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Competitive sorption and desorption between BDE-47 and BDE-99 by different river- and farmland-based aquifer media

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ABSTRACT

Two main PBDEs that have potential endocrine disrupting properties—2,2,4,4′-tetrabromodiphenyl ether (BDE-47) and 2,2′,4,4′,5-tetrabromodiphenyl ether (BDE-99)—have been detected in environmental samples and have drawn public attention. In a single solute system, three aquifer media, Beijing river aquifer media, Beijing farmland soil, and Fujian farmland soil (FN), with different properties were collected as the main sorbents to investigate the sorption and desorption characteristic of BDE-47. The results indicate that a two-compartment first-order model could adequately describe the sorption kinetics of BDE-47. FN has the largest adsorption capacity, showing that a high organic matter content could improve the soil adsorption capability. In binary-solute systems, a series of BDE-99 with different concentration suppresses the sorption of BDE-47. The result indicates that the sorption capacity of BDE-47 significantly decreases with the increasing concentration of BDE-99, and the decreasing tendency becomes more obvious when the content of BDE-47 is high. By contrast, BDE-47 does not show a competitive sorption effect on BDE-99 sorption. The BDE-47 desorption from soils exhibits hysteresis with the addition of BDE-99, especially for FN. These results could be used to predict a potential pathway for the removal of PBDEs and for the evaluation of ecological risks when using reclaimed municipal wastewater.

Keywords: BDE-47; Sorption; Desorption; Binary-solute system; Competitive adsorption

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are commonly used in industrial materials, including electrical equipment, textiles, foam furniture, insulating foams, and other building materials [1]. Because of regulations aimed at reducing death and injury from fires, the market for flame retardants has grown rapidly in recent decades [2]. Consequently, the fraction of bromine used to produce brominated flame retardants (BFRs) has increased from 8% in 1975 to 38% in 2000 globally [3]. The total

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concentration of PBDEs ranged from 4 to 29 ng/L in wastewater discharged effluent, with the highest PBDE abundance consisting of 2,2´,4,4´,5-tetrabromodiphenyl ether (BDE-99) and 2,2,4,4´-tetrabromodiphenyl ether (BDE-47). Over the last two decades, BDE-99 and BDE-47 were the highest priority PBDEs, ranked even above BDE-209, with an average concentration of 2.6 ng/L in the Xijiang River of the Pearl River Delta [4]. The total PBDE concentrations in soils were in the range of 2,720–4,250 ng g^{-1} dry weight. In the Pearl River Estuary, the total concentrations of PBDEs ranged from 2.15 to 127 pg L^{-1}, with a mean of 29.0 pg L^{-1} [5]. Moreover, even in non-industrial area, such as the Yangtze River Delta [6] and the central Loess Plateau [7], PBDEs can be easily detected. Although PBDEs were added to the list of banned chemicals included in the Stockholm Convention in 2009, the potential environmental threat posed by PBDEs will not disappear immediately because of new products composed of recycled PBDE-containing materials, the use of PBDE-containing equipment, and the disposal of e-waste [4,8].

All PBDEs have low solubility (<1 μg kg^{-1}) and high K_{OW} values (>5), but the lower congeners have substantially higher vapor pressure than the highly brominated compounds. Therefore, BDE-47, which has four bromine atoms, is usually highly concentrated in air samples. BDE-47 is followed by BDE-99, which is more prevalent in commercial pentaBDE mixtures [9]. PBDEs, like other persistent organic pollutants (POPs), can be transported via a variety of processes, including atmospheric deposition, land runoff, and direct industrial and domestic wastewater discharges [10]. PBDEs are detected in organisms and various environmental media, such as air, water, soil, dust, and sediment [3,11–13]. Several studies have discussed long-range transport of PBDEs [14,15], indicating that PBDEs are easily spread to distant areas via environmental media, leading to multiple types of pollution. For example, PBDEs were detected in soils of the Tibetan Plateau, the highest plateau in the world, where BDE-47 was found to be the main congener, accounting for approximately 40% of total PBDEs [4]. Evidence to date demonstrates that PBDEs have the potential to adversely affect both human and environmental health [16]. PBDEs have received a great deal of attention to date due to their potential toxicity, environmental persistence, and bioaccumulation ability, especially those congeners that have fewer bromine atoms [17,18]. Lower brominated congeners (those with four to seven bromines) are more bioaccumulative and persistent [19,20]. Limited evaluations of the ecological effects of PBDEs have been conducted. In general, the lower brominated mixtures are more toxic than the higher brominated congeners. PentaBDE is more toxic than OBDE, whereas DBDE is essentially nontoxic to invertebrates [21].

With water shortages in many countries, the recharge of groundwater with treated reclaimed wastewater provides many advantages, such as the reduction of groundwater level decline, mitigation of declining groundwater levels, and storage of reclaimed water for future usage [22]. However, as the main source of reclaimed wastewater, current wastewater treatment plants (WWTPs) are not specifically designed to eliminate micropollutants, also termed "emerging contaminants," including PBDEs [23]. Thus, by virtue of their persistency, their continuous introduction or both, PBDEs are able to pass through wastewater treatment processes and can then be introduced in groundwater via artificial recharge using reclaimed water [24]. As soil is the major pathway for groundwater pollution by some micropollutants [25], the study of the adsorption behavior and degradation in soil is essential. Soil adsorption is one of the important ways that organic pollutants in the environment are removed because of soil's sorption quality and holding capacity [26]. Sorption of micropollutants by soil mainly relies on the hydrophobicity of the compound. In most cases, K_{OW} is used to predict the adsorption of micropollutants [23]. A general rule for estimating sorption is that when $\log K_{OW} > 4$, the sorption potential is high [27]. Therefore, soil might have a strong ability for the sorption of PBDEs; hence, soil becomes one of the largest gathering places for PBDEs. Therefore, the research of adsorption behavior for PBDEs is of vital importance.

