Research article

Characterization of soil organic matter by FT-IR spectroscopy and its relationship with chlorpyrifos sorption

María Eugenia Parolo

Mónica Claudia Savini

Ruth Miriam Loewy*
rmloewy@gmail.com

LIBIQUIMA, Departamento de Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, 8300, Neuquen, Argentina

*Corresponding author.

Abstract

Sorption of non-ionic organic compounds to soil is usually expressed as the carbon-normalized partition coefficient (K_{OC}) assuming that the main factor that influences the amount sorbed is the organic carbon content (OC) of the soil. However, K_{OC} can vary across a range of soils. The influence of certain soil characteristics on the chlorpyrifos K_{OC} values variation for 12 representative soils of the Northpatagonian Argentinian region with different physicochemical properties was investigated for this study. The chlorpyrifos sorption coefficients normalized by the OC content were experimentally obtained using the batch equilibrium method; the K_{OC} values ranged between 9000–20,000 L kg^{-1}. The soil characteristics assessed were pH, clay content and spectral data indicative of soil organic matter (SOM) quality measured by FT-IR on the whole soil. The bands considered in the spectroscopic analyses were those corresponding to the aliphatic components, 2947–2858 cm^{-1} (band A) and the hydrophilic components, 1647–1633 cm^{-1} (band B). A significant relationship was found ($R^2 = 0.66$) between chlorpyrifos sorption (K_{OC}) and the variables pH and A/B height band ratio. The correlation between the values predicted by the derived model and the experimental data was significant ($r = 0.89$ $p < 0.05$). Thus, this methodology could be used to estimate chlorpyrifos sorption coefficient through the use of a simple, rapid, and environmentally-friendly measurement. K_{OC} analysis 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.

Keywords: Organic matter; Sorption; Pesticides; FT-IR spectroscopy

1 Introduction

Degradation and sorption are key processes affecting the fate and transport of organic chemicals in the environment. Degradation is a fundamental attenuation process for pesticides in soil. This process is governed by both abiotic and biotic factors that often work in tandem, and is affected by a variety of interactions among microorganisms, various soil constituents, and the specific chemical involved. Similarly, sorption is significant to control compounds advective-dispersive transport, transformation and bioaccumulation processes (Boivin et al., 2005). For non-ionic pesticides one of the key factors that determines the extent of such sorption is the organic carbon content of the soil (Wauchope et al., 2002; Weber et al., 2004).

It is thus typically assumed that the parameters that best quantify this process are the sorption coefficient (K_D) and the organic carbon normalized sorption coefficient (K_{OC}). A considerable variability in the K_{OC} values of hydrophobic contaminants in soils has been reported (Ahangar et al., 2008; D'Acqui et al., 2010; Ehlers et al., 2010; Mosquera et al., 2010). The chemical composition of soil organic matter (SOM) is known to have a substantial influence on the sorption of pesticides and other organic pollutants. Several authors analyzed this topic; Ahmad et al. (2006) reported the significance of the relationships between the K_{OC} of carbaryl and phosalone and the molecular nature of organic matter in the studied soils. Among the estimated molecular components, lignine and charcoal contents correlated best with the sorption of carbaryl and phosalone. Aliphatic, carbohydrates and protein contents were found to be negatively correlated with the K_{OC} of both pesticides. Furthermore, Farenhorst et al. (2010) observed variations in the 2,4-dichloro phenoxyacetic acid sorption with variations in the characteristics of SOM at field-scale. These authors suggest that such variations in the herbicide K_{OC} values are induced by changes in SOM aromaticity, determined by solid state ^{13}C NMR spectroscopy.

