Sorption and desorption of diuron in Oxisol under biochar application

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ABSTRACT: The objective of this study was to verify the kinetics of sorption and desorption of diuron in an Oxisol under application of biochar. The samples were collected in a field experiment conducted in randomized design blocks consisted of 2 base fertilization levels (0 and 400 kg·ha^{-1} NPK 00-20-20 fertilizer formula) and 3 doses of biochar (0, 8 and 16 Mg·ha^{-1}). In the evaluation of sorption and desorption, Batch Equilibrium method was used. The kinetics of sorption and desorption of diuron, total organic carbon, fulvic acid, humic acid and humin, pH and partition coefficient to organic carbon were evaluated. The Freundlich isotherm was adjusted appropriately to describe diuron sorption kinetics in all the studied treatments. The application of biochar provided increment in the sorption (Kf) and reduction in the desorption of diuron in 64 and 44%, respectively. This effect is attributed to the biochar contribution to the total organic carbon and C-humin and of these to diuron through hydrophobic interactions and hydrogen bonds. The positive correlation between the partition coefficient to organic carbon and Kf confirms the importance of soil organic compartment in the sorption of diuron. There was no competition of NPK fertilizer for the same sorption site of diuron. The increase and reduction in sorption and desorption, respectively, show that the application of biochar is an important alternative for the remediation of soil leaching of diuron, especially in sandy soils.

Key words: leaching, persistence, soil organic matter, herbicide, pyrogenic carbon.

INTRODUCTION

In Brazil, large-scale agriculture has demanded high consumption of pesticides, especially herbicides, which accounted for approximately 57% of the total traded volume in the 2014/2015 harvest year (SINDIVEG 2014). Among the herbicides, diuron [3-(3.4-dichlorophenyl)-1.1-dimethylurea] is widely used in demanding crops such as cotton and sugar cane.

Diuron is a broad-spectrum herbicide, recommended for applications in pre- and post-emergence of mono and dicotyledonous weeds (Rodrigues and Almeida 2011). Diuron tended to maintain its molecular structure and showed no sensitivity to ionize in soil solution. However, even with pKa equal to zero, it may exhibit polarity and be potentially influenced by the physical and chemical characteristics of the soil, such as pH, clay minerals and organic matter (Rodrigues and Almeida 2011; Rocha et al. 2013b).

Diuron is expected to have low mobility in soil due to molecular stability, hydrophobicity and low water solubility. However, there are reports in the literature (Inoue et al. 2008; Britto et al. 2012) about the high mobility of this molecule in the soil, especially after intense precipitation. This characteristic becomes even more important as diuron half-life is considered relatively long (Stork et al. 2008; Rocha et al. 2013b), which may result in high leaching potential and, consequently, contamination of subsurface water.

The sorption process may mitigate the possible effects of diuron leaching on the soil, greatly reducing its mobility. Sorption is a physicochemical process in which pesticide molecules are retained on a solid surface (e.g. soil organic matter) by mechanisms such as covalent bonds, ionic and hydrogen bonding, van der Waals forces and hydrophobic interactions (Lavorenti et al. 2003). However, these processes do not exhibit total hysteresis to pesticide molecules, that is, they can return to the soil solution in a process known as reversibility or remobilization. Under these conditions, the molecules attached as residue may have partial reversibility and again be adsorbed to the sorption sites and/or be mineralized.

Thus, soil organic matter (SOM) can act as an adsorbent with high mitigation potential of diuron leaching, especially in sandy soils. Some studies show a positive correlation between SOM and diuron sorption (Chaplain et al. 2008; Rocha et al. 2013a). The sorptive interaction between SOM and pesticides depends on their physicochemical characteristics. The dynamics of this interaction in the pesticide sorption kinetics can be better understood with the chemical fractionation of SOM. This study allowed to quantify the humic acid and humin, fractions that have higher reactivity and stability, respectively.

