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Potential contributions of clay minerals and organic matter to pentachlorophenol retention in soils

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Abstract

Sorption of pentachlorophenol (PCP) by pure minerals and humic acids were measured to obtain additional perspective on the potential contributions of both clay minerals and soil organic matter (SOM) to contaminants retention in soils. Four types of common soil minerals and two kinds of humic acids (HAs) were tested. The sorption affinity for PCP conformed to an order of HAs $\gg$ K-montmorillonite $\gg$ Ca-montmorillonite $\gg$ goethite $\gg$ kaolinite. Such a difference in sorption capacity could be attributed to the crucial control of HAs. Clay minerals also had their contribution, especially K-montmorillonite, which played an important, if not dominant, role in the controlling process of PCP sorption. By removing 80% (on average) of the organic carbon from the soils with H_2O_2, the sorption decreased by an average of 50%. The sorption reversibility had been greatly favored as well. Considering the uncharged mineral fractions in soil before and after H_2O_2-treated, the main variation in sorption behavior of the soil might thus be related to the removed organic carbon and the reduced pH. This testified rightly the interactive effect of SOM and clay minerals on PCP sorption as a function of pH.

Keywords: Pentachlorophenol (PCP); Sorption; Minerals; Humic acids (HAs)

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1. Introduction

Pentachlorophenol (PCP, C_6Cl_5OH) is a kind of ionizable hydrophobic organic contaminants (HOCs). As a pesticide, herbicide, and antiseptic, it was once used worldwide, and has been designated as a priority pollutant and a probable human carcinogen (US Environmental Protection Agency, 1980). In the 1970s PCP was popularly used in China in fighting against snail fever and as a herbicide. Its biodegradation is slow; hence it is not surprising that it still caused environmental problems at many locations (Sanjoy et al., 1996). The highest concentrations of PCP are usually found in soil and aquatic sediments (Maatela et al., 1990; Abrahamsson and Klick, 1991; Sung-Kil and Angela, 2003). PCP can remain for a very long time. Understanding the behavior of PCP requires an assessment of the processes influencing its fate, transport, bioactivity and persistence in soils. The investigation on sorption and desorption behaviors, and the controlling key factors involved may be a possibly helpful and effective way.

It has been well established that the retention of HOCs in soil–water systems is strongly correlated with soil organic matter (SOM) content and that soil mineral fractions play a comparatively minor role except in the absence of water. SOM is viewed as providing a partition phase for the uptake of HOCs (Kile et al., 1995; Weber and Huang, 1996; Xing and Pignatello, 1997; Xia and Ball, 1999). And the SOM-partition model appears valid for organic contaminants containing nonpolar or slightly polar functional groups (e.g., –Cl). It is, however, frequently extended to organic contaminants in general, including those containing polar functional groups such as many pesticides. This is illustrated by the common use of soil organic matter (or carbon)-normalized sorption coefficients (K_{OM}, K_{OC}) to predict pesticide mobility in soils. It is now clear that for important categories of pesticides (e.g., triazines,

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carbamates, nitrophenols) and organic contaminants (e.g., nitroaromatic compounds), sorption by clays may equal to or exceed that by SOM (Haderlein et al., 1996; Sawhney and Singh, 1997; Boyd et al., 2001; Sheng et al., 2002; Li et al., 2003). For example, nitro-substituted aromatics, including explosives and some dinitrophenol pesticides, are also significantly adsorbed by clays (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1998). K^+-saturated smectite (i.e., SWy-2) was a more effective sorbent for pesticides such as 4,6-dinitro-*o*-cresol and 2,6-dichlobenil compared to sorption by an organic soil (Sheng et al., 2001). Using sorption data from soils of variable clay and SOM contents, Karickhoff (1984) attempted to evaluate conditions under which mineral-phase sorption of organic contaminants in whole soils was important. For the *N*-heterocyclic simazine and biquinoline, mineral contribution to overall sorption became apparent (i.e., greater than that predicted from K_{OM} values) at clay/organic matter ratios of >30. Sorption of pyrene, however, was not affected by clay content. It was then concluded that the contribution of mineral-phase sorption was a direct function of the polarity of the compound. The studies cited above, along with experimental evidence from earlier studies (Bailey and White, 1970), clearly indicate the ability of pure minerals to effectively bind organic molecules. However, such exact ability of clay mineralogy compared to SOM varied with contaminant types, which was less direct and has not been forthcoming for ionizable HOCs such as PCP.