Chlorpyrifos (CPF), the insecticide used in this study, has great stability and is effective against a wide range of pests, making it one of the most commonly used insecticides in the world (Gebremariam et al., 2012). The continuous and excessive use of CPF has already led to widespread environmental contamination in many countries. This insecticide has been detected in marine sediments, streams, sumps, sloughs, rivers, urban storm drains, freshwater lakes, groundwater, fog, rain, and air (Gilliom et al., 2006; Loewy et al., 2011; Wightwick and Allinson, 2007; Zhang et al., 2012). The fate and transport of CPF in the subsurface is affected by a complex, time-dependent interplay between sorption and mineralization processes. Gebremariam et al. (2012) reported, from several other authors, that a key process that results in CPF degradation involves enzymatic or clay-/metal-catalyzed hydrolysis leading to cleavage of the phosphorothioate ester bond to form the 3,5,6-trichloro-2-pyridinol metabolite (TCP). Also a rapid increase in the rate of hydrolysis was observed with increasing pH, increasing temperature and in the presence of catalytically dissolved Cu(II). Similarly, CPF undergoes photolytic degradation in sunlight. CPF has been reported to be resistant to enhanced degradation which was attributed to the antimicrobial activity of TCP (Racke et al., 1990). Later in the literature, a variety of microorganisms capable of degrading CPF has been reported, some of them showing to be effective to degrade both, chlorpyrifos and TCP (Anwar et al., 2009; Lakshmi et al., 2008; Yang et al., 2006). Recently, Cycon et al. (2013) reported that the strain *Serratia marcescens* was capable of using chlorpyrifos (CPF), fenitrothion (FT) or parathion (PT) as growth substrates in mineral salt medium. The growth curves and chemical data showed that *S. marcescens* has a higher potential to remove PT than to remove CPF and FT. This might result from the different chemical structure and/or toxicity to bacterial strain of the tested organophosphate pesticides as well as to the appearance of TCP.

The CPF sorption onto soils has also been described by several authors (Rogers and Stringfellow, 2009; Yu et al., 2006; Zhang et al., 2012). Yu et al. (2006) studied the adsorption/desorption behaviour of chlorpyrifos, butachlor and myclobutanil on five types of soil with various physical and chemical properties using batch equilibrium techniques and they concluded that the process was mainly controlled by SOM content and the octanol/water partitioning coefficient. More recently, the adsorption and desorption of CPF was discussed in a comprehensive review (Gebremariam et al., 2012), showing that CPF has a large potential to adsorb to soil. As CPF is a pesticide with hydrophobic characteristics, its sorption increases as SOM content increases. However, the sorption coefficient cannot be entirely explained only by the fraction of organic carbon present in the soil, since OM quality also plays an important role.

The nature of organic matter (OM) varies between soils from different regions because of its origin, age, environmental conditions and possible cultural practices, among other factors (Ahangar et al., 2008; Ahmad et al., 2001; Bernier et al., 2013; Capriel et al., 1995; Demyan et al., 2012). The use of spectroscopic techniques, such as 13C NMR, IR, UV–Vis and fluorescence, has led to considerable advancements in the understanding of SOM structure (Bonfleur et al., 2016; Savini et al., 2017). IR spectroscopy is a method used to analyze bulk soil. It is quick, environmentally friendly and non-destructive. Infrared (IR) spectroscopy characterizes the components that constitute SOM as it provides information about the associated functional groups (Parikh et al., 2014). Margenot et al. (2015) analyzed soils from 13 organically managed tomato fields by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and they found significant differences in relative band intensities among them; in particular, a relative increase in absorbance of bands representing aliphatic C

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H was positively associated with soil organic carbon. Ellerbrock et al. (2015) characterized the amount and composition of SOM and OM fractions along a hillslope by transmission Fourier transform infrared (FTIR) spectroscopy, and identified those OM fractions that strongly reflect soil erosion effects. Unlike other spectroscopic techniques, such as ^{13}C NMR, UV–Vis and fluorescence, IR spectroscopy does not require a pre-extraction or treatment stage involving possible conformational changes in OM structure. Moreover, the analysis of the isolated soil organic fraction would not take into account the interactions between OM and other inorganic soil components (Ahmad et al., 2006; Ellerbrock and Gerke, 2004; Farenhorst et al., 2010).

Up to the moment, the adsorption of non-ionic pesticides has been extensively investigated in relation to soil fractions obtained by a sequential extraction with sodium hydroxide followed by sodium pyrophosphate and the humic fraction characterized by UV-V spectroscopy. Solid state 13C NMR on HF treated soil was also used for determining SOM structural characteristics, which can be then correlated with the K_{OC} values (Ahmad et al., 2001; Farenhorst et al., 2010).