However, in the tropics, the maintenance of SOM stocks are hampered especially by high humidity and high temperatures, accelerating the waste decomposition process. Thus, the adoption of management practices designed to bring higher organic carbon input into the soil becomes an important tool in the sorption interaction process with soil pesticides, such as the use of biochar. Recent studies (Petter et al. 2012; Fei et al. 2015) have demonstrated that the application of biochar increased the carbon content in the soil and the interactions with the humic acid fraction. According to Petter and Madari (2012), as the partial oxidation of aromatic edges of biochar structures happens, the charge exposure increases. These features can enhance the interaction with ionizable molecules or not, since SOM physicochemical composition is highly variable.

To this end, we hypothesized that biochar affects SOM fractions, providing greater physical and chemical interaction by increasing the reactivity (humic acid fraction) and molecular stability (humin), thus contributing to greater sorption of pesticides. Thus, this study aimed at verifying the dynamics of diuron sorption and desorption into the soil after biochar application and observing in which way biochar and SOM apparently contribute to the sorptive interaction processes.

MATERIAL AND METHODS
Study site

The study was conducted using soil samples collected in a field experiment in Nova Xavantina, Mato Grosso State, in the Cerrado biome. The soil was classified as Oxisol dystrophic, with medium texture (clay: 307 g·kg^{-1}; silt: 73 g·kg^{-1}; sand: 620 g·kg^{-1}). Soil chemical parameters were: pH (H$_2$O) = 5.6; P (Mehlich method) = 6.7 mg·dm^{-3}; K$^+$ = 61.5 mg·dm^{-3}; Ca^{2+} = 1.4 cmol$_c$·dm^{-3}; Mg^{2+} = 0.4 cmol$_c$·dm^{-3}; Al^{3+} = 0.13 cmol$_c$·dm^{-3};

H$^+$ + Al^{3+} = 4.98 cmol$_c$·dm^{-3}; V% = 27%; CEC = 6.93 cmol$_c$·dm^{-3}; OM = 12.6 g·kg^{-1}; Fe: 75.0 mg·dm^{-3}; Mn = 49.0 mg·dm^{-3}; Zn = 45.0 mg·dm^{-3}; and Cu = 1.7 mg·dm^{-3}.

The study area was a Cerrado native forest until 1985. After forest removal, soybean culture started under no-tillage system, using millet as cover crop, until the year 2006.

From this, the experiment started as a randomized block design, consisting of 2 fertilization levels (0 and 400 kg·ha^{-1} 00-20-20 NPK fertilizer) and biochar doses (0; 8 and 16 Mg·ha^{-1}) randomly distributed, with 4 repetitions.

The samples were collected in the plots with the respective treatment in the 2013 year, that is, 7 years after the application of biochar. The samples consisted of a mixture of 3 sub-samples per plot.

Chemical

Diuron 99.5% [3-(3.4-dichlorophenyl)-1.1-dimethylurea] was supplied by Nortox SA (Brazil). All other solvents and reagents used were analytical standard.

Biochar

The biochar derived from the phyto-physiognomy of the Cerrado. It was produced in cylindrical furnaces by slow pyrolysis, in temperatures ranging from 200 to 450 °C at the initial and final stages of carbonization, respectively. It was subsequently grounded to particle size ≤ 2 mm, applied only once in September 2006, by manual hauling, and incorporated to a 0 – 15 cm depth using a rotary tiller. Table 1 shows biochar chemical composition.

The biochar sample was submitted to Nuclear Magnetic Resonance (NMR) analysis of ^{13}C to verify the functional groups (Figure 1). The spectrum showed clear signs of O-aromatic groups (C-aryl, ~ 130 ppm), responsible for the stability of the material and phenolic/carboxylic groups (~ 150 ppm), although at a lower ratio than the aryl groups, which are responsible for the chemical reactivity of vegetable biochar.

