Desorption-Resistance of Hydrophobic Organic Compounds in Natural Soils

Won Sik Shin

Water Environment Rsearch Team
Environment and Energy Division
Research Institute of Science and Technology
Pohang, 790-600, Korea
(E-mail: wshin@rist.re.kr)

Abstract

Sorption/desorption study was conducted to determine desorption-resistance of hydrophobic organic compounds in natural soils with low organic carbon content. Sorption/desorption characteristics of chlorobenzene and phenanthrene for both PPI (Petro Processors, Inc. Superfund site) and BM (Bayou Manchac) soils were investigated. Desorption was biphasic including reversible and desorption-resistant compartments. The biphasic sorption parameters indicated the presence of appreciable size of desorption-resistant phase in these soils. A finite maximum capacity of desorption-resistant fraction (q_{max}^{irr}) was observed after several desorption steps. The apparent organic carbon based partition coefficient, K_{oc}^{irr} was $10^{1.92 \pm 0.27}$ for PPI soil and $10^{1.92 \pm 0.27}$ for BM soil, respectively. The difference in K_{oc}^{irr} was attributed to different characteristics in soil organic matter. The results suggest that desorption-resistance should be considered in remediation and risk assessments in natural soils and sediments.

Key words: bioavailability, sorption, desorption, desorption-resistance, biphasic sorption, aging, sequestration, risk assessment

1. Introduction

Sorption and desorption have been received considerable attention as the most important processes controlling interaction between hydrophobic organic contaminants and sediments. Numerous studies have shown that the fate and transport of hydrophobic organic compounds (HOCs) in soil is highly dependent on sorption/desorption characteristics. Reliable estimation of the sorption/desorption processes is crucial for proper risk assessment of HOCs and for determining of

bioremediation treatments at contaminated sites. Sorption of organic compounds in soils and sediments has long been considered a reversible process in assessing risk and determining remedial endpoints. However, reversible models were not able to explain the long-term persistence of contaminants at many sites. The existence of a desorption-resistant (or sequestered) fraction of HOCs in soil has been identified and the quality of organic matter is critical in determining the magnitude of the desorption-resistant effect. Desorption is biphasic including labile fraction and highly resistant fraction. Desorption-resistance or irreversible sorption has been recognized as an important phenomenon for understanding fate of organic contaminants in soils and sediments, because it significantly affects chemical transport, toxicity, bioavailability and remediation strategies. Therefore, characterization and quantification of desorption-resistant phase should be better understood to develop more appropriate sorption-desorption models. In this study, sorption/desorption characteristics of chlorobenzene and phenanthrene in natural soils were investigated. Model parameters of the currently proposed biphasic-sorption model were investigated to explain the desorption-resistance.

2. Materials and Methods

Two different soils were used as sorbents in this study. A soil (PPI soil) was removed from a bottomland hardwood wetland near the Petro Processors, Inc. Superfund site near Baton Rouge, LA. A second soil (BM soil) was obtained from Bayou Manchac, LA.

Radiolabeled [^{14}C] compounds: chlorobenzene-UL-^{14}C (Sigma, 2.7 mCi/mmol) and [9,10-^{14}C] phenanthrene (ChemSyn Laboratories, 56.7 mCi/mmol) were used as sorbates. The [^{14}C] compounds were further diluted with unlabeled ^{12}C stock solutions (1,000 mg/L in methanol) to yield desired concentrations. ^{12}C-chlorobenzene (>99.9%) and -phenanthrene (>96%) were used. 200 mg/L of NaN$_3$ was added to the solution as a bacterial inhibitor. Chemical solutions were prepared before each sorption experiment using the ^{12}C stock solutions and an electrolyte solution containing 1 mM CaCl$_2$2H$_2$O, 0.5 mM MgCl$_2$, and 0.1 mM Na$_2$B$_4$O$_7$10H$_2$O (pH 8.0).

Experiments were performed in batch using successive sorption/desorption cycling. An adsorption/desorption cycle constitutes a series of 4 successive adsorptions (each sorption for 2 days) followed by successive desorptions. The sorption/desorption experiments were conducted in glass vials with a total volume of approximately 42-mL sealed with Teflon-faced silicone septa. Subsamples of the homogenized soil were transferred to the vial (water to soil ratio = 10:1, w/w%) before the addition of chemical solutions at concentrations of 100 mg/L for CB and 1.0 mg/L for Phen. The sediment/water mixture was horizontally mixed in a shaker bath at room temperature. After 48 hours, the sediment was separated from the solution by centrifugation at 2,500 rpm for 20 minutes and the chemical concentration in the supernatant was analyzed via liquid scintillation. Then, the sediments were re-spiked with the chemical

stock solution and the adsorption experiments were repeated step-wise 4 times before the desorption experiment began. Desorption was conducted with both electrolyte and iso-propanol cosolvent solutions. In repetitive desorption steps, approximately 75-90% of the supernatant was replaced with contaminant-free electrolyte solution followed by shaking for 3 days. At each desorption step, the solution was gently removed using a pipette. The solid phase chemical concentrations were calculated by assuming changes in solution-phase concentrations during adsorption or desorption result from changes in solid phase concentration. The solution phase chemical concentrations were determined by scintillation counting at each step (Beckman, LS 6000SC).

