

# Contribution of Soil Components on the Sorption of Chlorpyrifos

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**Abstract** It is generally assumed that the sorption of a nonionic pesticide on soil depends mainly on the content of soil organic matter (SOM); however, there are other factors that can contribute to this process. The possible causes of variation in the carbon-normalized partition coefficient ( $K_{OC}$ ) for chlorpyrifos (CPF) for a diverse set of ten soils have been investigated. On the one hand, the analysis of the chemical composition of the SOM was analyzed, and on the other hand, the likely interactions between the organic matter and the mineral phase were assessed. Sorption experiments of CPF were performed on whole soil, on soils treated with 2% hydrofluoric acid (HF), and onto calcined soil at 550 °C. Organic matter chemistry of soil was determined by  $^{13}C$  CP/MAS NMR spectroscopy;  $K_{OC}$  values were positively correlated with aryl C relative proportion and negatively correlated with alkyl C and O-aryl C proportions and prediction equation of  $K_{OC}$  was found ( $R^2 = 0.82$ ,  $p < 0.001$ ). To evaluate possible organo-mineral interactions, a mathematical model was proposed which calculates the concentration of CPF at equilibrium ( $C_{cal}$ ) considering adsorption coefficients

for the organic ( $K_{DHF}$ ) and inorganic ( $K_{D550\text{ °C}}$ ) soil constituents, separately. The comparison between  $C_{cal}$  and the equilibrium concentration obtained from experimental data ( $C_{exp}$ ) onto whole soil allowed us to confirm that interactions between the OM and clay affect the adsorption of CPF in whole soil. Such findings should be taken into account in the development of predictive models for the evaluation of the fate and transport of this pesticide in soil.

**Keywords** Pesticides · Soil · Organic matter quality ·  $^{13}C$ NMR · Organo-mineral interactions

## 1 Introduction

Sorption of organic pollutants to soils is an environmentally important process that affects properties such as bioavailability, ecotoxicity, rate of degradation, and their mobility (Smernik and Kookana 2015; Wauchope et al. 2002; Guerin and Boyd 1992; He et al. 2014; Ahangar et al. 2008a; Salloum et al. 2001; Ahmad et al. 2001). For these substances, the key factor that determines the extent of adsorption to the soil matrix is mainly the content of organic matter (OM) (Karickhoff 1981; Chiou 1989; Xing et al. 1994; Pignatello and Xing 1996). For hydrophobic species, the sorption process is considered as a partitioning between the solution and the soil organic matter (SOM), such sorption interaction is generally quantified by  $K_{OC}$ , the C-normalized partition coefficient (Ahmad et al. 2001).

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The analysis  $K_{OC}$  in relation to soil properties represents a valuable contribution to the understanding of the attenuation phenomena of the organic contaminants off-site migration in the environment. Fate and transport simulation models of pesticides in the environment require locally determined  $K_{OC}$  values as input data, which might be predicted using the methodology proposed in this study. In the last decade, several studies have shown that  $K_{OC}$  is a coefficient which depends not only on the adsorbate molecule but also on soil properties (Ahangar et al. 2008b; Singh and Kookana 2009; Gebremariam et al. 2012; Ehlers Clark et al. 2010). Other authors reported that  $K_{OC}$  values vary considerably within soil-landscape (Coquet and Barriuso 2002; Farenhorst et al. 2010) and both intrinsic factors (such as the natural condition of the soil) and extrinsic factors (management practices) can contribute to such variations (Farenhorst 2006). Wauchope et al. 2002 analyzed  $K_{OC}$  values from many different soils reported by several other authors finding that the coefficient of variation in  $K_{OC}$  values was generally around 30–60% and the ratio between the maximum values and minimum values of  $K_{OC}$  was generally around 3–10. It was suggested that about half of the variability in  $K_{OC}$  could be due to experimental error, whereas the rest of the variability reflects the differences in the nature of organic matter of soils. It has also been shown that different humic fractions from the same soil may have different values  $K_{OC}$  (Chiou et al. 2000; Mao et al. 2002; Gunasekara and Xing 2003; Kang and Xing 2005).

The most important types of soil particles that constitute the organic matter are humic and fulvic acids, whereas the mineral phase is constituted mainly by silica, metal oxides, and layered aluminosilicates with aggregation of colloidal and particulate materials. Interactions between organic matter and minerals are frequently invoked as the “reason” why the organic carbon is preserved in earth systems (Keil and Mayer 2014). The heterogeneous interactions between organic and mineral constituents, involving multiple binding points and aggregation, have the capacity to buffer or promote chemical reactions and to expose or protect organic matter from remineralization. Both the presence of minerals as well as the organo-mineral interactions in the whole soil can determine the adsorption of pollutants, either by representing a site adsorbent “per se,” clay

sorption sites (CL- sites), or by blocking of OM sorption sites (OC- sites) (Singh and Kookana 2009; Smernik and Kookana 2015; Bonfleur et al. 2016; Celis et al. 2006).