Sorption and desorption assays

The time required for the soil and the herbicide diuron to reach sorption equilibrium was previously determined. The method of batch slurry, based on the OECD (2000), was used. A solution containing 10 mg·L^{-1}, obtained from a 1,000 mg·L^{-1} diuron (Nortox SA, analytical standard, 99.5% purity) stock-solution, was prepared in CaCl$_2$ 0.01 mol·L^{-1}. Then, a 10-mL aliquot of the diuron-CaCl$_2$ solution was added to polypropylene tubes containing 2 g of soil. The tubes containing the solution and soil were sealed and placed vertically under agitation for different times (0; 0.5; 1.0; 2.0; 4.0; 8.0; 12; 16; and 20 h) at 25 ± 2 °C. After agitation, the samples were centrifuged at 2,250 g for 7 minutes. Part of the supernatant was filtered through a Millipore filter with

Table 1. Chemical composition (total values) of biochar used.

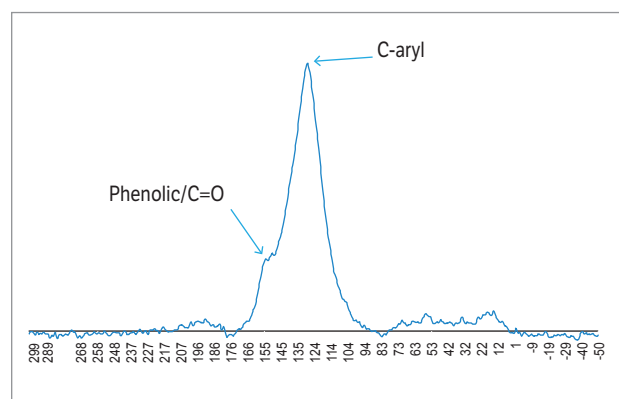| Elements	Concentration
Total Nitrogen (N)	6.6 g·kg^{-1}
Phosphorus (P$_2$O$_5$ citric acid)	0.3 g·kg^{-1}
Phosphorus (P$_2$O$_5$ total)	1.0 g·kg^{-1}
K$_2$O	3.3 g·kg^{-1}
CaO	5.7 g·kg^{-1}
MgO	1.1 g·kg^{-1}
Sulfur (S)	0.4 g·kg^{-1}
Copper (Cu)	7.0 mg·kg^{-1}
Zinc (Zn)	13.0 mg·kg^{-1}
Molybdenum (Mo)	2.0 mg·kg^{-1}
Cobalt (Co)	1.0 mg·kg^{-1}
Boron (B)	5.0 mg·kg^{-1}
Total carbon (C)	490.6 g·kg^{-1}
Moisture	50.0 g·kg^{-1}
Total mineral matter	280.0 g·kg^{-1}
C:N ratio	74.3 g·kg^{-1}

Figure 1. Spectrum of ^{13}C-NMR (VACP-TOSS) of vegetal biochar used.

0.45-μm PTFE membrane for further high-performance liquid chromatography (HPLC) analysis. The equilibrium time was defined as the time from which the solution concentration remained constant.

Diuron sorption into the soil was evaluated using working solutions prepared from the stock-solution in concentrations of 1, 2, 4, 8 and 15 mg·L⁻¹ of herbicide in 0.01 mol·L⁻¹ CaCl₂. A 10-mL aliquot of the solutions was added to the polypropylene tubes containing 2 g of soil. Then these tubes were constantly stirred at a temperature of 25 ± 2 °C for the duration of the equilibrium time, previously determined as 12 h. After agitation, the samples were centrifuged at 2,250 g for 7 min. Part of the supernatant was pipetted and filtered through a 0.45-μm PTFE membrane for chromatographic analysis. The desorption tests were conducted by adding the same volume of CaCl₂ 0.01 mol·L⁻¹ solution, free of herbicide, to tubes containing 8 mg·L⁻¹ diuron, before sorption testing. These tubes were subjected to further stirring under the same conditions that the sorption tests were performed. After agitation, the samples were centrifuged at 2,250 g for 7 min. After complete removal, the supernatant was filtered through 0.45-μm PTFE membrane for chromatographic analysis. This procedure was repeated for 3 consecutive times (12; 24 and 36 h).

Sorption and desorption analysis

Diuron quantity was determined by HPLC in a 20AT Shimadzu LC, with UV-Vis detector (Shimadzu SPD 20A) and stainless steel column (Shimadzu Shim pack VP-ODS 150 × 4.6 mm id). The mobile phase consisted of water and acetonitrile 50:50 (v/v) at a flow rate of 1.2 mL·min⁻¹, 20 μL injection volume, and 254 nm wavelength. Under these conditions, diuron retention time was approximately 10 min, identified by comparing the retention time with the analytical standard. Quantification followed the reference procedure (calibration with external standards).

