Environmental Pollution 184 (2014) 123–130

Contents lists available at ScienceDirect

Environmental Pollution

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

Synergistic role of different soil components in slow sorption kinetics of polar organic contaminants

Dongmei Zhang [a,c], Lei Hou [a], Dongqiang Zhu [b], Wei Chen [a,*]

[a] College of Environmental Science and Engineering, Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Nankai University, Tianjin 300071, China
[b] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu, China
[c] School of Environment, Northeast Normal University, Jilin, China

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form
1 August 2013
Accepted 5 August 2013

Keywords:
Slow sorption kinetics
Polar organic contaminants
Non-hydrophobic interactions
Soil components

ABSTRACT

We observed that the sorption kinetics of nitrobenzene and 2,4-dinitrotoluene (two model polar compounds) was significantly slower than that of 1,4-dichlorobenzene and phenanthrene (two model apolar compounds). The difference was attributable to the strong non-hydrophobic interactions between the polar molecules and soil. Interestingly, sorption kinetics of the polar sorbates to the soil organic matter-free soil, humic/fulvic acid-free soil, and extracted humic acids was very fast, indicating that different soil components played a synergetic role in the observed slow kinetics. We propose that slow sorption kinetics of highly polar sorbates stems mainly from the strong specific interactions (H-bonding, electron donor–acceptor interactions, etc.) with humic/fulvic acids; such specific interactions occur when sorbate molecules diffuse through humic/fulvic acids coiled, in relatively compressed confirmations, within the complex, tortuous, and porous soil matrices formed by mineral grains/particles and soil organic matter.

1. Introduction

Sorption is a critical process affecting the fate and transport of organic contaminants in the environment. In particular, contaminant transport in dynamic environmental systems (e.g., groundwater aquifers, rivers, estuaries) is largely controlled by sorption kinetics of contaminants from the aqueous phase to porous media, soils, and sediments. For example, slow sorption kinetics has been proposed as the primary factor resulting in the non-ideal breakthrough—such as asymmetrical breakthrough curves with both early breakthrough and tailing—of organic contaminants in groundwater (Brusseau and Rao, 1989).

A number of studies have been conducted to characterize the slow sorption kinetics of organic contaminants to natural soils and sediments (refer to two critical review papers – Brusseau et al., 1991; Xing and Pignatello, 1996). Most of these studies have focused on nonionic, apolar organic compounds such as polycyclic aromatic hydrocarbons and chlorinated benzenes, and slow sorption kinetics is typically linked to several slow diffusion processes, such as slow diffusion within soil/water interface, and slow diffusion in the tortuous intraparticle pore space retarded by local sorption to pore walls (Brusseau et al., 1991; Pignatello and Xing, 1996; Shih and Wu, 2002b). Additionally, it has been proposed that soil organic matter (SOM) is composed of both amorphous domain (e.g., low diagenetic humic substances, such as humic acids and fulvic acids, that are rich in flexible aliphatic structures) and condensed domain (e.g., condensed organic matter, such as humin, that is rich in aromatic and cross-linked structural components). Sorption kinetics to condensed SOM can be particularly slow, because condensed SOM has more rigid structures and may contain micropores, giving rise to very slow relaxation of the sorption matrix and slow pore diffusion (Ran et al., 2005; Weber and Huang, 1996; Xing and Pignatello, 1996).

Sorption kinetics of organic sorbates can be strongly affected by the nature of sorbate–sorbent interactions. For apolar, nonionic, hydrophobic organic compounds, sorbate–sorbent interaction is relatively simple, in that sorption to soil/sediment is driven predominantly by the hydrophobic effect (Rutherford et al., 1992; Schwarzenbach et al., 2003). For these compounds, the sorption kinetic constants are in general inversely related to the hydrophobicity of the sorbate molecules (Ball and Roberts, 1991; Brusseau et al., 1991; Valsaraj and Thibodeaux, 1999; Wu and Gschwend, 1986). For highly polar organic compounds, however, sorbate–sorbent interactions are often more complex and both

---

* Corresponding author.
E-mail addresses: wchen_17@yahoo.com, chenwei@nankai.edu.cn (W. Chen).

