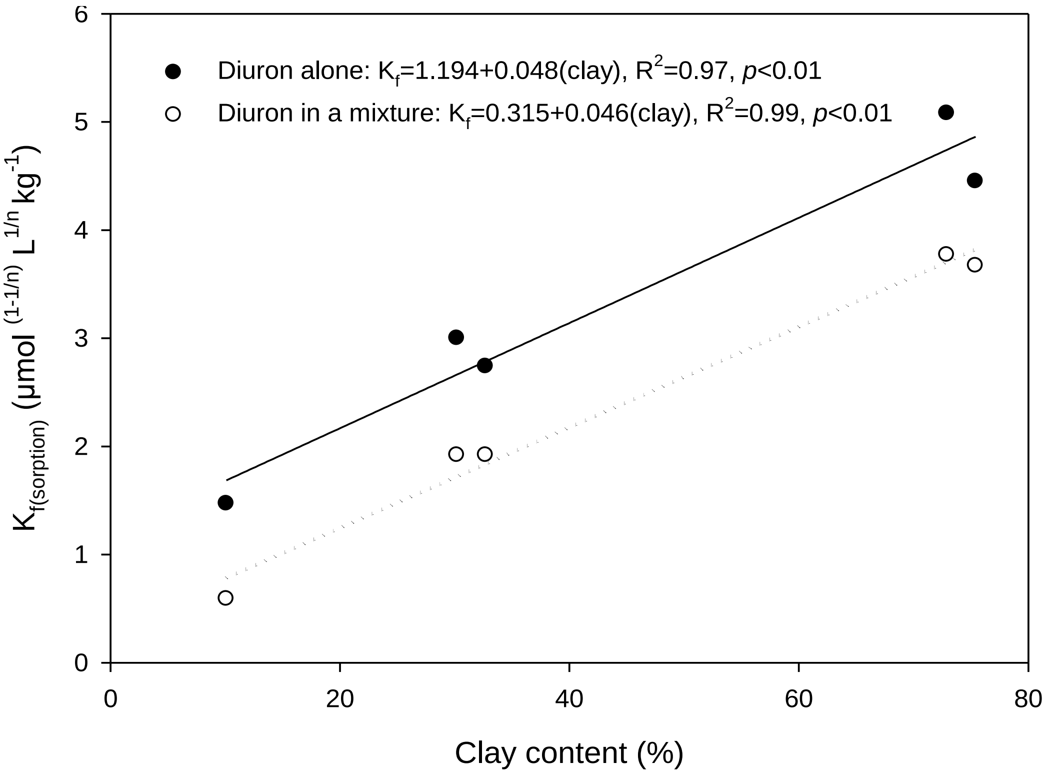

Figure 2. Relationship between the Freundlich sorption coefficient - K_f (µmol $^{(1-1/n)}$ L$^{1/n}$ kg^{-1}) mean of diuron applied alone and in a mixture with hexazinone, and the clay content (%) of five soils with different physicochemical properties.

explain the diuron sorption, which, due to its polarity, potentially binds to clay minerals sites; the greater the area of contact with the soil, the higher the sorption capacity. According to Oliveira and Reginato (2009), these adsorptive forces are highly relevant to herbicides with low solubility and polarity, such as diuron, and are also characterized by interactions of intermolecular forces, such as van der Waals and non-ionizable H bridges (neutral).

Several studies noted a positive correlation between diuron sorption and OC content in soils (Ahangar et al., 2008; Liu et al., 2010; Umali et al., 2012; Cáceres-Jensen et al., 2013). This fact is related to the low solubility of the herbicide and the greater affinity of the molecule with the hydrophobic compounds (Chaplain et al., 2008). For hydrophobic compounds, such as diuron, sorption is more influenced by organic compounds when the OC content in the soil is greater than 2.0% (Reddy and Gambrell, 1987). Like in the present study, soils presented a variation in the CO content between 1.0 and 2.0%, indicating that in this range the CO content of the soils had little effect on the sorption of the diuron alone and in the mixture. However, for diuron alone, Giori et al. (2014) found a correlation between herbicide sorption and soil OC (0.76-2.6%), as well as Sousa et al. (2018), who verified a correlation of diuron sorption both alone and in mixture with hexazinone, considering a greater range of OC (1.46-27.77%). This indicates that the type of organic material present in the soil can alter the retention dynamics of the herbicides in the soil, whether isolated or mixed. The sorption of diuron can also be correlated with the pH, due to the polarity of the molecule, despite being a non-ionic herbicide (Rodrigues and Almeida, 2011; Rocha et al., 2013). As mentioned by Chaplain et al. (2008), when there is a correlation between sorption and pH, K_f increases as the pH decreases, as also found by Liu et al. (2010) and Araujo and Melo (2012). However, in the pH range of arable soils, such as in this study (pH 4.45-5.93), in sugarcane cultivation areas for this soil property, there was no correlation with sorption.