Sorption coefficients

The herbicide that remained in the solution in equilibrium with the substrate (Ce) was quantified and expressed as μg·mL⁻¹. Subsequently, the equation $Cs = v/m (Cp - Ce)$ was used to calculate how much herbicide was sorbed into the soil (Cs), in mL·g⁻¹, where v is the volume of CaCl₂ 0.01 mol·L⁻¹ solution added to the herbicide (mL); m is the mass of substrate (g of soil); and Cp is the herbicide concentration in the added standard solution (μg·mL⁻¹). After determining the Ce and Cs values for each soil and biochar mix, the Freundlich equation ($Cs = Kf·Ce^{1/n}$) was adjusted to obtain the sorption coefficients, where Kf and 1/n are empirical constants that represent sorption capacity and intensity, respectively.

The quantity of desorbed diuron was calculated by the difference between the herbicide concentration in the soil before desorption and after each evaluated interval. Subsequently, the percentage of total desorption was calculated for each time interval (12; 24 and 36 h).

The organic carbon partition coefficient (Koc) was calculated by $Koc = (Kf/\%OC)·100$, where Kf is the sorption coefficient and %OC, the percentage of organic carbon in the soil.

Total organic carbon and chemical fractionation of soil organic matter

The total organic carbon (TOC) content was determined by the Dumas' method (dry combustion at high temperature) using an elemental analyzer (CHN-1110 Elemental Analyzer, Carlo Erba Instruments, Italy). For the chemical fractionation of SOM, we used the differential solubility technique modified from Benites et al. (2003) to obtain the organic carbon in fulvic (FA) and humic (HA) acids, as well as humin (HUM). Samples of 1.0 g TFSA were weighed, then added to an extraction mixture of NaOH 0.1 mol·L⁻¹, where the HA and FA fractions were solubilized. HUM was the insoluble solid residue resulting from fractionation process.

The HA and FA fractions were separated by centrifugation after precipitation in acid medium adjusted to pH 1 with 20% H₂SO₄. After washing, the HA fractions were resolubilized in NaOH 0.1 mol·L⁻¹. The carbon contents (C) in the FA, HA and HUM fractions were determined by oxidation of organic matter using potassium dichromate according to the methodology of Benites et al. (2003).

Statistical analysis

The data were subjected to regression analysis, and the coefficients of the equations were tested by *t*-test at

p < 0.05. Pearson's correlation analyses were performed between soil properties and sorption coefficients and biochar. Sorption coefficients for different biochar treatments and NPK fertilizer levels were compared by Scott-Knott's test at p < 0.05.

RESULTS AND DISCUSSION

Regardless of NPK + biochar treatments, diuron sorption kinetics behaved similarly in Oxisol, characterized by rapid sorption in the first 2 h, followed by a slow phase with subsequent stabilization after 12 h (Figure 2). Therefore, 12 h-stirring was used as the equilibrium time (dotted line in Figure 2) since the sorbed amount did not change significantly from that time on to justify using a longer period. The lower sorption values at equilibrium were verified in the treatments without biochar. Inoue et al. (2004) and Rocha et al. (2013a) have also reported the rapid sorption of diuron and concentration stabilization in soil solution after 12 h.

The non-linear sorption behavior is typical of the interactions between pesticides and solid phase (soil) and is due to the gradual filling of available sorption sites, as verified by Liu et al. (2010). These authors explain that there are abundant sorption sites available in the beginning; however, as these surface sites become occupied, increasing the repulsive forces between the solute molecules in the solid phase and the molecules in solution, the sorptive interaction is hindered. This effect is due to the decreasing attractive forces on the surface of the adsorbent, thus reducing the attraction of solute molecules in solution for a sorption-sorbent interfacial area (Pereira and Silva 2009).