To study PBDE pollution in the process of groundwater recharge with treated reclaimed wastewater in China because topsoil is affected by the biological climate or by human activity, leading to the organic matter, three typical topsoil samples—Beijing river aquifer media (BH), Beijing farmland soil (BN), and Fujian farmland soil (FN)—with different properties were collected as the main sorbents. BH represents the soil from northern China. FN represents the soil from southern China. BH represents the soil from rivers or sediment and is compared to the sorption of soil from farmland. This study demonstrates the sorption and desorption of BDE-47 not only in single systems but also in coexistence with BDE-99, which generally presents in the same contaminated soil. This approach can provide complementary information to analyze the mutual effects of the two solutes on sorption and desorption, as well as the mechanisms involved. The findings of this study can therefore support prevention and control measures for PBDE pollution during north- or south-based and river- or farmland-based artificial groundwater recharge using reclaimed water across China.

2. Materials and methods

2.1. Materials

Three topsoil samples—BH, BN, and FN—were collected from the Chaobai River bank and farmland at a depth of 0–20 cm in Beijing and Fujian. The physicochemical properties of the soil samples used in this study are listed in Table 1. After collection, the materials were freeze-dried, passed through a 2-mm sieve, and homogenized by graining. BDE-47 and BDE-99 were purchased from AccuStandard, Inc., USA with a purity > 98%. Some of their physicochemical properties are presented in Table 2.

The specific surface areas (SSAs) and micropore volume were defined by an Autosorb-iQ-C (Quantachrome, Boynton Beach, FL, USA) using the multi-point and HK (Horvath–Kawazoe) methods. The identities of the functional groups present were identified using a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher Scientific, Inc., USA). CEC was determined following the procedures defined by Chapman [28]. Total organic carbon (TOC) was determined using a solid TOC analyzer (SCSH, TOC-VCPH, Japan) [29].

Stock solutions (0.5 g L^{-1}) of BDE-47 and BDE-99 were prepared in methanol and stored at −20°C in the dark. High-performance liquid chromatography (HPLC) grades of methanol and hexane were purchased from Fisher (USA). All other chemicals ($CaCl_2$, NaN_3) were of analytical grade. To obtain a standard curve with different concentrations (5–50 μg L^{-1}) before instrument analysis, the stock solutions were diluted using methanol as a solvent.

2.2. Sorption and desorption experiments

All sorption and desorption experiments were conducted in glass vials sealed with screw-caps to avoid evaporation loss. Soil samples (10 mg) were mixed with 40 mL of a BDE-47 solution in 0.01 M $CaCl_2$ as the background electrolyte and 200 mg L^{-1} NaN_3 as a biocide. The concentration of BDE-47 initially added was 50 μg L^{-1} based on the individual water solubility (S_w, 50 μg L^{-1}) of BDE-47 [14]. In the single-solute systems, six initial concentrations of BDE-47 in the range of 5–50 μg L^{-1} were prepared. Each concentration was prepared in triplicate, and blank samples were also prepared without spiked BDE-47. Binary-solute systems were designed with the same sorbent-to-water ratios and simultaneously spiked with BDE-47 and BDE-99. The six initial concentrations of BDE-47 were prepared as in the single-solute systems, and a fixed amount of BDE-99 (10, 20, and 30 μg L^{-1}) was introduced as a cosolute to each vial. A preliminary study indicated that obvious equilibrium was reached within 48 h for both sorption and desorption processes; hence, suspensions were shaken for 48 h at 25°C throughout all of the sorption and desorption process.

After shaking, samples were allowed to set for sedimentation for approximately 4 h, and the supernatants (20 mL) were withdrawn and analyzed by a gas chromatography mass spectrometer (GC-MS) for analysis of BDE-47 and BDE-99. At the end of sorption experiments, aliquots of supernatant (20 mL)

Table 1
Physicochemical properties of three different soil samples

	Site	Organic matter (g kg^{-1})	CEC (cmol kg^{-1})	pH	Sand: silt: clay	Specific surface area (m^2 g^{-1})	BC (%)	SSA (m^2 g^{-1})
BH	N40.14° E116.65°	10.9	18.16	8.29	48:41:11	11.6482	0.059	19.94
BN	N40.45° E116.34°	15.2	12.20	8.59	8:79:13	13.4548	0.061	16.87
FN	N24.98° E116.43°	45.9	10.28	5.09	43:31:26	22.8213	0.080	15.47

Table 2
The properties of BDE-47 and BDE-99

	Number of Br	Molecular formula	Molecular weight (g mol^{-1})	Water solubility (μg L^{-1})	Log K_{ow}	Log D (pH 5–8)
BDE-47	4	$C_{12}H_6Br_4O$	485.82	94.7	5.9–6.2	3.74
BDE-99	5	$C_{12}H_5Br_5O$	564.75	38.8–54.1	6.6–7.0	3.82

were withdrawn, the same volume of background desorption solutions were added to replenish the sample, and the suspensions were shaken for an additional 48 h. The samples were then separated, and the concentrations of BDE-47 and BDE-99 were again analyzed. The procedure was repeated through at least three cycles [30].

To assess the loss of solute due to evaporation and surface sorption, samples with no sorbent were prepared similarly with the same reactors. The results indicated that average system losses were less than 5% of the initial concentration for BDE-47 and BDE-99, indicating that the uptake by the glass walls and volatilization during sorption were negligible.

2.3. GC-MS detection

The sample extracts for PBDEs were determined according to a method modified from Fontana et al. [31]. The determination of BDE-47 and BDE-99 was performed using a 7890 gas chromatograph equipped with a 5975 MSD. The GC was operated in splitless injection mode. The carrier gas was He. A DB-5 MS chromatography column (15 m × 0.25 mm (i.d.) and 0.1 μm (film thickness)) was used in a constant flow mode with the flow rate set at 1.0 mL min^{-1}. The temperature rise program was set as follows: initial temperature of 140℃ maintained for 1 min; increased to 170℃ at a rate of 15℃ min^{-1} and maintained for 1 min; and increased to 240℃ at a rate of 8℃ min^{-1} and maintained for 1 min. Later, the temperature was increased to 310℃ at a rate of 35℃ min^{-1} and maintained for 4 min to remove any possible residual impurities. The MS was run in electron impact ionization (EI) mode, in which the interface temperature was 280℃ and the ionic source temperature was 250℃ with an electron energy of 70 eV and quadrupole temperature of 150℃. The selective ion mode was used for the final quantification [30].

