



Influences of binding to dissolved organic matter on hydrophobic organic compounds in a multi-contaminant system: Coefficients, mechanisms and ecological risks



Yi-Long Li^a, Wei He^a, Wen-Xiu Liu^a, Xiang-Zhen Kong^a, Bin Yang^a, Chen Yang^a, Fu-Liu Xu^{a,b,*}

^a MOE Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871, China

^b Research Centre for Water Sciences, Peking University, Beijing, 100871, China

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ABSTRACT

The complexation flocculation (CF) method was successfully employed to identify binding coefficients (K_{doc}) of specific organic contaminants to dissolved organic matter (DOM, often indicated by dissolved organic carbon, DOC) in a multi-contaminant hydrophobic organic contaminant (HOC) system. K_{doc} values were obtained for most of the evaluated 33 HOCs, indicating the feasibility and applicability of the CF method in a multi-contaminant system. Significant positive correlations were observed between binding coefficients and octanol–water partition coefficients (K_{ow}) for organic halogen compounds, such as polybrominated diphenyl ethers (PBDEs) ($R^2 = 0.95$, $p < 0.05$) and organic chlorine pesticides (OCPs) (methoxychlor excluded, $R^2 = 0.82$, $p < 0.05$). The positive correlations identified between the $\lg K_{doc}$ and $\lg BCF$ (bioconcentration factor) for PBDEs and OCPs, as well as the negative correlation observed for polycyclic aromatic hydrocarbons (PAHs), indicated that different binding or partition mechanisms between PAHs and organic halogen compounds exist. These differences further result in discriminative competition partitions of HOCs between DOM and organisms. Assuming that only freely dissolved HOCs are bioconcentrative, the results of DOM-influenced bioconcentration factor (BCF_{DOM}) and DOM-influenced lowest observed effect level ($LOEL_{DOM}$) indicate that the ecological risk of HOCs is decreased by DOM.

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1. Introduction

Hydrophobic organic contaminants (HOCs) are a group of chemicals that are toxic to humans and pose potential risks to the ecosystem. In an aquatic environment, the fate, transport and risk of HOCs are influenced by interactions with dissolved organic matter (DOM) (Cho et al., 2002; Laor and Rebhun, 1997; Moeckel et al., 2013). DOM has a major impact on the transport of HOCs in surface water and groundwater by enhancing solubility of contaminants (Yu et al., 2011). In most cases, the presence of DOM diminishes the bioavailability of HOCs. Studies demonstrate that DOM mitigates the bioconcentration factor (BCF) and biotoxicity of several HOCs for various organisms, including invertebrates,

terrestrial plants, and vertebrates (Bejarano et al., 2005; Chen et al., 2008; Haitzer et al., 1998; Landrum et al., 1987; Yang et al., 2006). Furthermore, DOM can alter photolysis and transformation rates of organic pollutants (Ajoud et al., 2003; Burns et al., 1996). Binding of HOC to DOM is regarded as the most likely mechanism explaining these interactions (Burns et al., 1996; Krop et al., 2001) because only freely dissolved compounds are assumed to be taken up and accumulated by organisms (Gourlay et al., 2003; Haitzer et al., 1999).

Experimental determination of binding coefficients (K_{doc}) of HOCs began in the 1970s (Krop et al., 2001) and has become a subject of intense interest due to the need to monitor and control HOCs. Initially, studies investigated PAHs (e.g., pyrene and naphthalene), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) (Carter and Suffet, 1982; Chiou et al., 1986; Cho et al., 2002; Laor and Rebhun, 1997; McCarthy and Zachara, 1989). Additionally, di-(2-ethylhexyl) phthalate (DEHP) was the only compound studied in

* Corresponding author. MOE Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871, China.

E-mail address: xufl@urban.pku.edu.cn (F.-L. Xu).

the phthalic acid ester (PAE) class (Carter and Suffet, 1983). As a result of increasing awareness regarding emerging contaminants, the binding coefficients of a variety of other contaminants are currently being investigated. These contaminants include polybrominated diphenyl ethers (PBDEs) (Kuivikko et al., 2010; Wang et al., 2011), other PAEs (Yamamoto et al., 2003), endocrine disruptors (Lee et al., 2011; Yamamoto et al., 2003), synthetic pyrethroids (Delgado-Moreno et al., 2010), pharmaceuticals and personal care products (Maoz and Chefetz, 2010), and other pollutants (e.g., naphthol (Ahmed et al., 2012)).