The Freundlich isotherm was adequate to describe diuron sorption kinetics in Oxisol treated with biochar in all treatments, with coefficients of determination (R^2) higher than 0.97 (Figure 3), corroborating the studies of Chaplain et al. (2008) and Wang and Keller (2009). The isotherms were fitted to the L-type, with non-linear concave slope, the most common type of sorption interactions between herbicides and solid phase. Regardless of the treatment, the sorption intensity (1/n) did not differ for biochar and NPK application, demonstrating the increased total capacity of sortive sites, however, without effect on the interaction forces between diuron and the solid phase.

Regardless of NPK fertilization, biochar treatment significantly increased (p > 0.05) the diuron sorption coefficient (Kf), especially for the highest dose (16 Mg·ha⁻¹). The obtained values of 12.82 (with NPK) and 11.91 (without NPK) (Table 2) are 74 and 53% higher, respectively, compared to the control treatment without biochar. On the other hand, the sorption capacity of the soil did not change significantly with or without NPK fertilization as shown by the average values of Kf isotherms (p > 0.05), indicating that the fertilizer nutrients did not compete for the same physicochemical sorption site of diuron.

There was a positive correlation between the Kf and TOC (r = 0.76), HA (r = 0.75), HUM (r = 0.76), and Koc (r = 0.91), demonstrating the high SOM contribution to diuron sorption (Table 3). These results corroborate Rocha et al. (2013a) and El-Nahhal et al. (2013), who reported a positive correlation between Kf and SOM in Latosols with different textures and in sandy soil, respectively.

Positive correlations between biochar and TOC (r = 0.94) and the HUM fraction (r = 0.73) were also observed. Similarly, Petter et al. (2016) reported a significant increase in TOC contents with the application of
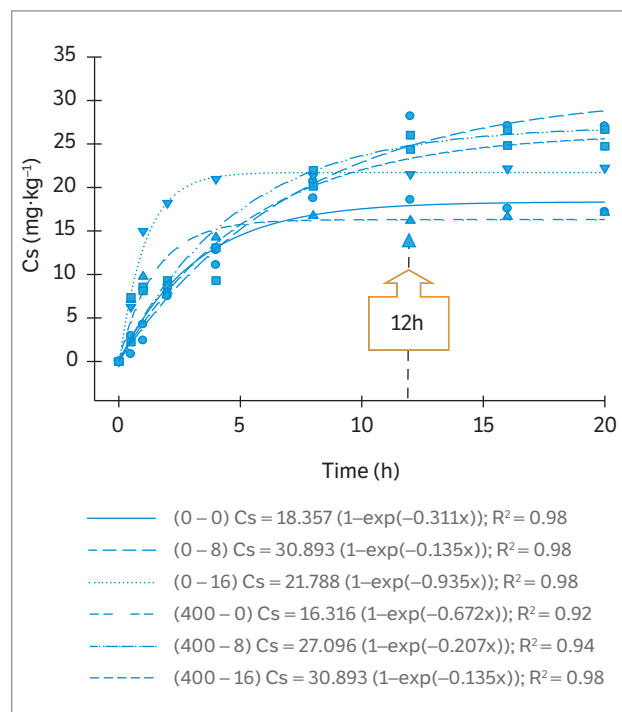

Figure 2. Estimates of diuron sorption kinetics curves in Oxisol after biochar application (0, 8 and 16 Mg·ha⁻¹) in the presence and absence of chemical fertilizer (0 and 400 kg·ha⁻¹ NPK) over time.

32 Mg·ha⁻¹ of biochar. The biochar effect of increasing TOC is associated with the presence of aromatic structures and the high C/N ratio, increasing the stability of organic matter, since this material decomposition is slow. On the other hand, the contribution to the carbon-HUM may be related to weathering or oxidative natural depolymerization of biochar (Kramer et al. 2004) and the high aromaticity of biochar, which are closely related (Rumpel et al. 2006). While there is no direct correlation between biochar and carbon content in the HA fraction, there may be physical-chemical interactions as verified by Fei et al. (2015). Wang et al. (2014) concluded that the catalytic ability of biochar seems to be an important contributor to the formation of carboxylated and condensed aromatic structures of humic acids.