The use of spectroscopic techniques, such as  $^{13}\text{C}$ -NMR, IR, UV-Vis, and fluorescence, has led to considerable advance in the knowledge of soil chemistry (Kaiser and Ellerbrock 2005; Forouzangohar et al. 2009; Demyan et al. 2012; Bernier et al. 2013; Carstea et al. 2014). Particularly, the solid state cross polarization and magic-angle spinning  $^{13}\text{C}$ -nuclear magnetic resonance technique ( $^{13}\text{C}$  CP/MAS NMR) spectroscopy enables the quantitative evaluation of the structural environment of each C atom in organic materials (Heckman et al. 2014; Bonfleur et al. 2016).

Several researchers have suggested that sorption coefficients such as  $K_{OC}$  can be calculated using the structural characteristics of soil organic matter (SOM). Recently, Smernik and Kookana (2015) investigated the adsorption of diuron (nonionic pesticide) on 34 different soils of Sri Lanka, and they found a large variation in the  $K_{OC}$  values, either in whole soils or in HF-treated soils. They also analyzed the chemistry of organic matter using  $^{13}\text{C}$  NMR spectroscopy and concluded that  $K_{OC}$  increased with aryl C content and decreased with the O-alkyl C and alkyl C content. Farenhorst et al. (2010) reported that  $K_{OC}$  values for the 2,4-D (weakly acidic herbicide) varied from 76 to 315 L kg<sup>-1</sup> in soils obtained along a slope transect from an agricultural area in Manitoba, Canada. This study, in which SOM structure was characterized by NMR technique, showed that there is variation in field scale for  $K_{OC}$  values of 2,4-D attributed to variation of aromaticity in the SOM given by the relative proportion of aryl C and O-aryl C. Similar results were obtained by Ahmad et al. (2001) for carbaryl and phosalone (both nonionic pesticides) in soil from different regions of Australia and Pakistan. Kile et al. (1999) reported that  $K_{OC}$  for carbon tetrachloride for 19 soils and 9 sediments was negatively correlated with the proportion of “polar organic carbon” (O-alkyl C + carbonyl C).

Previous studies conducted in our laboratory have shown that among other organophosphate pesticides, chlorpyrifos (CPF) is one of the most frequently detected in water, both surface and subsurface, of the region under study. Leaching and preferential flows were the main transport routes contributing to subsurface contamination (Loewy et al. 2011). Since sorption is one

of the main attenuation mechanisms known to minimize the risk of groundwater contamination, in the present work, CPF sorption behavior onto ten soils of varied physicochemical properties was investigated.

In the present study, the sorption results are combined with ( $^{13}\text{C}$  NMR) data in order to explain the variation in CPF  $K_{\text{OC}}$  values by the soil organic matter chemistry. In order to assess how organic matter-mineral phase interactions, occurring in the whole soil, can influence on the adsorptive behavior of CPF, a simple theoretical model is used to explain the sorption data.

## 2 Materials and Methods

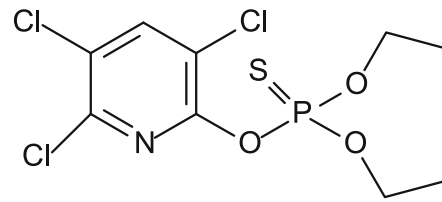
### 2.1 Soil and Chemical

The sorption studies were carried out on soils from the North Patagonian region, Neuquen Province, South Argentina ( $39^{\circ}$ – $41^{\circ}$  S;  $71^{\circ}$ – $64^{\circ}$  W). Ten soils, with varied physicochemical characteristics in terms of texture, clay and organic carbon (OC) content, and pH (Table 1), were collected from the A horizon. The soil samples were air-dried and sieved through a 2-mm mesh.

Chlorpyrifos (O,O-diethyl-3,5,6-trichloro-2-pyridilphosphorotriate) (Chem Service, chemical purity >99%) was used for sorption studies; is a non ionizable compound ( $\log K_{\text{ow}} = 4.7$ , water solubility  $1.05 \text{ mg L}^{-1}$ ; IUPAC PPDB - Pesticides Properties DataBase 2015). The CPF structural formula is given in Fig. 1. This chemical is a worldwide-applied insecticide; particularly in the North Patagonian Region, it is used for *Cydia pomonella*, a fruit widespread pest.