2.4. Data analysis

The two-compartment first-order kinetic model (Eq. (1)) was used to describe the BDE-47 sorption kinetics:

$$\frac{q_t}{q_e} = f_1(1 - e^{k_1 t}) + f_2(1 - e^{k_2 t}) \tag{1}$$

In Eq. (1), t (h) is the reaction time and q_t (μg g^{-1}) and q_e (μg g^{-1}) are the concentration at the time of t and the equilibrium concentration of BDE-47 absorbed on the sorbent matrix, respectively. Also in Eq. (1), k_1 (h^{-1}) and k_2 (h^{-1}) represent the sorption rate constants of fast and slow sorption compartments, respectively; f_1 and f_2 represent the fractions of the fast and slow compartments, respectively; and $f_1 + f_2 = 1$.

Studies have shown that the Freundlich isotherm model is widely used to describe the adsorption behavior of hydrophobic organic contaminants in soils and sediments [32]. The Freundlich isotherm model has the following form:

$$q_e = k_f \times C_e^n \tag{2}$$

where C_e is the liquid phase equilibrium concentration in μg L^{-1}; q_e is the concentration on the solid phase in μg g^{-1}; k_f is the Freundlich affinity coefficient [(μg g^{-1})/(μg L^{-1})^n]; and n is the isotherm linearity parameter, an indicator of site energy heterogeneity.

The hysteresis index (HI) for the sorption–desorption isotherm is calculated using the formula [33]:

$$\mathrm{HI} = \frac{n_d}{n_s} \tag{3}$$

where n_s and n_d represent the Freundlich isotherm nonlinearity index of the adsorption and desorption isotherms, respectively, fitted according to Eq. (2). The fitting was processed using Origin 8.0.

3. Results and discussion

3.1. Kinetics of sorption of BDE-47 and contribution of fast sorption

To clarify the sorption mechanism of BDE-47 in three different soil systems, the connection between the sorption time and amount is presented in Fig. 1. The results indicate that the adsorption amount increases rapidly in the first 10 min and then remains unchanged after 2 h, and the slow sorption compartment gradually increases until the adsorption equilibrium is reached. The fast sorption remains substantially unchanged throughout the whole adsorption process, agreeing with reports by Liu et al. [34]. The two-compartment first-order model fits the kinetics of sorption well, and the detailed fitting results of the model parameters are summarized in Table 3. The fast sorption rate k_1 is higher than the slow sorption rate k_2, and the value of k_1 for the three soil samples is in the order of BN > BH > FN, whereas the SSA of soils was in the reverse order, indicating that fast sorption cannot be ascribed to the partitioning function and surface sorption merely by SSA. Apart from the fast sorption, the slow sorption should not

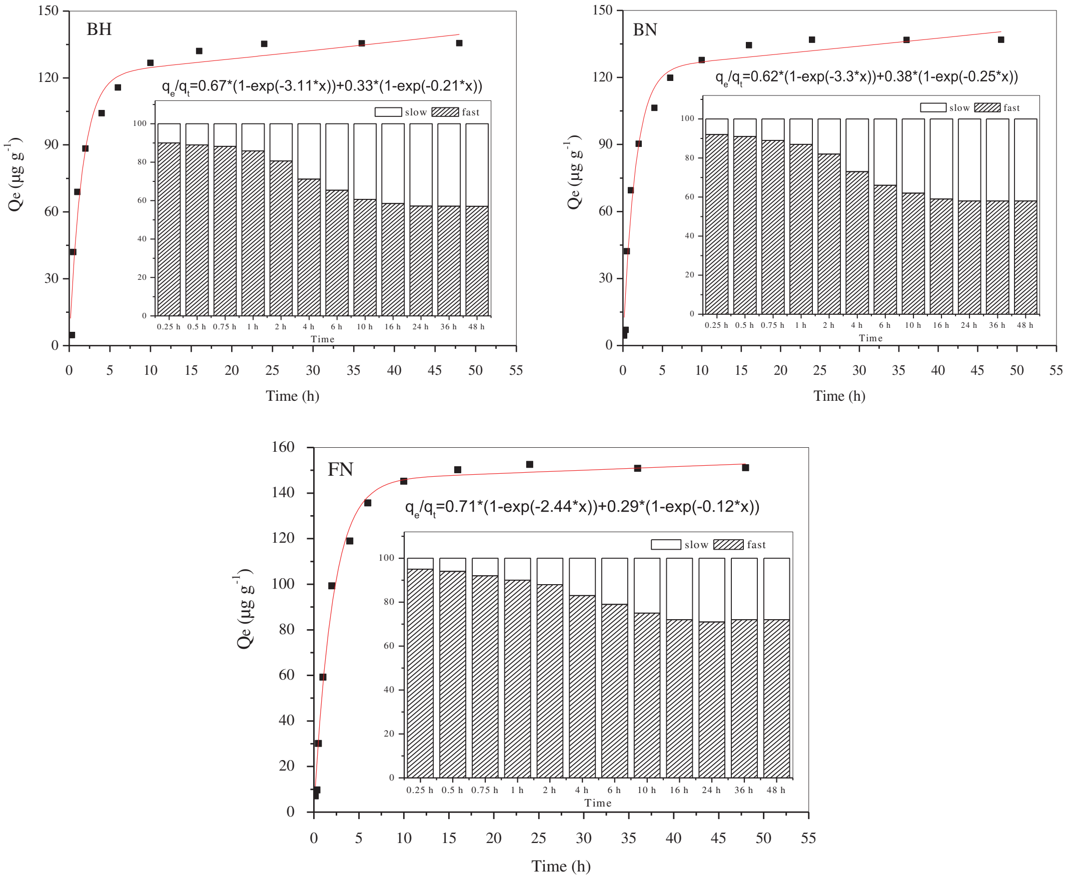

Fig. 1. Sorption kinetics of BDE-47 in soils and the fitting results of the two-compartment first-order model.