Various methods, including solubility enhancement (Chiou et al., 1986), membrane dialysis (Carter and Suffet, 1982), fluorescent quenching (Backhus and Gschwend, 1990), solid-phase microextraction (Wang et al., 2011), and complexation flocculation (Laor and Rebhun, 1997), have been developed to determine K_{doc} values. These methods each have advantages and limitations. Generally, a simple HOC-DOM interaction system includes only one pure HOC is utilized to determine the binding coefficient. Recently, multi-contaminant systems in which more than one HOC is present have been intensively investigated because a combination of pollutants more closely represents the real environment (Moeckel et al., 2013; Wang et al., 2011). Complexation flocculation was considered to be suitable for all classes of compounds in a multi-contaminant system (Krop et al., 2001).

In previous multi-contaminant systems, the researchers have primarily investigated only a specific group of chemical species, such as PAHs (Moeckel et al., 2013), and little attention was devoted to other existing chemicals. Therefore, the values obtained could provide only limited information concerning multi-contaminant circumstances. No studies are currently available for K_{doc} determination in a multi-contaminant system with different groups of chemical species. A set of updated K_{doc} s would better reflect the real environment and would provide a more accurate means of monitoring and forecasting the fate of HOCs. Moreover, due to the binding behavior of HOCs with DOM, their BCFs and ecotoxicity may be altered (Bejarano et al., 2005; Haitzer et al., 1998; Landrum et al., 1987; Yang et al., 2006; Zhang et al., 2011). In addition, the BCF is influenced by DOM (BCF_{DOM}) and ecotoxicity. For instance, the lowest observed effect level (LOEL) is affected by DOM ($LOEL_{DOM}$). These influences have seldom been evaluated and warrant further study. Overall, the objectives of this paper are to 1) calculate binding coefficients in a multi-contaminant system using the CF method, 2) investigate correlations between K_{doc} and properties of HOCs (e.g., K_{ow} , BFC, and LEOL), and 3) evaluate the real BCF_{DOM} and $LOEL_{DOM}$ under the influence of DOM.

2. Materials and methods

2.1. Reagents and chemicals

In total, five PAHs (fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BAA), chrysene (CHR), and benzo[k]fluoranthene (BKF)), four PAEs (dihexyl phthalate (DnHP), hexyl 2-ethylhexyl phthalate (HEHP), dicyclohexyl phthalate (DCHP), and di-n-propyl phthalate (DPP)), eleven PBDEs (BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, and 154) and thirteen organochlorine pesticides (OCPs) (α -HCH, γ -HCH, δ -HCH, aldrin, γ -chlordane, *o*, *p*'-DDE, α -endosulfan, α -chlordane, *p*, *p*'-DDE, *o*, *p*'-DDD, *p*, *p*'-DDD, *p*, *p*'-DDT, and methoxychlor) were selected. All selected HOCs were in solution and purchased from AccuStandard Inc. (New Haven, CT, USA). Lake humic acid (HA) reference (1R105H) was selected as the experimental DOM and obtained from the International Humic Substances Society (<http://www.humicsubstances.org/>). All other solvents and chemicals were of gas chromatography grade or analytical grade.

The stock solution (20 mg-C/L) was prepared by fully dissolving the HA in ultrapure water and subsequently diluted to 5 different proportions (1/5, 2/5, 3/5, 4/5, and 5/5 of the original concentration). The pH of each solution was adjusted to 6.00 ± 0.05 by 0.1 mol L^{-1} NaOH and 0.05 mol L^{-1} H_2SO_4 , and the ionic strength was adjusted to 0.5 mequiv/L by 0.5 mmol L^{-1} NaHCO_3 . A coagulant solution of aluminum sulfate (40 g L^{-1} $\text{Al}_2(\text{SO}_4)_3$) was prepared for the flocculation experiments (Laor and Rebhun, 1997; Moeckel et al., 2013).