Although all the investigations mentioned above provide important insights into the effect of SOM in hydrophobic pesticides sorption, the study of the relationship between sorption of CPF and the chemical characteristics of SOM should be deepened. This investigation would allow for the understanding of the processes that regulate the fate and behaviour of this pesticide in soil and its implication on the risk assessment. The specific objectives of this study were: a) to characterize SOM using FT-IR spectroscopy, identifying the main bands associated to the major SOM components, in soils with widely different physical and chemical properties; b) to determine the CPF sorption coefficients (K_D) in soils using batch equilibrium techniques, in order to identify the main soil factors affecting the CPF sorption by means of a correlation analysis; c) to evaluate the possible relationship between the sorption coefficients normalized to the organic carbon content (K_{OC}) and the spectral data indicative of SOM quality.

2 Materials and methods

2.1 Soil samples

The soils used in this study came from the North of the Argentine Patagonia. Twelve (12) soil samples were selected in locations from 39° to 41° S and 71°–64° W. Nine (9) samples were taken from the Neuquén River Alluvial Plain (AP) and three (3) of them were collected from the mountainside of the Andine Region (AR).

Soil samples from the AP region belong to the order Aridisols. This region is characterized by its intensive fruit production, especially of pears and apples; the application of pesticides and the flood irrigation being part of the cultivation practices associated with this activity. Moreover, one of the remarkable hydrological characteristics of these sites is that sub-surface water is highly shallow; the water table depth ranges from 1.0 to 2.5 m. Andisols soils (from the AR region) are volcanic in origin and correspond to a predominantly woodland region, where there are no anthropogenic activities. However, similar soils in other regions of the world, such as Chile, Costa Rica, Colombia, Ecuador and Mexico, are intended for agricultural production activities with the possible introduction of organic contaminants; particularly this type of soil is widespread and abundant in Central-Southern Chile, accounting for approximately 69% of the arable land (Cáceres et al., 2010).

The physicochemical characteristics of the soils were obtained using standard characterization methods. Soil sample preparation included air-drying and sieving to obtain the fraction under 2 mm pH value was determined in a solution with a soil:water ratio of 1:2.5. Total carbon (TOC) was determined using the Leco CR-12 dry combustion infrared carbon analyzer. In order to convert TOC to OM, the Van Bemmelen coefficient of 1.724 was applied; according to this factor 58% of OM is organic carbon (Tabatabai, 1996). Textural analysis was performed using the Robinson pipette method (Kilmer and Alexander, 1949).

2.2 Chemicals

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) is an insecticide commonly known as Dursban® or Lorsban®, trademarks of Dow AgroScience, LLC (IN, USA). The compound is moderately hydrophobic; when compared to most other organophosphorus pesticides, CPF exhibits lower water solubility, 1.05 mgL^{-1} at 20 °C (IUPAC PPDB - Pesticides Properties DataBase, 2015) and a high log K_{OW} (4.7) Analytical grade chlorpyrifos (Chem Service, chemical purity >99%) was used in the sorption experiments.

2.3 Sample preparation for FT-IR. Obtaining and processing the spectra

To obtain the IR absorption spectra of the soil samples, pellets were made by mixing 1 mg of soil with 200 mg of KBr (Buck Scientific, spectroscopic grade); weights were performed with a high-resolution Mettler Toledo AB-S/FACT analytical balance with a readability of 0.01 mg. The mixture was then ground with an agate mortar. Both the KBr and the soil sample were dried for 24 h at 105 °C prior to pellet preparation, avoiding the interference produced by water molecules absorption. Moreover any alteration in organic matter is negligible due to this drying effect (Kiersch et al., 2012). A hydraulic press was used to make the pellets by applying 14 tons of weight. The pellets were prepared in duplicate to ensure reproducibility. FT-IR spectra were recorded with a Lumex FT08 spectrometer equipped with a high-resolution deuterated triglycine sulfate (DTGS) detector. Analyses were carried out in the mid-infrared spectral region, from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 2 cm^{-1}. The number of scans for each sample was 256 and they were averaged to obtain the spectrum. The background spectrum of each sample was KBr. The correction for atmospheric conditions (absorption of IR radiation due to carbon dioxide and water) was performed using StartspectralLUM software. The ORIGIN 8.0 software was used for processing spectral data to correct the baseline (connecting line method), to calculate the maximum absorbance, to reduce noise and to integrate bands.