Thus, the greater sorptive capacity of the soil after the biochar is applied can be attributed to 2 main effects. The first is the direct effect of biochar on components of organic matter (TOC and HUM) and of these on Kf; the second is the direct effect on diuron retention through charges generated by the oxidation of biochar poly-condensed aromatic structures. Some studies observed, by spectroscopic analysis of FTIR and NMR, oxidation of biochar aromatic structures associated with HA and HUM, increasing the reactivity (carboxylic groups C = O) (Kramer et al. 2004; Prost et al. 2013; Wang et al. 2014).

The formation of C = O groups resulting from the biochar-HA interaction is assigned to H-bond mechanism that occurs in the more polar surfaces of biochar (Fei et al. 2015). Therefore, the increase in
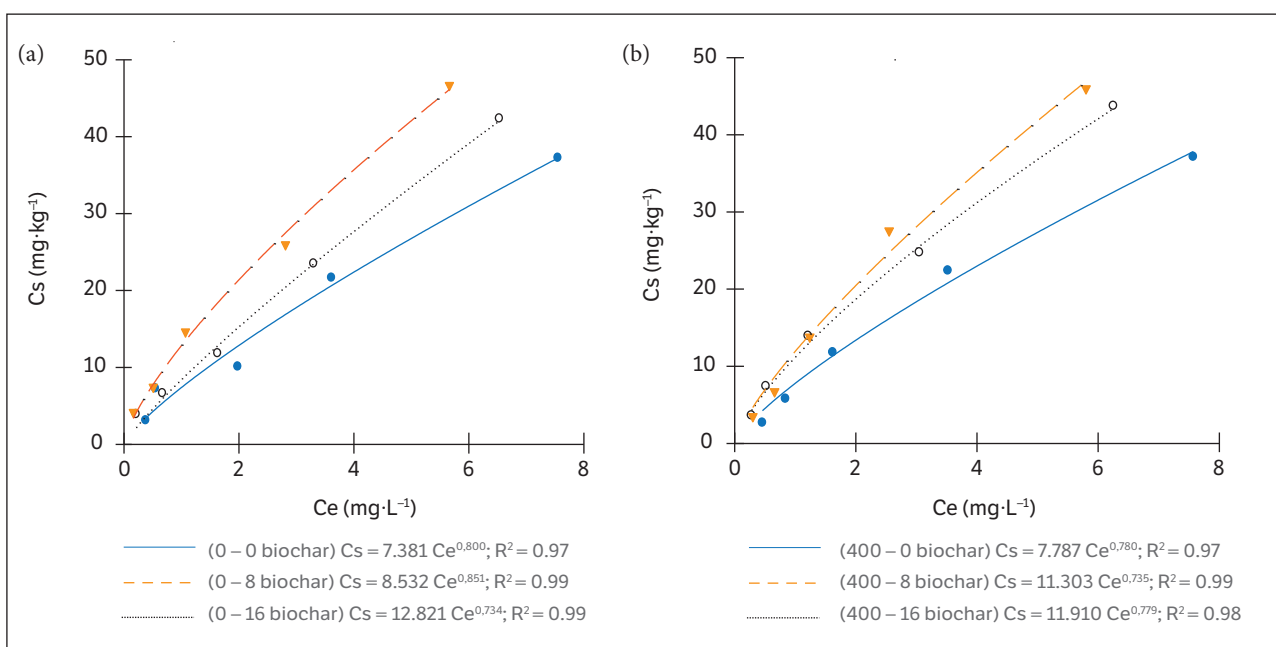

Figure 3. Estimates of Freundlich sorption isothermals for diuron in Oxisol after biochar application (0, 8 and 16 Mg·ha⁻¹) (a) in the absence and (b) in the presence of 400 kg·ha⁻¹of chemical fertilizer (NPK).

Table 2. Estimates of sorption coefficients (Kf and 1/n) and coefficients of determination (R^2) of diuron sorption isothermals in Oxisol after application of biochar in the presence and absence of chemical fertilizer.