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.08.022

the SOM fraction and the clay mineral fraction of the soil/sediment can make significant contribution to sorption (Charles et al., 2006a; Chiou and Kile, 1998; Schwarzenbach et al., 2003). Moreover, highly polar organics can interact with multiple soil components via strong non-hydrophobic interactions, such as charge transfer, H-bonding, and electron donor–acceptor interactions (Brusseau and Rao, 1991; Zhu et al., 2004), and each of these specific interactions could have its characteristic effects on the sorption kinetics. Depending on the compositions and structural properties of the soil/sediment, highly polar contaminants can exhibit distinctively different sorption kinetic patterns from apolar contaminants. Thus, sorption kinetics of highly polar organic sorbates is much less understood compared with that of apolar, nonionic organics.

To date, only a few studies have been conducted to systematically understand the sorption kinetics of polar sorbates. Brusseau and Rao (1991) found that the sorption kinetic rate constants (obtained by fitting the breakthrough curves of column tests) of atrazine, simazine, cyanazine, and trietazine were at least one order of magnitude lower than those of the nonionic, low-polarity compounds, such as chlorinated benzenes, unsubstituted and alkyl-substituted aromatics, and chlorinated ethanes and ethenes. They proposed that the slow sorption kinetics of pesticides may result from some combination of diffusive constraint (due to the complex functional groups of these pesticides) and specific sorbate–sorbent interactions. Chang et al. (1997) investigated diffusion of toluene, n-hexane, and acetone in dry, compressed humic acid disks, and found that acetone, with the smallest van der Waal volume and lowest partition coefficient, showed similar (or even lower than hexane) diffusivity. They proposed that weak molecular interactions (e.g., hydrogen bonding between acetone and hydroxyl groups of humic acid) may be responsible for the slow diffusion of acetone. Later on, Shih and Wu (2002a) made similar observations with compressed humin disks and drew the same conclusion. While these studies all indicate the potential role of specific sorbate–sorbent interactions in the slow sorption kinetics of highly polar sorbates, the specific contributions of different soil components are unclear.

The objective of this study was to further understand the roles of specific interactions between polar compounds and different soil components in sorption kinetics. To systematically understand the effect of sorbate polarity on sorption kinetics, two model apolar compounds (1,4-dichlorobenzene and phenanthrene) and two representative polar compounds (nitrobenzene and 2,4-dinitrotoluene) were selected. In addition to polar interactions (such as H-bonding), both nitrobenzene and 2,4-dinitrotoluene can induce strong π–π electron donor–acceptor interactions with SOM (Zhu et al., 2005; Zhu and Pignatello, 2005) but the interaction is expected to be stronger for 2,4-dinitrotoluene because it contains two nitro groups (strong π-electron-withdrawing functional group). 1,4-Dichlorobenzene was chosen to compare with 2,4-dinitrotoluene: the two sorbates are structurally similar but sorption of 1,4-dichlorobenzene is predominantly through non-specific interactions. Phenanthrene (with larger molecular size and greater hydrophobicity than 1,4-dichlorobenzene) was selected as another model apolar compound to compare with 1,4-dichlorbenzene. The sorbents included a natural soil, a humic/fulvic acid (HA/FA)-free soil (obtained by removing the humic and fulvic acid fractions of SOM from the original soil), a SOM-free soil (obtained by removing the SOM fraction of the original soil), and extracted humic acids from the original soil. Batch sorption kinetics and batch sorption isotherms of different sorbates to different sorbents were examined and modeled. Potential mechanisms controlling the sorption kinetics of polar versus apolar compounds are analyzed.