2.4 Adsorption studies

The sorption coefficients (K_D) of bulk soils were determined by recording the isotherms for CPF concentrations ranging from 0.120 to 0.800 mg L^{-1} (C_i), using the batch equilibrium method (Rogers and Stringfellow, 2009). Since the solubility of CPF was low in aqueous solutions, standard solution stock (1000 mg L^{-1}) was prepared in methanol and the working pesticide aqueous solutions to the required concentration were freshly prepared by dilution in 0.01M CaCl$_2$ p.a. as a background electrolyte (methanol content <2%).

In order to prevent sorption of CPF to the tubes wall, all the experiments were carried out in glass flasks fitted with Teflon caps. A series of glass flasks was prepared from 0.400 ± 0.001 g of soil and CPF solution, maintaining a constant solution volume:soil mass ratio of 20:1. Each sorption experiment was performed in triplicate. The flasks were stirred in dark with a Bioamerican Science horizontal stirrer at 134 rpm at constant temperature (22±2 °C). A contact time of 16 h was chosen from previous kinetic experiments as a period sufficient to achieve sorption equilibrium (data not shown). Blanks without soil were treated in the same way, as degradation controls. Blanks containing soil, but without CPF solution, were treated in the same way, as laboratory method blanks. Degradation controls, blanks and replicate samples were analyzed with each round of samples for quality control.

After stirring, samples were centrifuged in a Sartorius 2-16P centrifuge at 3000 rpm for 20 min. The supernatant was separated and aliquots of 5 mL were transferred to 10 mL glass centrifuge tubes and extracted with 2.0 mL of hexane on a vortex shaker for 2 min. Preliminary tests on extraction procedures were performed and minimal improvements in extraction efficiencies were found through multiple extractions with hexane. The obtained recoveries were constant and better than 90%. No corrections for recovery were done. Internal standard (methyl chlorpyrifos) was used for the chromatographic quantification in order to minimize volume differences. The equilibrium concentration (C_{eq}) was determined from the hexane phase by gas chromatography. Chromatographic analysis of the samples was performed using an Agilent 6890N gas chromatograph equipped with an HP-5MS column

(30 m × 0.25 mm x 0.25 µm) and an µECD detector. The concentration of CPF sorbed to the soil (C_s) was calculated as the difference between the initial concentration (C_i) and the equilibrium concentration (C_{eq}). Thus, it was assumed that processes such as degradation, volatilization or photolysis were not significant during the 16 h period (Dolaptsoglou et al., 2007).

2.5 Statistical analysis

Descriptive statistical analyses were carried out using the Statistica software package version 7.0 (StatSoft France, Maison-Alfort, France). This included the construction of linear correlation models and a Principal Component Analysis (PCA). Independence, normality, linearity, and homoscedasticity were tested (results not shown) before Regression and PCA analyses were performed.

3 Results and discussion

Table 1 shows the physicochemical characteristics of the soils investigated in this study. Aridisols (AP 1-9) have mainly clay-loam or silt-loam textures, while andisols (AR 1-3) present sandy-loam texture, with a clay percentage under 12% in all cases. Andisols tend to be slightly acidic, while aridisols are neutral to slightly basic. Andisol soils, of volcanic origin, have a highly pH-dependent charge and are generally rich in minerals such as kaolinite, gibbsite, hematite and allophane (Mon et al., 2009). In terms of %OC, Andisols (AR) tend to have greater values compared to Aridisols (AP). Given its hydrophobic characteristics, the sorption of CPF is recognized as closely linked to SOM content. However, it is important to consider other soil components that, under certain circumstances, could acquire relevance in the sorption process, probably because of organomineral interactions that play significant roles on sorption on the whole soil (Bonfleur et al., 2016).