**Table 1** Physicochemical characteristics of soils

Soil	Texture	OC (%)	pH	Clay (%)
S1	Loam	2.52	8.2	21.9
S2	Silt loam	1.62	8.2	21.9
S3	Loam	1.91	7.4	21.9
S4	Clay loam	2.03	7.5	36.4
S5	Silt loam	4.72	5.6	18.0
S6	Silt loam	1.76	5.5	19.0
S7	Silt loam	3.28	5.9	20.0
S8	Sandy loam	6.82	5.3	3.8
S9	Sandy loam	2.21	6.2	11.8
S10	Sandy loam	4.91	6.1	6.3



**Fig. 1** Structural formula of chlorpyrifos

### 2.2 Soil Treatments

#### 2.2.1 HF Treatment

Soil samples were treated with hydrofluoric acid (HF) to concentrate the organic fraction and remove the paramagnetic materials (Ahmad et al. 2001). Briefly, finely ground (<200  $\mu\text{m}$ ) of each soil (3 g) and 50 mL of 2% HF were shaken into centrifuge tubes for 1 h and centrifuged at 3000 rpm for 20 min, and the supernatant solution was discarded. This procedure was repeated five times and then followed by other four similar HF treatments using longer shaking time (three for 16 h and one for 64 h). After the final extraction, the residue was washed three times with deionized Millipore water and then freeze-dried.

#### 2.2.2 Thermal Treatment

In order to remove the soil organic matter, 5 g of each whole soil was calcined at  $550^{\circ}\text{C}$  during 36 h in heating muffle.

### 2.3 $^{13}\text{C}$ NMR Analysis

The solid-state  $^{13}\text{C}$  NMR spectra of HF-treated soils were obtained with a Bruker Avance III HD 400 MHz Wideboard instrument operating at a frequency of 100.63 MHz for  $^{13}\text{C}$  using zirconium rotors of 4 mm OD with KEL-F-caps. The cross polarization magic angle spinning (CPMAS) technique was applied during magic-angle spinning of the rotor at 14 kHz. A contact time of 1 ms and a  $90^{\circ}$   $^1\text{H}$ -pulse width of 3.5  $\mu\text{s}$  were used for all spectra. The spectra were corrected for spinning sidebands. The quantification for the different functional group regions of organic matter was carried out by subdividing the spectra into four chemical shift ranges (Table 2): 0–45 ppm, alkyl C; 45–110 ppm, O-alkyl C and N-alkyl C; 110–160 ppm, olefinic/aryl C; and 160–220 ppm, carboxyl C and

**Table 2** Peaks assignment in the solid state  $^{13}\text{C}$  NMR spectra to typical C groups in soil samples (referenced to tetramethylsilane = 0 ppm) (Knicker and Ludeman 1995)

Chemical shift range (ppm)	Assignment
0–45	Alkyl C in fatty acids, aminoacids, or paraffinic structures
45–110	O- and N-alkyl C
45–60	Aliphatic C-N, methoxyl
60–90	Alkyl-O (carbohydrates, alcohols)
90–110	Acetal and ketal carbon (carbohydrates) and some aromatic C
110–160	$\text{sp}^2$ -hybridized C
110–140	Aryl-H and aryl-C carbons, olefinic C
140–160	Aryl-O and aryl-N carbons
160–220	Carbonylic C/carboxylic C/amide C
160–185	Carboxyl and amide C
185–220	Aldehyde and ketone C

carbonyl C, according to Knicker (2011). The proportional contribution of these types of C was determined by integration of the different spectral regions. Aromaticity of OM in each soil was calculated by dividing the fraction of aromatic C (aryl C plus O-aryl C) by the sum of the fractions of all components of carbon.

## 2.4 Sorption Experiments

Sorption isotherms were registered in order to obtain the sorption coefficients ( $K_D$ ,  $K_{OC}$ ,  $K_{DHF}$ , and  $K_{D550\text{ }^\circ\text{C}}$ ) and thus deepen about the mechanisms governing the distribution and fate of pesticides in the environment. Sorption of CPF in soil was measured using a batch equilibrium method. The soil samples and aqueous solution (0.01 M  $\text{CaCl}_2$ ) of CPF at different initial concentration ( $C_0$ ) between 0.120 and 0.800  $\text{mg L}^{-1}$ , in a ratio 1:20, were shaken at 134 rpm in glass flasks fitted with Teflon caps in the dark at 20 °C for 16 h. Preliminary kinetics experiments indicated that this time was sufficient to attain the equilibrium. At the end of the equilibration period, suspensions were centrifuged at 3000 rpm for 30 min. Then, the supernatant was separated and CPF concentrations were determined by chromatographic analysis using an Agilent 6890N GC instrument equipped with an HP-5MS column and  $\mu\text{ECD}$  detector.