Table 3
Summary of model fitting results of BDE-47 for the soils

	Two-compartment first-order kinetic						
Sorbents	k_1 (h^{-1})	k_2 (h^{-1})	k_1/k_2	f_1	f_2	f_1/f_2	R^2
BH	3.11	0.21	15.05	0.67	0.33	2.03	0.976
BN	3.30	0.25	13.04	0.62	0.38	1.63	0.985
FN	2.44	0.12	19.89	0.71	0.29	2.45	0.990

be neglected because it probably affects the transport, degradation (including biodegradation), and final fate of PBDEs in the natural soil system [24]. Soil organic matter (SOM) is ranked FN > BN > BH, with FN having the largest adsorption capacity, showing that a high organic matter content could improve soil adsorption capability. This finding corresponds with that of a previous study [30]. The adsorption process is promoted by the high content of SOM and fine particles, especially for BDE-47 because BDE-47 has two Benzene rings that promote the π–π bonds formed that contribute greatly to surface adsorption [35].

The FT-IR spectra of the three soil samples before and after sorption are depicted (Fig. 2) to identify various functional groups that are capable of adsorbing PBDEs. In the case of the original soils, the band at 3,620 and 3,500 cm^{-1} could be assigned to OH stretching vibration. Other bands could be attributed as follows: 1,615 cm^{-1} (–C=O stretching), 1,021 cm^{-1} (–C–O–C stretching vibrations) [36]; the peaks at 502, 577, and 826 cm^{-1} correspond to –C–I, –C–Br, and –C–Cl, respectively.

After the sorption experiment, some significant changes occurred in the spectrum. Several peaks shifted in soils: BH (1,435–1,459 cm^{-1} and 525–520 cm^{-1}), BN

(1,032–1,027 cm^{-1}), and FN (1,109–1,114 cm^{-1}). Some new peaks were observed, such as a peak at 3,412 cm^{-1} of BH (b) and peaks at 3,396 and 2,517 cm^{-1} in BN (b). These new peaks could be due to the formation of new interactions between soils and BDE-47.

3.2. *BDE-47 sorption in single- and binary-solute systems*

As the cosolute, BDE-99 was added to BDE-47. It is important to understand their respective sorption amounts in single-solute systems for a better understanding of the mutual influence on their sorption behaviors in binary-solute systems. Nevertheless, due to an obvious difference between their solubility, the sorption isotherms at their respective concentration gradients would be insufficient to express their dissimilar sorption behavior. Therefore, the same concentration of 25 μg L^{-1} of BDE-99 and BDE-47 was chosen for the sorption experiments to compare their sorption amount. In most cases, the sorption capacity of BDE-99 was higher than that of BDE-47 (Fig. 3). There was a large difference in the molecular size of SOM. SOM could be divided into two states: dissolved and adsorption. Research indicates that dissolved organic matter improves the solubilization of pollutants in water, and solubilization becomes stronger when hydrophobic organic compounds have a lower water solubility [37]. For the characteristic of the lower solubility, the high hydrophobicity of BDE-99 was proposed to account for BDE-99's stronger affinity with sorption sites.

The sorption isotherm of BDE-47 onto three soil samples in single- and binary-solute systems fitted the Freundlich models well (Fig. 4). All three soil samples showed high sorption capacities for BDE-47 in single systems, with their Q_e ranging from 10.71 to 152.22 μg g^{-1} at a C_e gradient of 2.32 to 11.95 μg L^{-1}. In both the single and binary systems, the adsorption amount of FN to BDE-47 was higher than that of BH or BN. In binary-solute systems, a series of BDE-99 concentrations, including 10, 20, and 30 μg L^{-1}, suppressed the sorption of BDE-47. The result demonstrated the effect of competitive adsorption between the two PBDEs (Table 4). With the increased concentration of BDE-99, a significant decrease in the BDE-47 sorption capacity was observed and the decreasing tendency appeared more obviously at higher concentrations of BDE-47. From this concentration-dependent phenomenon, Xin et al. concluded that the sorption of BDE-47 could be affected in two different ways: through competitive effects and surface modification [30]. However, when the concentration of BDE-99 remained unchanged in the binary-solute system and the BDE-47 ranged from 0 to 50 μg L^{-1}, BDE-47 caused no competitive sorption effect on BDE-99 sorption. At lower solubility, the high hydrophobicity gave an advantage to BDE-99 sorption, which we propose accounts for its stronger affinity with sorption sites, thus making it less influenced by BDE-47.

The isotherm linearity parameter, represented by n, is an indicator of site energy heterogeneity in Freundlich models. When $n < 1$, the model indicates that the soil adsorption of BDE-47 is mainly nonlinear. According to the fitted results (Table 4), this phenomenon applies to FN, but not to the other two soil samples. When SOM is high, chemical adsorption seizes the advantage; when SOM is relatively low, physical adsorption dominates the whole process. The diffusion through the inter-particle may be the main factor for PBDEs adsorption onto soils. Different levels of nonlinearity adsorption were presented, and the main adsorption mechanism was physical adsorption.