Table 1 Physicochemical characteristics of the soil samples.

alt-text: Table 1

Soil samples	Texture	OC(%)	pH	Clay(%)
AP1	Loam	2.52	8.2	21.9
AP2	Loam	1.79	7.4	21.9
AP3	Clay loam	2.03	7.5	36.4
AP4	Silt loam	4.72	5.6	18.0
AP5	Silt loam	3.28	5.9	20.0
AP6	Loam-Silt loam	1.50	8.3	23.8
AP7	Loam-Silt loam	1.48	8.2	10.5
AP8	Sandy loam	1.25	8.1	14.5
AP9	Silt loam	1.76	5.5	19.0
AR1	Sandy loam	4.91	6.1	6.3
AR2	Sandy loam	2.21	6.2	11.8
AR3	Sandy loam	6.82	5.3	3.8

Soil analysis by FT-IR was performed to characterize soils and study the chemistry of the organic matter. Fig. 1a and b show the FT-IR spectra corresponding to AP and AR soils, respectively.
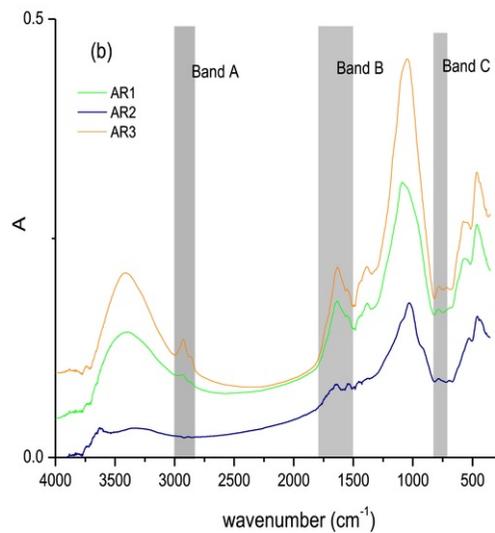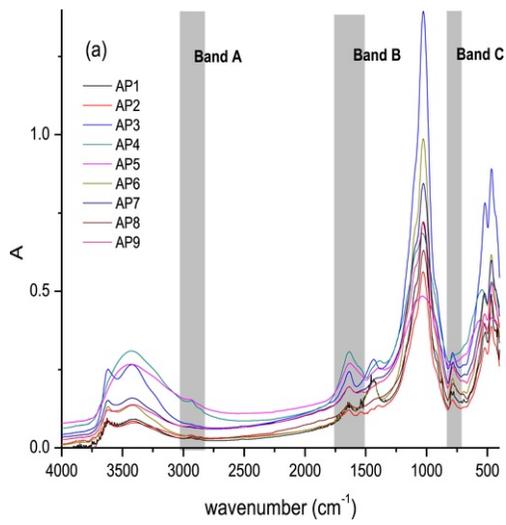
Fig. 1 FT-IR soil spectra a) soils from the alluvial plain (AP); b) soils from the Andean Region (AR).Band A Band B and Band C intervals associated with absorbance of aliphatic CH groups, hydrophilic components and quartz, respectively.

alt-text: Fig. 1

The absorption bands observed correspond to the main organic and inorganic soil components and are consistent with those reported previously in the literature (Bernier et al., 2013; Ellerbrock and Gerke, 2004).

Table 2 shows functional group allocations for the absorption bands observed in the spectra of this study and those reported in the literature. The position of each peak remained within the expected range for all the samples analyzed.

Table 2 Band positions in the FT-IR spectra observed in the current study and reported in the literature, and proposed assignments.