Blanks without soil were analyzed to evaluate CPF degradation in the experimental conditions, and it was considered that such process was not significant during 16 h. Blanks containing soil and 0.01 M  $\text{CaCl}_2$  solution,

without CPF, were treated in the same way as laboratory method blanks for quality control. All sorption experiments were carried out in triplicate.

The CPF sorbed amount onto soil ( $C_s$ ) was calculated from the difference between the initial solution concentration ( $C_0$ ) and equilibrium solution concentration ( $C_{eq}$ ).

$$C_s = \frac{(C_0 - C_{eq}) \times V}{m}$$

where  $V$  is the CPF solution volume (L) and  $m$  is soil mass (g).

The  $K_D$  values were obtained as the ratio between the sorbed concentration on the solid phase and the equilibrium concentration in the solution from the linear region of the isotherms performed (Baskaran et al. 2003; Rogers and Stringfellow 2009).  $K_{OC}$  values were calculated as ratio between  $K_D$  values and fraction of organic carbon in soil,  $f_{OC}$ .

## 2.5 Modeling

A mathematical model was applied which compares the adsorption capacity of the whole soils ( $C_{exp}$ ) with that calculated from the organic and inorganic soil components separately ( $C_{cal}$ ). The adsorption data were fitted with a mathematical model that takes into account the binding between the CPF and organic and mineral soil components. The binding is assumed to take place at localized OC- sites (onto organic matter) and CL- sites (onto mineral surface), whose abundance was determined by physicochemical analyses. The binding of CPF to the

OC- is represented by the following equilibrium reaction (Eq. 1):

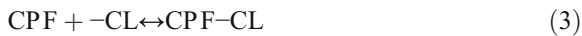


where -OC, obtained by treating soil with HF represents the organic carbon in the absence of mineral. The mass action law of this reaction is represented in Eq. 2.

$$K_{\text{DHF}} = \frac{(\text{CPF-OC})}{[\text{CPF}]} \quad (2)$$

where  $K_{\text{DHF}}$  ( $\text{L kg}^{-1}$ ) is the CPF sorption coefficient on soil organic matter, symbols within parentheses represent the sorbed amount ( $\text{mg kg}^{-1}$ ), and symbols within square brackets represent the solution concentration ( $\text{mg L}^{-1}$ ).

Similarly, the binding of CPF to clays is represented by the equilibrium reaction (Eq. 3) and by the mass action law in Eq. 4.



$$K_{\text{D550}^{\text{C}}} = \frac{(\text{CPF-CL})}{[\text{CPF}]} \quad (4)$$

The model needs to be completed with the mass balance for CPF (Eq. 5).

$$C_o = [\text{CPF}] + [\text{CPF-OC}] + [\text{CPF-CL}] \quad (5)$$

where  $[\text{CPF-OC}]$  and  $[\text{CPF-CL}]$  represent the concentrations ( $\text{mg L}^{-1}$ ) of CPF sorbed on organic carbon and sorbed on clays, respectively.

Considering Eqs. 2, 4, and 5, the CPF equilibrium concentration ( $C_{\text{cal}}$ ) can be easily calculated (Eq. 6).

$$C_{\text{cal}} = \frac{C_o}{1 + K_{\text{DHF}} \times [\text{OC}] + K_{\text{D550}^{\text{C}}} \times [\text{clay}]} \quad (6)$$

## 2.6 Statistical Analyses

Descriptive statistical analyses were carried out using the Statistica software package version 7.0 (StatSoft France, Maison-Alfort, France). The relationship between pesticides sorption parameters and SOM chemistry was examined using stepwise multiple regression. Independence, normality, linearity, and homoscedasticity were tested (results not shown) before regression analyses were performed.

