Geoderma 232–234 (2014) 309–316

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

A new adsorption model to quantify the net contribution of minerals to butachlor sorption in natural soils with various degrees of organo-mineral aggregation

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ARTICLE INFO

Article history:
Received 15 September 2013
Received in revised form 14 February 2014
Accepted 25 May 2014
Available online 7 June 2014

Keywords:
Butachlor
Sorption
SOM–mineral association
Aggregate size fraction
Quantified contribution

ABSTRACT

The effect of interactions between soil minerals and organic matter as a function of aggregate size on butachlor sorption was quantified in natural soils with various degrees of organo-mineral aggregation. The smallest size clay microaggregates sorbed most butachlor (58% to 71%) and the fine sand fraction sorbed the least (less than 4.3%). When normalized to organic carbon, butachlor sorption to the clay microaggregates was even smaller than to the silt and sand fractions under specific soil conditions. The sum of sorption to the different fractions was, on average, above 78% greater than sorption to the bulk soils, with the greatest differences in the soils with relatively higher ratios of clay to soil organic carbon (RCO). This suggests that minerals can physically protect favorable sorption sites within soil organic matter (SOM), and inhibit butachlor sorption by influencing SOM physical conformation. Comparisons of changes in butachlor sorption coefficients (both K_d and K_{oc}) in two different series of soils, with the same mineral components but gradients of total organic carbon (TOC) and RCO values also showed that minerals can directly contribute to soil butachlor sorption processes, which may be even more pronounced in soils with relative higher RCOs. A new adsorption model was proposed and verified to quantify the net contribution of minerals to butachlor sorption, based upon 38 different soils. This study has increased our ability to quantify the positive direct contribution of soil minerals and their negative indirect contribution through associated effects on SOM physical conformation during butachlor sorption in natural soils.

1. Introduction

The soil matrix is not simply a mixture of discrete soil organic matter (SOM) and minerals, but is a multi-component and structurally organized combination of aggregates formed from organo-mineral complexes (Amelung et al., 1998; Brady and Weil, 2008; Zhou et al., 2004). Therefore, better understanding of the associations between SOM and minerals is required in the study of sorption mechanisms since there is increasing evidence that measurement of SOM concentrations alone is insufficient to provide reliable indicators of the sorption behavior of organic pollutants (OPs) in soils. Many studies have shown that the association of minerals with SOM may block sorptive functional groups on SOM surfaces. Therefore, the extent of sorption of OPs could decrease when the configuration of SOM is changed when associated with minerals (Feng et al., 2006; Garbarini and Lion, 1986; Lambert et al., 1965; Pusino et al., 1992, 1994; Salloum et al., 2001; Wang and Xing, 2005a,b), indicating a negative contribution of minerals to OP sorption by soils.

However, other studies have also emphasized that the different soil constituents may complement each another, leading to enhanced sorption by the resultant aggregates (Celis et al., 1999; Huang et al., 1984; Khan, 1980). Recent investigations showed a dual function of minerals vs. SOM for OP sorption in soils, such as butachlor (Liu et al., 2010). Besides the negative contribution through blocking some sorption sites on SOM, minerals may also positively contribute to OP sorption in specific soils (e.g. those of very low SOM contents) where mineral–SOM interactions are small, so that their surface could be highly exposed, increasing the extent of OP sorption (He et al., 2011). It was also suggested that 1) the relative importance of SOM and minerals in butachlor sorption depends on the ratio of clay to soil organic carbon (RCO), and 2) the positive contribution of minerals to overall sorption may become apparent when RCO values increase to a critical value (Liu et al., 2008). These studies collectively highlight the importance of minerals for OP sorption in determining the accessibility of sorption sites within the soil matrix. But how the natural association between minerals and SOM affects the physicochemical nature of soil organo-mineral aggregates, and therefore influences the sorption of OPs in soils, remains uncertain. To answer this question, more direct information is required on how

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http://dx.doi.org/10.1016/j.geoderma.2014.05.021
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adsorbed OP in bulk soils distributes among their different size aggregates, which has different degrees of organo-mineral association.

Selecting butachlor (a chloracetamide) as a model OP, we examined its sorption by bulk soils and respective organo-mineral aggregates with contrasting degrees of association of minerals and SOM. The soil organo-mineral aggregates were fractionated by ultrasonic dispersion in water without chemical pretreatment to minimize any alteration to their composition or structure. Soils were also treated with hydrogen peroxide (H_2O_2) to remove SOM to various degrees. We hypothesized that variation of the physicochemical nature of organo-mineral association in different soil aggregates would result in corresponding differences in butachlor sorption capacity of soils as a function of aggregate size. We also hypothesized that minerals could provide sites for butachlor adsorption, and when SOM was removed from soils, the original, and now largely SOM free, mineral surface would be exposed and so would contribute directly and positively to butachlor sorption by soils. Our objective was to develop an effective method to quantify the dual roles of minerals vs. SOM in the sorption of OPs, such as butachlor, in natural soils with various degrees of organo-mineral aggregation. To do this, a new adsorption model was proposed and verified to quantify the net contribution of minerals to butachlor sorption, based upon 38 different soils.