alt-text: Table 2

Peak position (cm⁻¹)		Proposed assignment[a]
Current study	Literature	
3629–3618	3698–3622	Stretching of O—H bond in kaolinite
3430–3401	3600–3400	Stretching of O—H bond in water, carboxyl and hydroxyl groups
2947–2858 (Band A)	3020–2800	Symmetric and asymmetric C—H stretching of CH_3 and CH_2 groups[b]
2514–2507	2550–2515	Vibrations of CO_3^{2-} in calcite and minerals of the calcite and dolomite groups.
	2000, 1880, 1790	Overtones and combination bands for quartz and silicates
1647–1633 (Band B)	1650–1515	NH_2 and NH bending in primary and secondary amides (amide II band)
	1650–1640	C=O stretching vibrations in amides (amide I band)
	1650–1580	NH bending vibration of primary amines
	1650–1550	NH bending vibration of primary amines
	1630	Bending of water molecules in hydration layers of soil phyllosilicate. Hydrogen-bonded C=O of carbonyl or quinone.
	1625–1600	Stretching of the C=C group conjugated with another C=C group, aromatic ring, C=O and/or COO- in unsaturated, carboxylic acids and amides[b]
1453–1416 1396–1383	1450–1430	Vibrations of CO_3^{2-} in calcite and minerals of the calcite and dolomite groups; C\H bending vibrations of CH_3 and CH_2 groups
	1420–1330	Symmetric stretching vibrations of COO^-
	1384–1350	Vibrations associated with nitrate
1046–1025	1035	Stretching of Si—O in kaolinite
	1300–1100	In-plane bending of the aromatic ring C—H bonds; the C—O stretching vibration in alcohols, ethers, phenols, carboxylic acids and esters; stretching of C—O in polysaccharides; C—N stretching vibrations in aliphatic and aromatic amines
	1100–1000	Vibrations associated with phosphate groups PO_4^{3-}
	915	Fundamental vibrations in illite
	887–866	Vibrations of CO_3^{2-} in calcite and minerals of the calcite and dolomite groups
798–779 (Band C) 698–686	800–795, 780–775	Symmetric Si—O stretching in quartz[c]
	800–666	Out-of-plane NH wagging in amides
	900–675	Out-of-plane bending of the aromatic ring C—H bonds

| 716–713 | 715–712 | Fundamental vibrations of CO_3^{2-} in calcite |

[a] Silverstein et al. (2014).

[b] Ellerbrock and Gerke (2004); Simkovic et al. (2008).

[c] Bosch Reig et al. (2002); Ravisankar et al. (2011).

The main bands identified in the spectra correspond to the —

OH groups of clay mineral structure (3629–3618 cm⁻¹), hydration water and the oxygenated groups of organic matter (3430–3401 cm⁻¹); bands at 2947–2858 cm⁻¹ correspond to the vibrations of symmetric and asymmetric stretches of aliphatic C —

H bonds (—

CH_2 and —

CH_3) that contribute to the nonpolar component of the SOM; absorption bands at 1647–1633 cm⁻¹ are assigned to relatively polar functional groups containing nitrogen and/or oxygen atoms; and bands at 1046–1025 cm⁻¹ and 798–779 cm⁻¹ correspond to the stretching vibrations of the Si —

O mineral group.

Band intensity indicates the quantity of functional groups responsible for IR absorption for each frequency. The analysis of these intensities reflects the physicochemical composition of these soils. Among the AP soils, it was observed that AP3 presented the greatest intensity for bands at 3629–3618 cm⁻¹ and the band at 1046–1025 cm⁻¹, which would be expected considering its high clay content. Among the AR soils, AR3 had a high OC content, presenting bands with the greatest intensity at 2947–2858 cm⁻¹ compared to the soil samples AR1 and AR2.

In order to analyze the chemical nature of SOM, three absorption bands were selected and the height peak was determined at their maximum absorbance. Band "A" represents the aliphatic fraction of SOM (2947–2858 cm⁻¹); band "B" represents the hydrophilic component of SOM (1647–1633 cm ⁻¹); and band "C" is associated to the Si —

O bond in quartz (798–779 cm⁻¹).

Table 3 presents the quantification results for integration by peak height corresponding to bands A, B and C. Unlike the integration by calculating areas, the integration by height is considered to minimize the interference due to band overlap.

Table 3 Integration of absorption peaks corresponding to the aliphatic and hydrophilic fractions of the SOM. Relationship between the heights of peaks A[a] and B[b] compared to peak C.[c]

alt-text: Table 3

Site	A/C	B/C	A/B
AP1	0.0997	0.8662	0.1151
AP2	1.1052	0.6767	1.6333
AP3	0.0299	1.2560	0.0238
AP4	1.6795	17.2604	0.0973
AP5	1.6898	24.4036	0.0692
AP6	0.0113	0.5151	0.0219
AP7	0.0225	0.5414	0.0415
AP8	0.2668	2.2712	0.1175
AP9	0.0524	0.7645	0.0685

AR1	1.1041	9.8664	0.1119
AR2	0.1172	2.5368	0.0462
AR3	2.8056	5.7993	0.4838

[a] A = peak height at 2930 cm^{-1} of Band A (2947–2858 cm^{-1}).