## 3 Results and Discussion

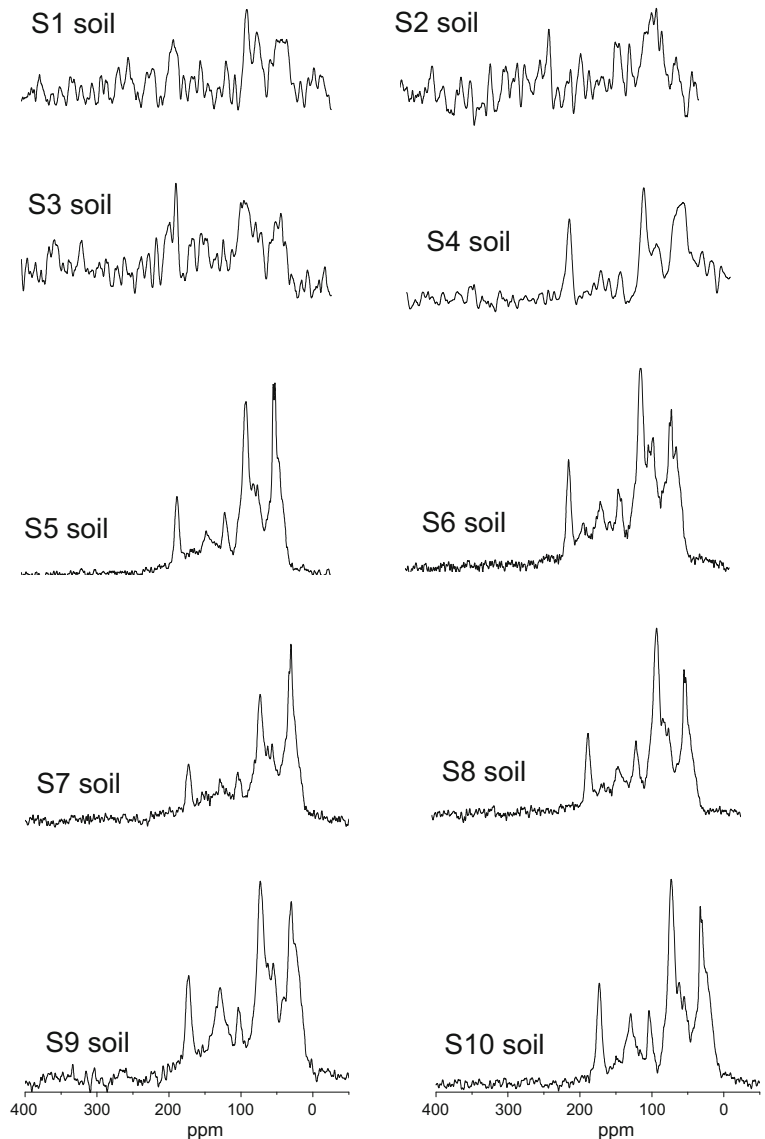
The  $^{13}\text{C}$  NMR spectra of the ten soils after HF- treatment showed a similar profile; however, the relative integrals of the selected regions differ depending on the soil sample (Fig. 2), indicating that there are differences in the chemistry of the organic matter between the soils.

For a quantitative comparison, solid state  $^{13}\text{C}$  NMR spectra were divided into six chemical shift regions: 0–45 ppm (alkyl C), 45–110 ppm (O-alkyl C and N-alkyl C), 110–140 ppm (aryl C), 140–160 ppm (O-aryl C), 160–185 ppm (carboxyl C), 185–220 ppm (aldehyde/ketone C). The O-alkyl C and N-alkyl C region (45–110 ppm) predominated in almost all the soils studied whereas alkyl C was found to be the second most abundant C type and aromatic C was the third in order of importance component. Both carboxyl C and carbonyl C were the smallest contribution to the SOM. One exception is given by S2 and S4 soils where the alkyl C region predominated over the O-alkyl C region. Overall, the proportion of O-alkyl C region in the SOM ranged from 27 to 51%, alkyl C from 17 to 43%, and the aromatic- C (aryl C + O-aryl C) varied from 5 to 19%, as shown in Fig. 3.

In the literature, it was reported that alkyl C component of SOM accumulate selectively in the clay fraction (Baldock et al. 1992). Skjemstad et al. (1986) studied Vertisols that contain organic matter, which is dominated by alkyl structures. Although a range of organic structures was evident, the highest fractions in alkyl material are more intimately associated with the soil clay components. These authors suggested that sorption to clay minerals can increase the stability of materials with highly aliphatic structures. In our study, the S4 is the highest clay content soil and the one with the largest contribution of alkyl C, a result consistent with those previously reported by the authors mentioned above.

The chemical characteristics of organic matter of the soils studied are similar to those reported by Mahieu et al. (1999) who based their study on NMR data collected from the literature on >300 soils, in which the O-alkyl C was the most abundant group followed by alkyl C and aromatic groups, with carbonyl group always being the least abundant group. However, soils analyzed in this study are characterized in general, by a low content of aromatic component (Fig. 3) in relation to the results reported by other authors. Farenhorst et al. (2010) found in soil from an agricultural field in Manitoba, Canada, proportions of aromatic C (O-aryl C + aryl C) between 24 and 37% of the total area in the

**Fig. 2** Solid-state  $^{13}\text{C}$  NMR spectra of ten HF-treated soils samples (S1–S10), acquired on the 400 MHz spectrometer with a 14-kHz MAS rate