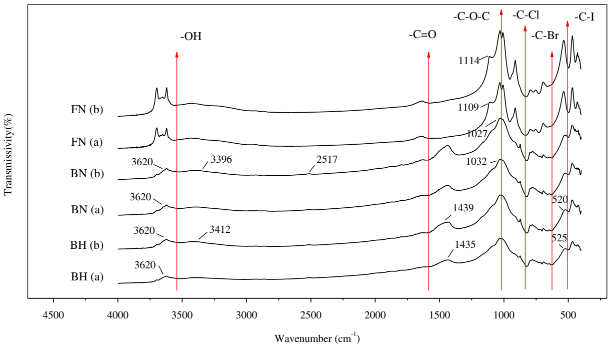

Fig. 2. FT-IR spectra of soils before (a) and after (b) sorption of BDE-47.

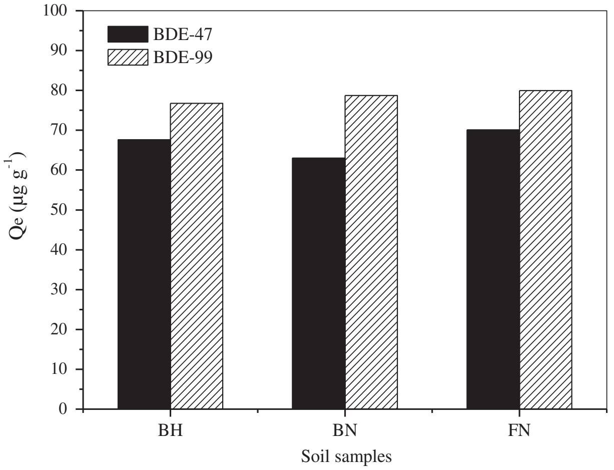

Fig. 3. Sorption amounts of BDE-47 and BDE-99 onto three soil samples with an initial concentration of 25 μg L^{-1}.

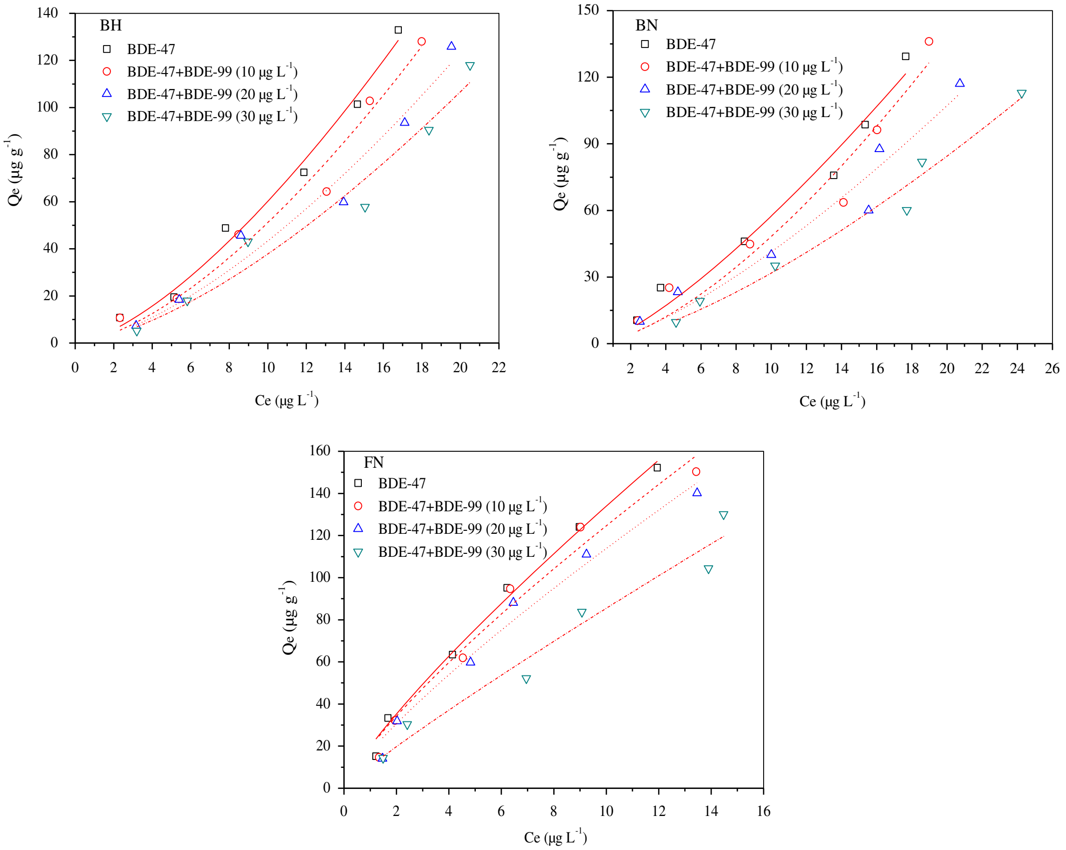

Fig. 4. Sorption isotherm of BDE-47 onto three soil samples in single- and binary-solute systems.

Table 4
Fitted results of BDE-47 sorption to three soil samples in single- and binary-solute systems by the Freundlich model

Sorbents		K_f	n	R^2
BDE-47 sorption in single-solute systems				
BH		2.051	1.468	0.986
BN		2.752	1.399	0.981
FN		19.883	0.828	0.991
BDE-47 sorption in binary-solute systems				
BH	BDE-47+BDE-99 (10 μg L^{-1})	1.495	1.534	0.970
	+BDE-99 (20 μg L^{-1})	1.356	1.505	0.960
	+BDE-99 (30 μg L^{-1})	1.208	1.496	0.955
BN	BDE-47+BDE-99 (10 μg L^{-1})	1.508	1.505	0.952
	+BDE-99 (20 μg L^{-1})	1.750	1.374	0.956
	+BDE-99 (30 μg L^{-1})	1.241	1.409	0.971
FN	BDE-47+BDE-99 (10 μg L^{-1})	19.626	0.803	0.970
	+BDE-99 (20 μg L^{-1})	17.419	0.815	0.976
	+BDE-99 (30 μg L^{-1})	10.515	0.910	0.961

Moreover, hydrophobicity was considered to be the major mechanism for BDE-47 sorption onto soils. Sorption was influenced by the physicochemical properties of BDE-47, TOC and the amorphous structure of organic matters. Liu et al. proposed that the different sorption behaviors corresponded to the soil organic fraction that had an amorphous and condensed structure [34]. Olshansky et al. found that in addition to the amount of SOM, its structure and properties also affect the sorption of PBDEs [38]. The relevant studies indicated that the adsorption mechanism for hydrophobic organic compounds of SOM is different when the liquid phase equilibrium concentrations are changed. At a low concentration, the surface microporosity term, which represents a pore-filling mechanism, contributed significantly to this relationship. When the concentration increased, surface functionality related to surface adsorption became more dominant [35].