Desorption isotherms of diuron alone and in mixture

The K_f values for diuron desorption ranged from 3.13 (Loam-1) to 9.47 µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1} (Sand) when applied alone and from 4.42 (Clay-1) to 7.22 µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1} (Sand) in a mixture (Table 3). Therefore, the behavior of diuron in soils, regarding the application forms, corroborated the sorption data. For desorption of the isolated diuron and mixture, the Freundlich's isotherms were suitable (R^2 > 0.87) (Table 3). In both application modes, the $1/n_{desorption}$ values were less than 1, indicating

Table 3. Freundlich desorption parameters and hysteresis coefficient (H) for the diuron alone and a mixture with hexazinone in the five soils with different physicochemical properties.

Herbicide	Soil[a]	$K_{f\ (desorption)}$	$K_{foc\ (desorption)}$	1/n (desorption)	R^2	H	Desorption (%)
		(µmol $^{(1-1/n)}$ L$^{1/n}$ kg^{-1})					
Diuron alone	Clay-1	7.45 (7.16-7.71)[b]	413.89 (397.78-428.33)	0.49 ± 0.01[c]	0.96	0.96	6.01
	Clay-2	6.66 (6.21-7.09)	666.00 (621.00-709.00)	0.47 ± 0.01	0.99	0.96	6.24
	Loam-1	3.13 (3.08-3.16)	260.83 (256.67-263.33)	0.40 ± 0.01	0.93	0.85	9.34
	Loam-2	4.79 (4.65-4.90)	299.37 (290.62-306.25)	0.53 ± 0.01	0.99	1.10	11.57
	Sand	9.17 (8.55-9.68)	458.50 (427.50-484.00)	0.86 ± 0.02	0.95	1.72	16.01
Diuron in a mixture	Clay-1	4.97 (4.62-5.22)	276.11 (256.67-290.00)	0.42 ± 0.02	0.97	0.98	5.87
	Clay-2	4.42 (4.33-4.49)	442.00 (433.00-449.00)	0.40 ± 0.01	0.98	0.91	6.60
	Loam-1	1.87 (1.83-1.91)	155.83 (152.50-159.17)	0.28 ± 0.01	0.90	0.82	10.13
	Loam-2	2.02 (1.98-2.05)	126.25 (123.75-128.12)	0.34 ± 0.01	0.89	0.89	12.13
	Sand	7.22 (7.05-7.38)	361.00 (352.50-369.00)	0.21 ± 0.02	0.87	1.17	17.39

[a] Clay-1: Oxisol Typic Hapludox, Clay-2: Oxisol Typic Hapludox, Loam-1: Nitosol Eutrophic, Loam-2: Udult soil, and Sand: Typic Quartzipsaments. [b] Number in parentheses are confidence intervals of the mean, *n* = 2. [c] Mean 1/n value ± standard deviation of the mean.

L type isotherms, as also observed for the sorption. The desorption history values (H < 1) were lower than the sorption. Namely, less herbicide returned to the soil solution (Figure 1), as likewise found in some soils studied by Liu et al. (2010). However, in the present study there was more desorption of the diuron when applied in isolation (H > 1) to the Loam-2 and Sand soils, as well as in Sand with the diuron in mixture with hexazinone, respectively, when compared with the other soils. Such behavior was possibly due to the low soil CEC (44.4 for Sand and 62.6 mmol$_c$ dm^{-3} for Loam-2) relative to the other soils tested, thereby having fewer sorption sites for herbicide retention.

In general, there was an increase of 10.00 and 11.52% in the desorption of the diuron isolated and in the mixture, respectively, when the soil profile was changed from Clay-1 soil to sand (Table 3). That is, in soils with comparatively higher clay content, less herbicide returned to the soil solution, with 6.01% desorption for diuron isolated and 5.87% for diuron mixture, in the soil Clay-1. These data confirm a correlation of the clay content with diuron sorption, where the clay proportion was 72.9% for Clay-1 and 10.1% for sand, respectively. In this sense, Rocha et al. (2013) found elevated diuron desorption values in "*Latossolos vermelhos"* with low clay content (27%) and OC (0.8%), which can be attributed to the poor interaction of herbicide with a soil surface.

Conclusion

Diuron sorption was similar when isolated compared to the application of the herbicide in the mixture (Table 2).

For soils with comparatively high clay content and low OC content, the clay fraction had a marked influence on diuron sorption. The desorption of diuron was most pronounced in soils with relatively low clay content, for both forms of application. The application of this herbicide may not affect the transport through leaching, due to the little effect on the retention process. The results of this study contribute to the information regarding the positive correlation between diuron retention and soil clay fraction. In this context, knowledge of the physical and chemical properties of the soil is essential before recommending this herbicide in weed management. Therefore, regardless of the mode of application, in soils with low OC content the availability of herbicides in the control of dying plants can be higher than in soils with high OC content. In this same sense, soils with higher clay content can retain more diuron isolated and in mixture, interfering in the control dynamics of these herbicides in the soil. Herbicide transport studies, such as surface runoff, are encouraged to complement the retention findings, especially in the tropical soil conditions, with various rainfall indices, and for a widely used herbicide, such as diuron.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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