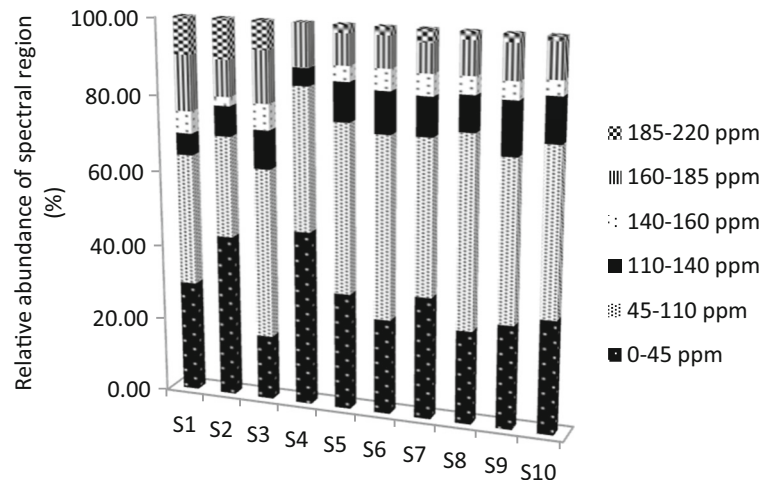


spectra of  $^{13}\text{C}$  NMR. Ahmad et al. (2006) studied the nature of SOM of 25 soils of Australia and Pakistan and reported proportions of aromatic C between 11 and 28%. These structural differences in the SOM are related to various factors such as degree of decomposition of the organic matter, origin, parent material, and environmental factors (Ahmad et al. 2001; Ahmad and Kookana 2002). In particular, the type of vegetation from which the SOM originates and the degree of decomposition of the SOM affect the chemical composition of soil. The O-alkyl C groups decrease during decomposition while the proportion of alkyl C tends to increase and aromatic C may increase or decrease. Aromaticity of organic

matter depends in part on biological alteration during pedogenesis (Chen and Pawluk 1995) and the mode of geological diagenesis (Grathwohl 1990). Ahmad et al. (2006), using  $^{13}\text{C}$  NMR data and elemental composition in a molecular mixing model estimated the molecular components of SOM in 24 soils from various agroecological regions. These authors reported that signals assigned to O-alkyl C and N-alkyl C regions are associated mainly to the presence of carbohydrates, while signals corresponding to O-aryl C + aryl C (110–160 ppm) regions were attributed mainly to the presence of lignin and charcoal.



**Fig. 3** Relative integrals of different functional group regions of  $^{13}\text{C}$  NMR spectra of ten soil samples (S1–S10)



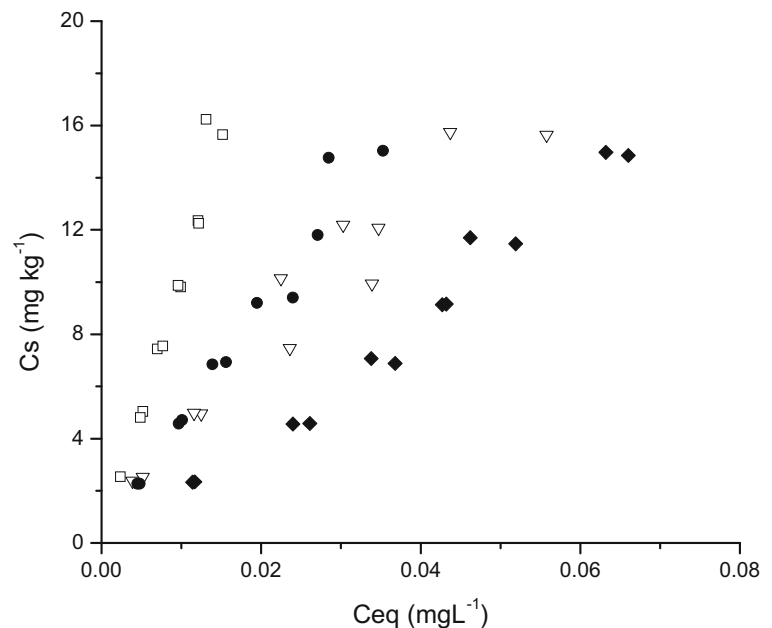
Sorption isotherms for CPF in soils were registered and linear plot was observed along the concentration range analyzed. This behavior is expected considering that the sorption of nonionic organic compounds occurs mainly by partition into SOM, and thereby  $K_D$  was positively correlated with  $f_{\text{OC}}$ ,  $R^2 = 0.92$  ( $p < 0.001$ ). Figure 4 shows four of these isotherms (soils S2, S6, S8, and S9). Sorption coefficient values ( $K_D$ ) were calculated from the slopes of the plot.