[b] B = peak height at 1640 cm^{-1} of Band B (1647–1633 cm^{-1}).

[c] C = peak height at 780 cm^{-1} of Band C (798–779 cm^{-1}).

The peak heights of band "A" and band "B" were normalized using the height of a peak of band "C", considered as an internal reference (798-779 cm^{-1}) given that quartz is present in all the soils, its absorption band is distinctive, and other minerals do not affect its signal, among other reasons (Bernier et al., 2013). The normalization relative to the internal reference facilitates a quantitative comparison and minimizes signal variability associated with environmental conditions during sample preparation. In this study, the ratio of the peak heights of the A/C and B/C bands were used to evaluate the contribution of aliphatic and hydrophilic components of SOM, respectively. The A/B ratio was used to determine an index for the relative abundance of hydrophobic and hydrophilic functional groups (Bernier et al., 2013; Capriel et al., 1995; Ellerbrock and Gerke, 2004; Nadav et al., 2013).

The lowest A/B ratios among studied soils were found in the AP3 and AP6 soils, indicating more contribution of hydrophilic substances, while the highest A/B ratio was observed in AP2 soil, revealing the predominance of more hydrophobic substances.

The presence of hydrophilic and hydrophobic functional groups on SOM defines the spatial arrangement of the structure of the carbon chains. At the same time, these functional groups are responsible for the chemical reactivity and adsorptive properties of the organic matter, as they determine the capacity to establish hydrophobic interactions, hydrogen bound interactions or cation-exchange with the adsorbate and with other soil components, such as clay minerals (Ahangar et al., 2008; Smernik and Kookana, 2015).

The adsorptive properties of the soils studied were analyzed determining the CPF sorption coefficients. Table 4 presents the values obtained for the K_D coefficients and %OM of the soils used in the adsorption assays. The K_D values ranged from 130 to 1100 L kg^{-1} for soils with %OM between 2.13 and 11.6. The K_D coefficients derived experimentally were within the range of values reported in the literature, which ranged from 45 to 1315 L kg^{-1} (Garcia et al., 1992; Huang and Lee, 2001; Wu and Laird, 2004).

Table 4 Chlorpyrifos sorption coefficients (K_D and K_{OC}) and soil organic matter (%OM).

alt-text: Table 4

Soils	% OM	K_D (L kg^{-1})[a]	K_{OC} (L kg^{-1})
AP1	4.43	274	10661
AP2	3.07	330	18539
AP3	3.50	182	8966
AP4	8.03	921	19764
AP5	5.57	346	10712
AP6	2.55	184	12432
AP7	2.51	147	10068
AP8	2.13	138	11220
AP9	2.99	239	13815
AR1	8.34	444	9192

| AR2 | 3.75 | 435 | 20046 |
| AR3 | 11.6 | 1103 | 16414 |

The K_D coefficients of the studied soils correlated significantly with %OM (r = 0.90). For soils with higher organic matter content, the affinity of CPF by solid phase increases, which emphasizes that this is the determining factor of the soil retention capacity for hydrophobic pesticides. Although the CPF sorption depends mainly on SOM content, it can be observed that some soils with similar OM percentages present dissimilar K_D values (Table 4). Comparable results were found by other authors for pesticides with low solubility and a wide variety of soils (Gebremariam et al., 2012). In order to explain this behaviour it is appropriate to use the K_D normalized by the content of soil organic carbon. K_{OC} values obtained experimentally varied between 9000 and 20000 L kg^{-1}, confirming that, regardless of the amount of OM, other factors such as the chemical composition of the SOM, the pH and clay content may impact on CPF sorption.