	Oxisol							
Coefficient	**0 kg·ha⁻¹ NPK (00-20-20)**				**400 kg·ha⁻¹ NPK (00-20-20)**			
	Biochar (Mg·ha⁻¹)				**Biochar (Mg·ha⁻¹)**			
	0	**8**	**16**	**Mean**	**0**	**8**	**16**	**Mean**
Kf	7.38c	8.53b	12.82a	9.57A	7.78b	11.30a	11.91a	10.33A
1/n	0.80	0.85	0.73	0.79ⁿˢ	0.78	0.73	0.78	0.76ⁿˢ
R^2	0.99	0.99	0.99	-	0.99	0.99	0.99	-

Means followed by the same letter in the row do not differ by the Scott-Knott's test at 5%; ⁿˢNon-significant.

Table 3. Estimates of Pearson's correlations between diuron and biochar sorption coefficients and the chemical characteristics of the treatments in Oxisol.

Coefficient/ biochar	Total organic carbon	Fulvic acid	Humic acid	Humin	pH	Organic carbon partition coefficient
Kf	0.76**	0.19^{ns}	0.75*	0.76*	0.52^{ns}	0.91*
Biochar	0.94*	0.24^{ns}	0.08^{ns}	0.73*	0.96*	0.31^{ns}

^{ns}Non-significant; **and*Significant at $p < 0.01$ and $p < 0.05$, respectively.

carboxyl groups (C = O) in the HA and HUM fractions after biochar application contributed to diuron sorptive interactions via H-bonds, while the higher biochar-HUM aromaticity would stimulate increased retention by the hydrophobic partition. Studies show (Kasozi et al. 2010; Armanious et al. 2014) that interactions between humic substances and other compounds happen mainly by hydrophobic adsorption mechanisms and electrostatic interactions.

Therefore, even though diuron is non-ionizable in the soil solution, the presence of diuron polarity would justify the sorption mechanism via H-bonds. On the other hand, the low solubility and hydrophobicity of diuron would explain the sorption mechanism via hydrophobic partitioning by the physical partitioning of the hydrophobic surfaces. The sorption interaction mechanisms via hydrophobic partition and H-bonds have been identified as the main diuron sorption mechanisms in the soil (Wauchope et al. 2002; Fontecha-Cámara et al. 2008; Araujo et al. 2012). In this sense, Ferri et al. (2005) observed high contribution of the HUM fraction to the sorption of acetochlor, which, as diuron, is a non-ionic herbicide, confirming the importance of the HUM fraction in the herbicide retaining process.

The analysis of Koc, which is considered an important parameter for predicting the affinity of a molecule with soil organic fraction, confirmed the importance of SOM to diuron sorption since there is a direct correlation between Kf and organic carbon content (OC). For the average Kf values at doses of 0 (Kf = 7.58), 8 (Kf = 9.91) and 16 (Kf = 12.36) Mg·ha^{-1} of biochar, Koc values were 361, 388 and 430, respectively. The proportionality of Kf/OC values show that, in fact, SOM is primarily responsible for diuron sorption into tropical soils. However, these statements should not be extended as a rule to other pesticides with different physical and chemical characteristics. The high chemical variability of SOM might not present a direct correlation with

sorption. Weber et al. (2009) studied the sorption of the insecticide thiamethoxam in soil with and without organic matter and suggested using Kf as sorption coefficient, due to the non-proportionality between sorption and OC levels.

In contrast to the behavior of sorption data, diuron desorption was significantly reduced with the application of biochar (Figure 4). The diuron desorption rates for the 16 Mg·ha^{-1} dose, compared to control (without biochar), decreased 30 and 57% in the absence and presence of NPK, respectively. The desorption intensity also decreased as the biochar doses increased, which was verified by the decreasing angular coefficients of the regression equations. These results are important from the agronomic and environmental points of view because desorption determines the magnitude of the response regarding the release of diuron in the solution and, consequently, the potential mobility in the soil.