$K_D$  values of CPF ranged from  $175 \text{ L kg}^{-1}$  (soil S4) to  $1069 \text{ L kg}^{-1}$  (soil S8) for the soils studied, as shown in Table 3; such coefficient values were consistent with the

range of values reported in the literature for CPF sorption on soils (Huang and Lee 2001; Wu and Laird 2004; Gebremariam et al. 2012).

Sorption coefficients were normalized to OC content and sorption coefficients per unit mass of organic carbon ( $K_{\text{OC}}$ ) in these soils were obtained. The  $K_{\text{OC}}$  values for CPF ranged from  $8495$  to  $19,819 \text{ L kg}^{-1}$  for soils S4 and S9, respectively, indicating that the variability in  $K_{\text{OC}}$  values is not the same as in the  $K_D$  values. It is assumed that the soil sorption potential per unit mass of organic carbon for nonionic pesticide is the same for all soils, but this is not always true (Ahmad et al. 2001). In fact, S4

**Fig. 4** Sorption isotherms of CPF in soils S2 (triangle), S6 (diamond), S8 (square), and S9 (circle). Conditions: CPF concentration,  $0.120$ – $0.800 \text{ mg L}^{-1}$ ; ratio, 1:20 (soil mass/aqueous solution); contact time, 16 h. All experiments are performed at  $20^\circ\text{C}$  and circumneutral pH



**Table 3** Sorption coefficients ( $L\ kg^{-1}$ ) of CPF in whole soil ( $K_D$  and  $K_{OC}$ ), HF-treated soils ( $K_{DHF}$ ), and calcined soils ( $K_{D550\ ^\circ C}$ )

	Whole soils		Treated soils	
	$K_D$	$K_{OC}$	$K_{DHF}$	$K_{D550\ ^\circ C}$
S1	274	10,873	693	41
S2	168	10,370	490	45
S3	306	16,906	848	24
S4	175	8495	510	49
S5	784	15,967	2571	5
S6	287	16,307	354	14
S7	367	11,189	374	37
S8	1069	15,674	1555	22
S9	438	19,819	1452	18
S10	746	15,193	1468	16

and S9 soils have almost the same OC content, 2.03 and 2.21%, respectively (Table 1); however, the  $K_{OC}$  value of S9 soil is about twice the one corresponding to S4 soil. Moreover, the  $K_{OC}$  value of S6 soil is similar to the  $K_{OC}$  of S8 soil, although the content of OC in these soils is significantly different, 1.76 and 6.82%, respectively.

The  $^{13}C$ -NMR data of the SOM were considered in order to analyze whether differences in the nature of the organic matter could be contributing to the differences in  $K_{OC}$  values between the soils. The role of chemical components of SOM analyzed by  $^{13}C$  NMR and of the soil clay content on CPF sorption was examined using stepwise multiple linear regression between  $K_{OC}$ , the organic matter components (alkyl C, O-alkyl C and N-alkyl C, aryl C, O-aryl C, carboxyl C, and aldehyde/ketone C) and clay content, determining if a multivariable model might explain the data set. Our results show that the  $K_{OC}$  values for CPF are adequately predicted by the model shown in Eq. 7, using aryl C together with alkyl C and O-aryl C contents ( $p < 0.01$ )

$$K_{OC} = 25492 + 749(\text{aryl C}) - 412(\text{alkyl C}) - 1344(\text{O-aryl C}) \quad R^2 = 0.82 \quad (7)$$

The CPF  $K_{OC}$  values in the present study were observed to be strongly dependent on contents of aryl C component and a positive correlation was found accounting for 61% of the variance in  $K_{OC}$ . Whereas a negative correlation was observed for the contents of

alkyl C and O-aryl C components; these parameters account for 13 and 8% of  $K_{OC}$  variance, respectively. It can be inferred from these regression analyses that aryl C component of SOM is likely to be the key structural parameter that regulates sorption of this chemical. There was no significant correlation between  $K_{OC}$  values and the proportion of the O-alkyl C neither with N-alkyl C, carboxyl C, aldehyde/ketone C chemical component, nor with clay content. These results might show that only SOM chemistry explains the variability in sorption behavior of CPF while the soil inorganic component, quantified as clay content, does not represent an active site for retention of this pesticide.