3. Biphasic Sorption Model

The desorption data was modeled with a prevously proposed biphasic sorption-desorption model. The model describes desorption from two compartments: (i) to the reversible (or labile) compartment described by linear isotherm and (ii) to the desorption-resistant (or non-labile) fraction described by Langmurian-type expression:

$$q = q^{rev} + q^{irr} = K_{oc} \cdot f_{oc} \cdot C + \frac{K^{irr}_{oc} \cdot f_{oc} \cdot q^{irr}_{max} \cdot f \cdot C}{q^{irr}_{max} \cdot f \cdot K^{irr}_{oc} \cdot f_{oc} \cdot C}$$

where q = total concentration of sorbed compound in the soil phase ($\mu g/g$), q^{rev} = the concentration of sorbed compound in the labile fraction ($\mu g/g$), q^{irr} = the concentration of sorbed compound in the desorption-resistant fraction ($\mu g/g$), K_{oc} = organic carbon normalized partition coefficient (mL/g), f_{oc} = organic carbon content, C = solution phase concentration (mg/mL), K^{irr}_{oc} = partition coefficient of the desorption-resistant fraction (mL/g), f = fraction of compound residing in the desorption-resistant compartment, and q^{irr}_{max} = maximum capacity of the desorption-resistant fraction ($\mu g/g$).

4. Results and Discussion

The results of multiple sorption and desorption of chlorobenzene and phenanthrene are summarized in Table 1. The isotherms of four successive sorptions of chlorobenzene and phenanthrene were linear ($r^2 > 0.97$). The mean log K_{oc} values of chlorobenzene were 2.81 for PPI soil and 2.87 for BM soil are similar to the log K_{ow} (= 2.87) of chlorobenzene. After the desorption steps, q^{irr}_{max}, was approximately 483 μ g/g (21.4% of total sorbed amount) for PPI soil and 544 μg/g (25.6% of total sorbed amount) for BM soil, respectively. Clearly, q^{irr}_{max} of the BM soil was greater than that of PPI soil. The difference in log K^{irr}_{oc} value (mean of electrolyte and iso-propanol desorptions) of PPI soil (= 4.69) and BM soil (= 4.98) is mainly due to the characteristics of soil organic matter. The log K^{irr}_{oc} values of these soils were much smaller than the previous results of others (Kan et al., 1998; Chen et al., 2000). This indicates that their relationship of essentially constant K^{irr}_{oc} value may not be valid for

some soils and sediments. The result of soil analysis shows that organic carbon content in the PPI soil (1.35%) is greater than the BM soil (1.10%). Despite a lower organic carbon content in the BM soil, the maximum capacity of chlorobenzene in desorption-resistant compartment of the BM soil is greater than the PPI soil.

The Sorption/desorption of phenanthrene in PPI and BM soil exhibited similar behavior. The log K_{oc} values for phenanthrene were 3.90 for PPI soil and 4.12 for BM soil. For both soils, K_{oc} values were smaller than K_{ow} (= 4.57) of phenanthrene. The q_{max}^{irr} of the BM soil (16.7 μg/g, 19.8% of the total sorbed amount) was greater than the PPI soil (16.0 μg/g, 17.5% of the total sorbed amount) indicating that the maximum capacity of the desorption-resistant phase increases with soil age. The observations were consistent with the results of previous study (Shin, 2000). The apparent organic carbon based partition coefficients of the recently deposited young wetland soils are remarkably different from those of aged or normal soils with low organic carbon content.

4. References

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Table 1. Biphasic sorption parameters of chlorobenzene and phenanthrene in (a) PPI soil and (b) BM soil

Chemical	Soil	Exp.	q_0^c	log K_{oc}^d	r^2	q_{max}^{irr} ^{e}	C_w^{max} ^{f}	log K_{oc}^{irr} ^{g}
Chlorobenzene	PPI	1a^a	2,196.3	2.784	0.987	505.0	0.65	4.760
		1b^b	2,312.0	2.844	0.967	461.6	0.82	4.620
	BM	2a	2,163.5	2.878	0.984	575.0	0.57	4.962
		2b	2,088.6	2.851	0.989	512.6	0.46	5.006
Phenanthrene	PPI	3a	77.9	3.848	0.999	13.1	0.0066	5.166
		3b	88.4	3.942	0.983	16.1	0.0090	5.121
	BM	4a	84.0	4.093	0.999	15.7	0.0052	5.437
		4b	84.6	4.146	0.995	17.7	0.0100	5.205

^{a}Desorption with electrolyte solution. ^{b}Desorption with iso-propanol cosolvent solution. ^{c}Chemical concentration in soil phase at the end of sorption steps. Calculated from mass balance. ^{d}Organic carbon normailzed partition coefficient (mL/g OC). ^{e}Maximum capacity of desorption-resistant fraction (μg/g). ^{f}Aqueous phase concentration at equilibrium (μg/mL) when desorption-resistance is obtained at q_{max}^{irr}, and ^{g}Organic carbon normalized equilibrium partition coefficient for the desorption-resistant fraction (mL/g OC).