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Research article

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

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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.

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 bio-accumulation 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.

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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–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