In order to assess the contribution to the adsorption capacity of the different fractions that compose the soil,  $K_{D550\ ^\circ C}$  coefficients, which represent the potential for sorption by the mineral fraction, mainly clays, and  $K_{DHF}$ , which represents the sorption potential by the organic fraction of the soil, were determined (Table 3). An increase in the sorption coefficient of CPF after treatment of soil with HF ( $K_{DHF}$ ) was observed, suggesting that the adsorption potential of such material contributes significantly to the contaminant retention probably because the groups responsible for the interaction (mainly aryl C) are exposed for the pesticide retention. In contrast, the  $K_{D550\ ^\circ C}$  values decreased significantly in all soils, suggesting that the mineral is not the main component involved in the retention of CPF. Such behavior is expected for nonionic chemicals, because the natural clay presents negative structural charge and exhibits hydrophilic nature.

In view of the results obtained and in order to assess potential interactions between organic and mineral materials in the whole soil, the present study intends to analyze in depth the main factors responsible for the variation in adsorption behavior of CPF onto the soil components.

The equilibrium concentrations of CPF for the experiments performed on the whole soil ( $C_{exp}$ ), calculated by applying the proposed model ( $C_{cal}$ ) in Eq. 6, and the ratio  $C_{exp}/C_{cal}$  are shown in Table 4.

The  $C_{exp}$  values obtained were in all cases higher than those calculated with the model ( $C_{exp}/C_{cal}$  ratio values ranged from 1.24 to 2.04), indicating less adsorption of CPF by the whole soil. These results suggest that the sites involved in the retention pesticide in organic matter would not be available for adsorption due to interactions with the mineral, present in such matrix. The observations derived from



**Table 4** Equilibrium concentrations (mg L<sup>-1</sup>) of CPF for sorption experiment and calculated by sorption model

Soil	$C_o$	$C_{exp}$	$C_{cal}$	$C_{eq_{exp}}/C_{eq_{cal}}$
S1	0.3861	0.2818 ± 0.0003	0.1649	1.71
S2	0.3886	0.4048 ± 0.0022	0.2056	1.97
S3	0.2660	0.1985 ± 0.0032	0.1284	1.55
S4	0.4378	0.4811 ± 0.0036	0.1816	2.64
S5	0.2802	0.0737 ± 0.0006	0.0461	1.60
S6	0.2800	0.2581 ± 0.0024	0.1942	1.33
S7	0.2168	0.1944 ± 0.0016	0.1314	1.48
S8	0.2590	0.0491 ± 0.0002	0.0408	1.20
S9	0.1233	0.0567 ± 0.0002	0.0458	1.24
S10	0.6316	0.2845 ± 0.0001	0.1370	2.08

$C_o$  initial concentration,  $C_{exp}$  equilibrium concentrations of CPF from experimental data on the whole soil,  $C_{cal}$  equilibrium concentrations of CPF calculated by applying the proposed model

Tables 1 and 3 can be explained in view of the results obtained by the proposed model, in which it is observed that soils with similar content of OC (2.03 and 2.21% for S4 and S9 soil, respectively) but very different clay content (S4 and S9 with 36.4 and 11.8%, respectively) have sorption coefficient values markedly different. S4 soil presents a  $K_D$  coefficient significantly lower than S9 soil, which can be attributed to the blocking of OC- sites in S4 soil, due to high clay content in accordance with the highest ratio  $C_{exp}/C_{cal}$  observed. In addition, S4 soil has one of the lowest relative proportions of aryl C, so the adsorption is expected to be low.

S2 and S6 soils have similar OC and clay contents (Table 1), but differ significantly in their adsorption coefficient values (168 and 287 L kg<sup>-1</sup>, respectively); this could be explained considering that aryl C proportion is higher in S6 soil than in S2 soil, although, because of their similar composition, it is assumed that the organo-mineral interactions are similar. On the other hand, S8 soil has the lowest clay contents (3.8%), the highest organic carbon content (6.82%), and a strikingly high value of sorption coefficient, not only because of the great contribution of the OM but also because of the low clay content. This would imply a low blocking of sites responsible for adsorption. It should be noted that this soil is the one that has the lowest value of  $C_{exp}/C_{cal}$  ratio, very close to 1, which could suggest a less availability of active sites for the CPF sorption.

## 4 Conclusions

The results show that the CPF  $K_{OC}$  values varied between 8495 and 19,819 L kg<sup>-1</sup>; such values increase with the organic matter aryl C component and decrease along the SOM alkyl C and O-aryl C components. The proposed mathematical model, by which the CPF sorption on each soil fraction separately is assessed (OM and clay), allowed us to determine that the existing interactions between OM and clay in the entire soil affect the availability of active sites for the CPF sorption. Thus, the variability of the sorption capacity can be explained both, by the variability on the OM composition and by the interactions between the organic and inorganic fractions in the whole soil. These results represent a significant contribution in the development of predictive models for assessing the fate and behavior of hydrophobic contaminants in soil.

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