Northcott et al. suggested that a considerable fraction of polycyclic aromatic hydrocarbons (PAHs) assumed in previous studies may have been sequestered with the organic carbon and, to a lesser extent, mineral phases of soil. Northcott et al. also found a positive correlation between adsorbing quantities of polychlorinated biphenyls (PCBs) and the organic matter content of soils [39]. PCBs are a group of POPs. PCBs in the environment are ultimately deposited in soil. The adsorption process of PCBs in soil has received considerable attention as one of the most important processes affecting the mobility, degradation, and biological activity of PCBs in the environment. The content of SOM significantly influences the adsorption process. Soils with more organic matter adsorb PCBs faster. These research demonstrated that soil with smaller particles has a better adsorption ability, while the relation with the adsorption rate was unmarked [24,40]. Because PCBs and PBDEs share similar properties, the adsorption ability of BDE-47 was improved when SOM was increased.

3.3. BDE-47 desorption in single- and binary-solute systems

The sorption (n_s) and desorption (n_d) isotherm data (Figs. 5–7) for three soil samples allows the ratio of n_d/n_s, defined as the HI, to be calculated (Table 5), where HI < 1 represents the significance of hysteresis

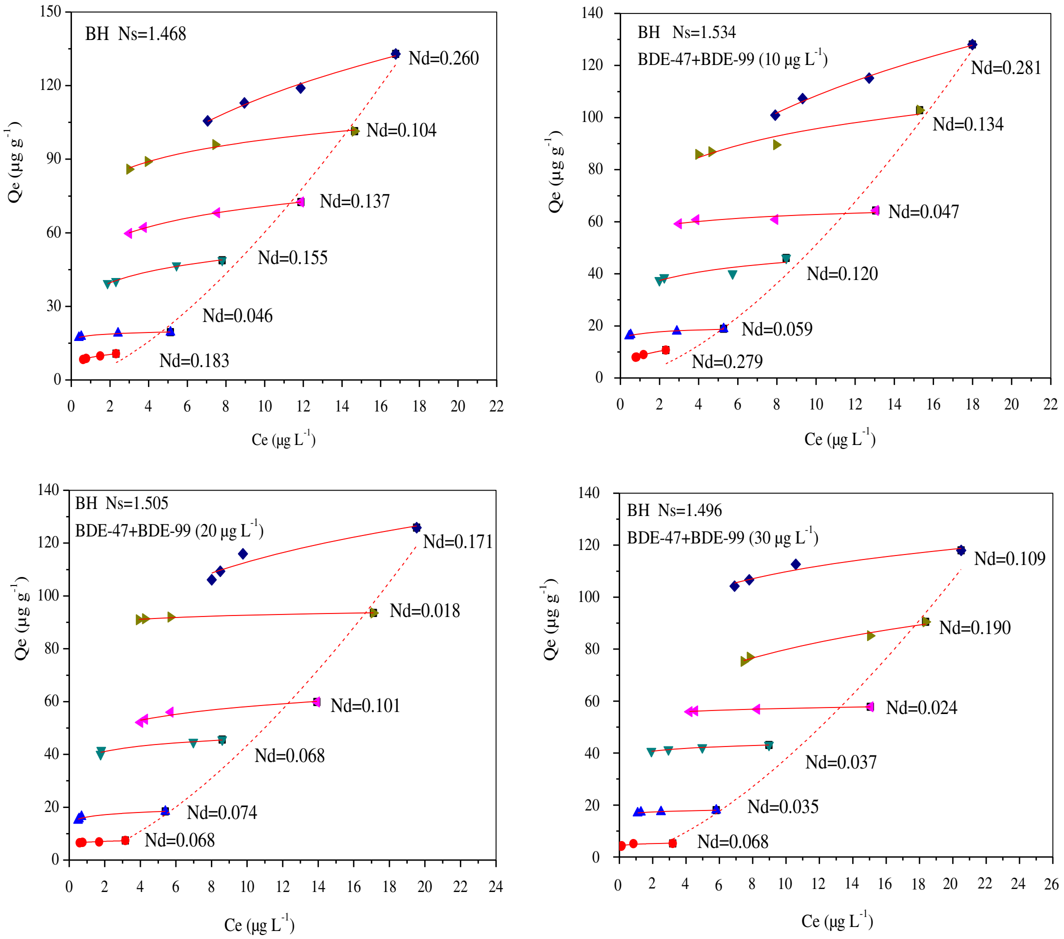

Fig. 5. Desorption of BDE-47 onto BH in single- and binary-solute systems.