The objectives of this study were (1) to provide sorption data for PCP by both pure minerals and humic acids over a wide range of PCP concentrations, (2) to determine the contribution to PCP sorption of common soil minerals (kaolinite, montmorillonite, goethite) and (3) to determine the contribution of SOM to PCP sorption, and thereby improve our understanding of soil parameters that control sorption of ionizable HOCs.

2. Materials and methods

2.1. Materials

Pure mineral phases. Four kinds of pure minerals were used to determine their contributions to sorption from common soil minerals. Kaolinite represented nonexpendable two-layer clay minerals. Homoionic K- and Ca-montmorillonite represented strongly expandable three-layer clay minerals with different valent exchangeable cations. Goethite represented common iron oxides. The selected minerals belonged to silicate and oxide minerals and therefore could represent different surface functional groups.

The synthetic goethite was prepared according to the methods of Boily et al. (2001). It was well crystalloid and had a high purity according to the X-ray analysis (data not shown). In order to obtain homoionic montmorillonite, the <2 μm clay-sized fractions were obtained by wet sedimentation and subsequently subject to K^+ and Ca^{2+} saturation, by dispersing 10 g clay samples in 1 l of 0.5 M KCl or 0.5 M $CaCl_2$ solution. The clay suspensions were shaken for 24 h, and then fresh chloride solutions were used to displace the original solutions after centrifugation. This process was repeated three times to ensure complete K- or Ca-saturation. The excess KCl or $CaCl_2$ was removed by repeatedly washing with Milli-Q water until Cl^- was negatively determined by reacting with $AgNO_3$ solution. The clay suspensions were then air-dried, and stored for later use.

Humic acid phases. Two kinds of humic acids (HAs) were used. One was purchased from Jufeng Co. (Shanghai, China) and designed as HAs_1. The other designed as HAs_2 was collected from a paddy soil with the total C of 20.7 g kg^{-1}, total N of 2.7 g kg^{-1}, and pH of 4.80 (Jinhua, Zhejiang, China). The detailed extraction and purification procedure were described by Chen and Pawluk (1995). Briefly, soil was mixed with 0.1 M $Na_4P_2O_7$ solution (1:10 w/v) under N_2 and shaken overnight. The alkali-soluble SOM was separated from mineral and humin fractions by high speed (20,000*g*) centrifugation. The supernatant was acidified with 6 M HCl to pH 1.0 to precipitate the HAs. The HAs were then treated with a dilute (0.5% V/V) HF/HCl solution to remove ash, dialyzed in Milli-Q water, freeze-dried, and ground to fine powders.

Selected physicochemical properties of the materials above are listed in Table 1. Organic carbon (OC) content was performed using a TOC analyzer (TOC-500, Shimadzum, Japan) with auto sampler after acidic digestion. Surface area (SA) was measured by multiple point nitrogen BET to be 4.0 m^2 g^{-1}. Cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (1986). And the pH was measured from the equilibrium supernatant after sorption.

H_2O_2-treated soil phases. Six referenced soils (Xie et al., 2003), from Zhejiang Province in southeastern China, were used for further investigation of the potential contribution of SOM to sorption by comparing the different retention behaviors before and after the removal of organic carbon with H_2O_2 treatment.

To remove organic matter from the soils, each 10 g of the air-dried soils was treated with approximately 25 ml of 35% H_2O_2 at room temperature for 4 days. This treatment was repeated twice, and the sediments were washed with Milli-Q water for four times and then air-dried. The organic carbon content was measured before and after removal of the organic carbon.

Chemical. PCP with purity more than 98% from Aldrich Chemical Co. was used as the model compound in this study. It is a highly chlorinated ionizable HOCs and a weak acid with a molecular weight of 266.5 g mol^{-1}, pK_a of 4.75, and $\log K_{ow}$ of 5.01 (Ferro et al., 1994; Joel and Jerald, 1998).

2.2. Sorption experiments

Sorption isotherms. Sorption was conducted in glass screw-PTFE-cap centrifuge vials. About 10–1000 mg (on