2. Materials and methods

2.1. Materials

A Chinese black soil, one of the most common types of soil in Northern China, was collected from near the surface (10–20 cm) from Tianjin; the characteristics of the soil was reported previously (Yang et al., 2008) and the soil contained no test sorbates. The soil was air-dried at room temperature, ground with a pestle, and sieved through a 1-mm mesh. A portion of the soil was treated with 30% H_2O_2 to remove SOM (Hyeong and Capuano, 2000). First, 500 g of the original soil was mixed with 500 ml of 30% H_2O_2 by periodical stirring until bubbling ceased. Then, the suspension was heated in a water bath at 50 °C until bubbling once again ceased. A total of three H_2O_2-treatments were done. Finally, the soil slurry was washed three times with distilled water, centrifuged, freeze-dried and stored at room temperature for future use. (Note that Mikutta et al. (2005) proposed that treatment with H_2O_2 can affect the properties of soil minerals. This artifact should have minimal impact on the overall observations in this study because the treated soil was used mainly to demonstrate that sorption was dominated by SOM). Another portion of the soil was treated with 0.5 M NaOH to remove the humic and fulvic acid fractions of SOM from the soil (Shi et al., 2010). First, 100 g of the original soil was mixed with 500 ml of 0.5 M NaOH and was continuously stirred under an atmosphere of N_2 (to avoid the oxidation of the SOM) for 24 h. Then, the soil slurry was rinsed thoroughly with deionized water, centrifuged, and freeze-dried (Hung et al., 2012). Humic acids were extracted from the soil using a previously developed method (Sun et al., 2008). First, the original soil was treated with 0.2 M HCl to remove carbonates. Then, the treated soil was mixed with 0.5 M NaOH and was continuously stirred under an atmosphere of N_2 (to avoid the oxidation of the SOM) at room temperature for 24 h. Then, the soil suspension was centrifuged, and the supernatant was collected and acidified with 6 M HCl (with the final pH adjusted to 1.5) to precipitate the humic acids, followed by a washing with a mixture of 0.06 M HCl and 0.14 M HF to remove mineral residues. The humic acids were then dissolved with 0.1 M NaOH and neutralized with 1 M HCl. The resulting humic acid solution was dialyzed using membrane tubes (500 Da, Union Carbide, Houston, TX, USA) and freeze-dried. The obtained humic acids were stored in a sealed vial for later use. The pH values of the original and treated soils were measured at 1:2.5 (w/v) soil to solution ratio in 1 M KCl solution (Jackson, 1967). Soil organic carbon content was determined using the dichromate oxidation (external heat applied) method, and soil texture was determined based on Stokes' law and transmission/extinction phenomenon of soil particles. Cation exchange capacity (CEC) was determined using 1 M NH_4Ac and 0.005 M EDTA at pH 7.0. Selected properties of the original and treated soils are given in Table 1.

Nitrobenzene, 2,4-dinitrotoluene, phenanthrene, and 1,4-dichlorobenzene were obtained from AccuStandard (New Haven, CT, USA). Selected physical–chemical properties of the chemicals are listed in Table 2. All organic solvents used were of high-performance liquid chromatogram grade or higher.

2.2. Sorption kinetics

In a typical sorption kinetic experiment, 2–30 g of soil or 0.63 g of extracted humic acids (the specific mass of sorbents are given in Table S1) was pre-wetted with approximately 100 ml of an electrolyte solution, containing 0.01 M $CaCl_2$ and 0.01 M NaCl to simulate soil solution, and 0.01 M NaN_3 as the inhibitor for bacterial growth (Chen et al., 2009; Yang et al., 2008) in a 220-ml glass centrifuge bottle for 24 h. Then, the bottle was filled with a freshly prepared aqueous solution of an organic solute (the initial aqueous phase concentrations are given in Table S1), and immediately sealed with a Teflon®-lined cap. Then the bottle was horizontally tumbled at 140 rpm. At predetermined time intervals the bottle was removed from the tumbler and centrifuged at 5000 rpm for 4 min. Approximately 0.4 ml of the supernatant was withdrawn to analyze the concentration of the sorbate (nitrobenzene, 2,4-dinitrotoluene, and 1,4-dichlorobenzene were extracted from an aliquot of the aqueous phase with hexane, and phenanthrene was analyzed directly). Afterwards, the bottle was sealed again, and tumbled until the next sampling time. For all the experiments, the total volume of the solution withdrawn during the repetitive sampling was less than 2.3% of the initial volume of the solution (~220 ml). Each sorption kinetic data was run in duplicate, and the experiments were carried on until the aqueous phase concentrations were essentially constant. Control samples that received the same treatment as the sorption samples but no sorbent were

Table 1
Selected physicochemical properties of soils.

Soil	f_{OC}[a]	pH	Sand (%)	Silt (%)	Clay (%)	CEC[b] (meq/100 g)
Original soil	0.022	7.5	8	50	42	22.4
SOM-free soil	0.0027	7.1	4	46	50	24.2
HA/FA-free soil	0.020	8.1	4	52	44	17.4

[a] Fractional organic carbon.
[b] Cation exchange capacity.