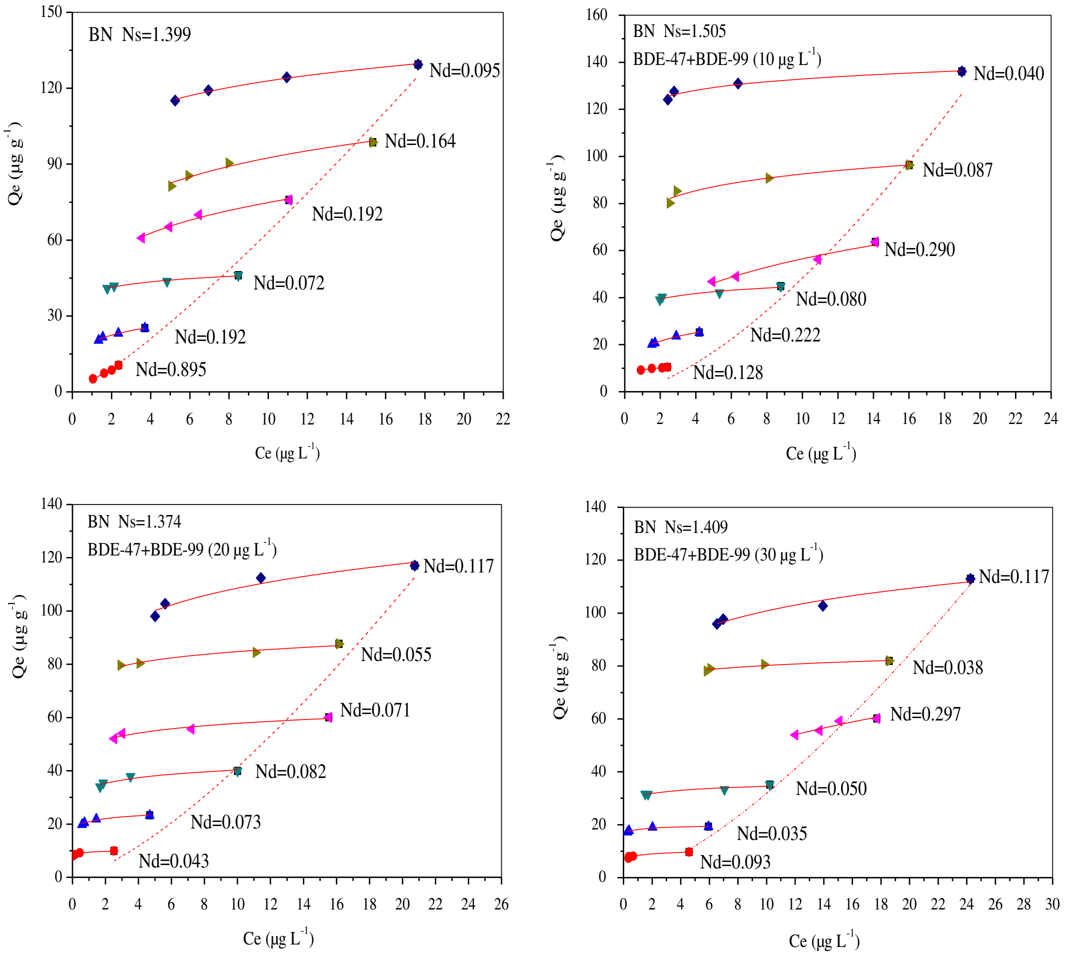

Fig. 6. Desorption of BDE-47 onto BN in single- and binary-solute systems.

and the smaller HI corresponds to the greater degree of hysteresis [33]. In single-solute systems, desorption hysteresis was observed in all three soils, with HI values ranging from 0.031 to 0.640. In almost all cases of FN, the value of HI decreased when the concentrations of BDE-47 increased, indicating that desorption hysteresis was enhanced. BN demonstrated similar HI properties as FN, except for the concentration of 20 μg L^{-1}. However, BH showed no obvious regularity. In binary-solute systems, the presence of BDE-99 strengthened desorption hysteresis, with HI values decreasing to 0.012–0.290. Finally, for BH, when the concentration of BDE-47 remained the same and the concentration of BDE-99 increased, the HI value decreased, elucidating the enhancement of desorption hysteresis.

The desorption isotherms of BDE-47 deviated significantly from the adsorption isotherms, indicating that the desorption process of soil was not the simple reverse of the corresponding adsorption process. Because adsorption was irreversible, PBDEs could potentially accumulate in the topsoil layer [38]. Desorption of BDE-47 was obvious hysteresis, which may be related to the heterogeneity of SOM and the existence of tiny pores in soil micelles. As a variety of action mechanisms exist between PBDEs and soils, the PBDEs adsorbed by soils could be classified into two states: easy desorption and difficult desorption. Distribution was predominant in the easy desorption state, corresponding to fast adsorption and desorption unit kinetics. The difficult part was mainly adsorbed by pore-filling effect and surface forces, corresponding to slow adsorption and desorption unit kinetics [41,42]. Meanwhile, the effect of pore-filling gave priority to BDE-47 adsorption at low concentration because the adsorbate molecule was wrapped in the pore, making it difficult to desorb. Distribution had the advantage in high concentrations, making it easy to desorb. Hence, soil desorption hysteresis increased when the concentrations rose.

Several previous studies observed that desorption processes of BDE-47 from soils could be classified into