The principal components analysis (PCA) was performed for all the variables, and those with major contribution to the factors 1 and 2 were selected (Fig. 2). By analyzing the main components, it can be observed that the first factor explained 53.21% of the variance (controlled mainly by the ratio A/C, pH and K_{OC}) while the second factor explained 29.23% of the variance (controlled mainly by the ratio A/B and pH). Thus, the 82.44% of the total variability could be explained by the two selected principal component axes.
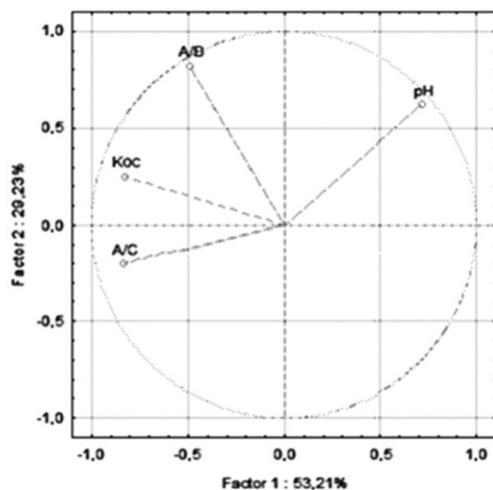
Fig. 2 Principal component analysis representation (projection on 1,2 plane) obtained for K_{OC}, A/B ratio, A/C ratio and pH from the 12 studied soils.

alt-text: Fig. 2

K_{OC} values obtained for CPF in the studied soils were analyzed by a multiple linear regression with the major eigenvalues contributors in each PCA factor. The derived model showed that both A/B ratio and pH contributed significantly (p < 0.05), leading to a linear predictive model: $K_{OC} = 22757 + 4364$ A/B $- 1564$ pH ($R^2 = 0.66$). The ratio of the peak heights A/B seems to influence favoring sorption and soil pH seems to have a significant opposite effect on sorption.

It can be observed that the parameter A/C does not participate in the equation, which might be explained considering its association with pH, as shown in Fig. 2. The results showed the affinity between a low polarity pesticide and the hydrophobic nature of the SOM, represented by the greater contribution of the band A with respect to the band B in the FT-IR spectrum of each soil. On the other hand, the pH determines the ionic state of the ionizable groups of the organic materials (carboxyl, hydroxyl, etc.) so that as the pH increases, the concentration of deprotonated groups in the humic substances increases and consequently decreases nonionic pesticide affinity with the adsorbent. The pH effect on CPF sorption is in agreement with previously reported studies (Hui et al., 2010). Chlorpyrifos sorption coefficients were calculated from the multiple linear regression equation and compared with the experimental data for the studied soils. The correlation between predicted and observed K_{OC} values was significant (r = 0.89, p < 0.05). The K_{OC} coefficients predicted by the obtained model in our study may be considered reliable, since they were established from a wide range of soil physicochemical properties. It is important to highlight that in the present study both the

sorption results and the spectroscopic data were obtained from intact soil, reproducing the natural conditions of interaction pesticide-soil components optimally. Under these experimental conditions, the possible effect of minerals was considered together with their association with OM, which might block the SOM active sites for contaminant retention.

4 Conclusions

Assessing the FT-IR spectra enabled the characterization of the soils studied. The chemistry of the OM represented by the contribution to the polar and aliphatic components of the SOM was specifically analyzed.

In this study the relationship between the K_D sorption coefficient of CPF, and physical and chemical soil properties was evaluated, finding a significant correlation with %OM (r = 0.90).

The relation between K_{OC} and soil chemical nature was also studied. Particularly, pH and chemical characteristics of OM play an important role in controlling the sorption behaviour (K_{OC}) of CPF insecticide ($R^2 = 0.66$). The results obtained in this study show that a higher adsorption occurs for soils with lower pH value and with greater contribution of the aliphatic components (band A) with respect to the hydrophilic components (band B), finding which was expected given the nonpolar nature of the pesticide studied.

The analysis of sorption coefficient (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.

Acknowledgments

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Highlights

- Polar and aliphatic components of soil organic matter were characterized by FT-IR.
- FT-IR spectroscopy allows analysing bulk soil keeping organic-inorganic interactions.
- Chlorpyrifos sorption behaviour is mainly affected by soil aliphatic components.
- Koc values obtained showed a significant relationship with soil pH and hydrophobicity.

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