Diuron can persist in the soil up to approximately 360 days in many cases (Giacomazzi and Cochet 2004), which is considered a long period by international standards. Therefore, diuron increased sorption and decreased desorption in soils with biochar application reduce leaching and, consequently, the contamination risk of subsurface waters. Leaching decreases because diuron remains longer in the surface layer becoming more prone to microbial degradation, which is a main pesticide dissipation mechanism, as the microbial activity is more intense in this layer. There is also the fact that biochar can enhance this process by increasing microbial activity, which is favored by the formation of microhabitat in the porous structures of biochar (Jindo et al. 2012). These characteristics are important as they contribute to reduce the persistence of diuron in the soil.

The results of this study improve the understanding of the physicochemical interaction processes between diuron and SOM and how the application of biochar
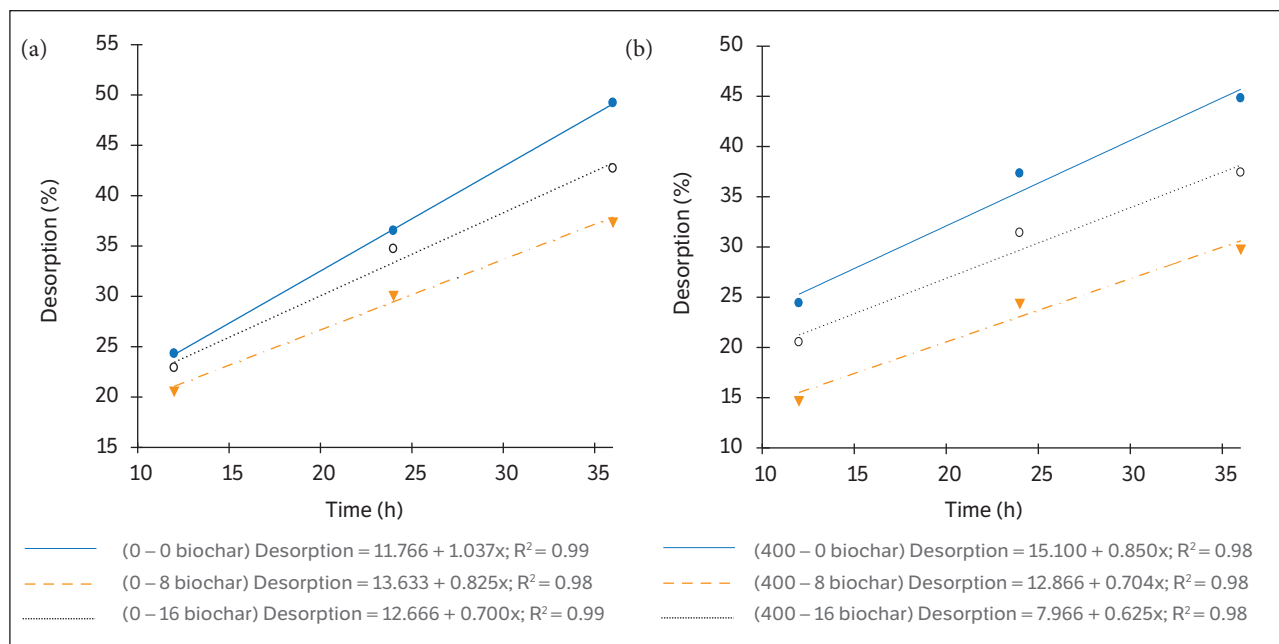
Figure 4. Desorption percentage of diuron in Oxisol after application of biochar (0, 8 and 16 Mg·ha⁻¹) (a) in the absence and (b) in the presence of 400 kg·ha⁻¹ of chemical fertilizer (NPK).

can help to mitigate the leaching process, particularly in sandy soils with low levels of organic matter.

CONCLUSION

The biochar application increased sorption and reduced desorption of diuron in Oxisol, confirming the hypothesis suggested in this study. Biochar contribution happens due to the increase of total organic carbon, humic acid and humin. The fractions of the organic matter, humic acid and humin are the main responsible for the increased sorption and reduced desorption of diuron in soil. The hydrogen bonds (diuron-humic acid) and the hydrophobic partition (diuron-humin) are suggested as the main mechanisms of diuron sorption, which is positively correlated with organic carbon.

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