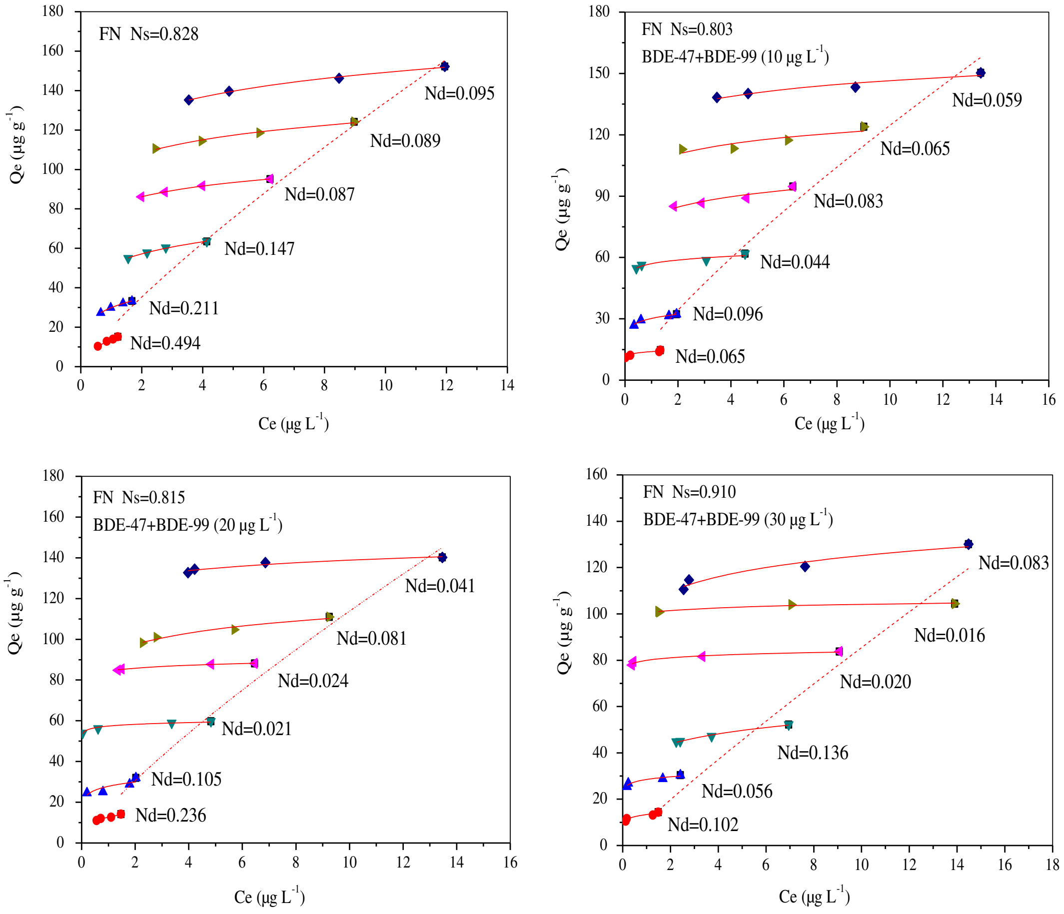

Fig. 7. Desorption of BDE-47 onto FN in single- and binary-solute systems.

Table 5
HI for BDE-47 desorption in single- and binary-solute systems

Sorbents		Initial concentrations ($\mu g\ L^{-1}$)					
HI for BDE-47 desorption in single-systems							
		5	10	20	30	40	50
BH		0.125	0.031	0.106	0.093	0.071	0.177
BN		0.640	0.137	0.051	0.137	0.117	0.068
FN		0.597	0.255	0.178	0.105	0.107	0.115
HI for BDE-47 desorption in binary-systems							
BH	BDE-47+BDE-99 (10 $\mu g\ L^{-1}$)	0.182	0.038	0.078	0.031	0.087	0.183
	+BDE-99 (20 $\mu g\ L^{-1}$)	0.045	0.049	0.045	0.067	0.012	0.114
	+BDE-99 (30 $\mu g\ L^{-1}$)	0.045	0.023	0.025	0.016	0.127	0.073
BN	BDE-47+BDE-99 (10 $\mu g\ L^{-1}$)	0.085	0.148	0.053	0.193	0.058	0.027
	+BDE-99 (20 $\mu g\ L^{-1}$)	0.031	0.053	0.060	0.052	0.040	0.085
	+BDE-99 (30 $\mu g\ L^{-1}$)	0.066	0.025	0.035	0.211	0.027	0.083
FN	BDE-47+BDE-99 (10 $\mu g\ L^{-1}$)	0.081	0.120	0.055	0.103	0.081	0.073
	+BDE-99 (20 $\mu g\ L^{-1}$)	0.290	0.129	0.026	0.029	0.099	0.050
	+BDE-99 (30 $\mu g\ L^{-1}$)	0.112	0.062	0.149	0.022	0.018	0.091

an initially fast and subsequently slow desorption. Liu et al. observed that the contribution of rapid desorption was relatively high in the early stage, gradually decreasing and ultimately becoming negligible fraction after 24 or 48 h, while slow desorption was predominant throughout the whole procedure [42]. Linear behavior was dominant at the initial stage; however, nonlinear characteristics gradually prevailed. The nonlinearity of desorption by n_d was apparently less than 1.0. Our research found the same results. In addition, during the three desorption processes of BDE-47, the reduction of the adsorption capacity gradually decreased, indicating that the speed of desorption became slower. The first desorption hysteresis was not obvious, but after three consecutive desorptions, it was difficult for BDE-47 to be desorbed from soils, indicating the significance of hysteresis. Olshansky et al. suggested that humin should be a major sorbent for PBDEs in soils because of a higher organic carbon content than bulk soils. However, compared to humin, bulk soils obtained a pronounced desorption hysteresis [38]. In the present paper, the SOM for FN was more than four times higher than for BH, and obvious desorption hysteresis was presented in FN in single-solute systems. Nevertheless, significant hysteresis was shown in BH with the presence of BDE-99 in binary-solute systems. Dissolved organic matter released from soil organic carbon may be one of the major factors influencing the desorption properties of the soil samples [43].

4. Conclusions

In this study, BDE-47 sorption and desorption onto and from different river- and farmland-based aquifer media were studied. It was concluded that the fast sorption made a dominant contribution to the total sorption amount in the whole process. Because of the high content of SOM, FN demonstrated the largest sorption ability for BDE-47. Considering the hydrophobicity of BDE-47, SOM was determined to supply most of the sorption domains. Compared to BDE-47, BDE-99, with its higher hydrophobicity, was proposed to adsorb to soils with larger sorption capacities, accounting for its stronger affinity with sorption sites in binary-solute systems. When the concentrations of BDE-99 were greater, the BDE-47 sorption capacity was significantly decreased, a tendency that became more obvious when the concentrations of BDE-47 were high. Soil desorption hysteresis was enhanced when the BDE-47 concentrations rose. Meanwhile, with the coexistence of BDE-99 and at greater concentrations of BDE-99, desorption hysteresis increased, as indicated by the smaller values of HI. These results could help predict a potential pathway for removing PBDEs and reducing the ecological risks of PBDEs when using reclaimed municipal wastewater.

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