2. Materials and methods

2.1. Reagents and soils

Butachlor, N-butoxymethyl-2-chloro-2′,6′-diethylacetanilide (>97.9% purity), was obtained from the Shenyang Research Institute of Chemical Industry (Shenyang, China). The soils used, with a wide range of RCO values (from 11.2 to 143.2), were seven of the referenced soils used previously (He et al., 2011; Liu et al., 2008). They were surface horizons (0–20 cm) of uncultivated soils collected in the Guizhou, Jiangsu, Henan, Zhejiang, Heilongjiang and Guangdong provinces of China. The physicochemical properties of the bulk soils and their fractions are listed in Table 1. The chemical properties of butachlor, soil classification, and the analytical methods for physicochemical properties of the bulk soils and their fractions are described in Supplementary information (SI) and Table S1.

2.2. Aggregate size fractionation of soils

Aggregate size fractionation of the bulk soils was conducted for soils 1–5 based on mechanical dispersion (Liu et al., 2010). The detailed fractionation procedures are described in SI. After fractionation, the fine sand (20–50 μm), silt (2–20 μm), and clay (<2 μm) fractions were freeze-dried and then weighed.

2.3. Treatment of bulk soil samples with H_2O_2

To verify that the adsorption model proposed for calculating the net contribution of soil minerals to butachlor sorption was quantitative, soils 6 and 7 were treated with different volumes of 30% H_2O_2 to obtain a series of soil samples of the same mineral compositions but with different total organic carbon (TOC) contents (He et al., 2006). The detailed steps are described in SI.

2.4. Sorption experiments

Sorption was measured using a batch equilibrium technique (He et al., 2011). In brief, approximately 0.30–0.65 g of freeze-dried bulk soil and their soil fractions were accurately and separately weighed into 25-mL centrifuge glass bottles with screw caps and equilibrated with 8 mL of 0.02 mol L^{-1} KCl solution (containing 0.02% NaN_3 to inhibit microbial activity) containing different concentrations of butachlor. Each isotherm consisted of 10 increasing concentrations of butachlor along a $\log_{10}$ scale, ranging from 0.1 to 16 mg L^{-1}, each with two replicates. One series of vials without butachlor served as a control. All sorption data were fitted to the logarithmic form of the Freundlich equation. The sorption partition coefficients (K_d) and the organic carbon (OC) content normalized partition coefficients (K_{oc}) were also determined. The mathematical manipulation of the sorption data is described in SI.

2.5. Building the adsorption model to quantify the contribution of minerals to butachlor sorption

2.5.1. Calculation of the K_d of minerals in soils

The K_d was assumed to be the sum of the mineral and SOM contributions as follows:

$$K_d = K_{d-min} + K_{d-oc} \quad (1)$$

Table 1

Selected properties of bulk soils and their fractions, and the distribution of each fraction in the bulk soils.[a]

Soil samples		TOC	SSA	AO-Fe	DC-Fe	W_f	pH	CEC	RCO
		g kg^{-1}	m^2 g^{-1}	g kg^{-1}	g kg^{-1}	%(W/W)	H_2O	cmol (+) kg^{-1}	
Soil 1	Bulk soil	25.0	13.6	6.0	24.6	100	4.09	10.5	14.4
	Clay	49.9	41.3	13.0	105.1	36.1			
	Silt	14.3	2.0	2.2	9.9	62.3			
	Fine sand	4.7	1.3	–	–	1.1			
Soil 2	Bulk soil	14.7	19.1	4.7	19.3	100	5.12	18.2	27.6
	Clay	26.3	33.1	8.9	57.3	40.6			
	Silt	4.8	1.1	0.5	5.1	58.2			
	Fine sand	4.0	0.5	–	–	5.6			
Soil 3	Bulk soil	4.4	6.8	1.8	9.8	100	8.36	9.9	57.9
	Clay	13.5	26.3	4.3	32.5	25.4			
	Silt	2.7	1.2	0.2	6.1	69.3			
	Fine sand	1.1	0.8	–	–	6.0			
Soil 4	Bulk soil	1.8	13.3	0.7	7.2	100	4.28	6.6	143.2
	Clay	6.8	31.4	0.8	31.9	25.2			
	Silt	2.3	2.7	0.1	10.1	61.2			
	Fine sand	0.4	1.4	–	–	21.6			
Soil 5	Bulk soil	4.5	38.0	2.9	25.0	100	4.59	9.7	124.1
	Clay	6.7	56.3	3.7	88.3	55.3			
	Silt	2.1	1.5	0.2	4.1	45.3			
	Fine sand	1.9	0.9	–	–	0.7			

[a] TOC, total organic carbon; SSA, specific surface area; AO-Fe, ammonium-oxalate extractable amorphous Fe_2O_3; DC-Fe, dithionite-citrate extractable free Fe_2O_3; CEC, cation exchange capacity; RCO, the ratio of clay to total organic carbon; W_f, the weight percentage of each soil fraction in bulk soil.