2.2. Binding experiments

The flocculation experiment was performed according to procedures in Laor and Rebhun (1997) and was slightly modified for the multi-contaminant system. Each binding experiment was performed in 20-mL glass bottles sealed with Teflon® caps. After preparing working solutions of HOCs, the multi-contaminant system was prepared by adding selected HOCs (40 ng of each PAH, 50 ng of each PAE, 10 ng of each PBDE, and 20 ng of each OCP) into the bottles. After evaporating the HOC solvent (*n*-hexane) to near dryness, the bottles were filled with the respective HA solutions and the reference solution. The bottles were later shaken (180 rpm) in a dark box at room temperature ($25 \text{ }^\circ\text{C}$) for 48 h, and 20 μL of the coagulant solution was added to each bottle. To achieve a sufficient flocculation reaction, the samples were shaken on a vortex mixer (1 min) and a shaker (60 rpm for 2 h). The samples were subsequently allowed to stand for 2 h. Next, the bottles were centrifuged (4500 rpm) for 20 min to separate the free and bound HOCs. More than 95% of organic carbon was removed in this way. Free HOC in the supernatant was extracted using dichloromethane (20 mL, 3 times). After removing the water, samples were reduced to 1 mL on a rotary evaporator, and 10 mL *n*-hexane was added to change the matrix. Finally, the *n*-hexane solutions were reduced to 1 mL, blown down to 0.5 mL under a gentle stream of nitrogen, and transferred to small amber vials before GC–MS analysis.

2.3. Instrument analysis

The total organic carbon concentration of each HA solution was measured by a total organic carbon analyzer (TOC-VWP, Shimadzu, Japan). PAHs and PAEs were analyzed by Agilent 6890GC-5973 inert mass detector (MSD) with an electron impact source. OCPs and PBDE were analyzed by Agilent 7890GC-5975C MSD with a negative chemical ionization source. The instrument conditions, the ions selected for identification/quantification, and the instrument limit(s) of detection are referred to in previous studies (He et al., 2013, 2014). All of the glassware was cleaned in an ultrasonic cleaner and baked at $450 \text{ }^\circ\text{C}$ for 6 h. The samples and blanks in each binding experiment were performed in triplicate. The samples were corrected by blanks accordingly.

2.4. Binding coefficient calculations

The binding coefficients (K_{doc} , L/kg-C) are calculated using the following equation (Laor and Rebhun, 1997):

$$\left(\frac{C_{\text{free+bound}}}{C_{\text{free}}} \right) / C_{\text{free}} = 1 + K_{\text{doc}}[\text{DOC}] \quad (1)$$

where C_{free} is the free concentration of HOCs as determined by the results for HA solutions, $C_{\text{free+bound}}$ is the total concentration represented by the results for reference solutions, and [DOC] is DOC concentration in mg-C/L.

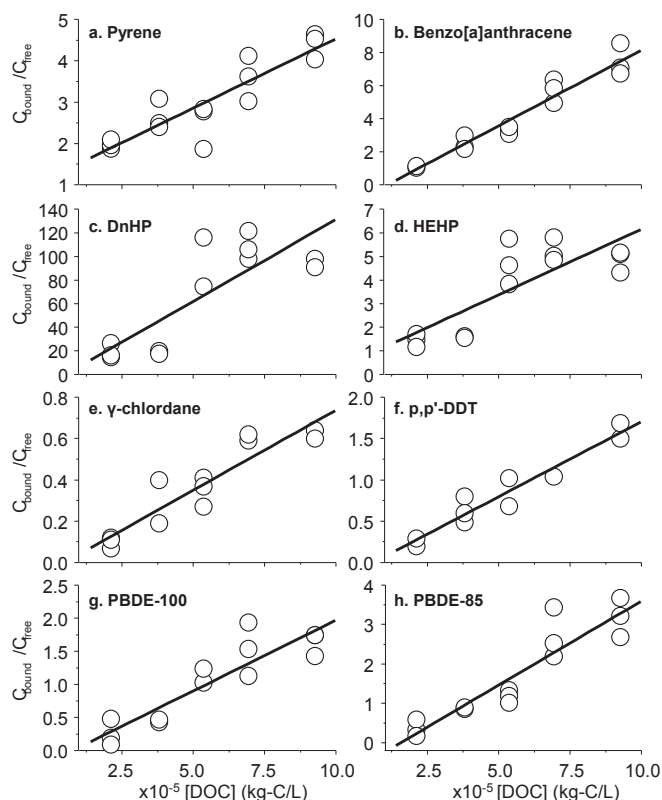


Fig. 1. Linear relationship between $C_{\text{bound}}/C_{\text{free}}$ and [DOC] for different groups of HOCs.

3. Results and discussion

3.1. Binding coefficients in a multi-contaminant system

The linear relationship between concentration ratios ($C_{\text{bound}}/C_{\text{free}}$) of selected HOCs and DOC concentration ([DOC]) are constructed in Fig. 1 and binding coefficients were calculated in Table 1. The binding coefficients of selected HOCs in references are also summarized in Table 1. Significant positive correlations were found between $C_{\text{bound}}/C_{\text{free}}$ and DOC in all 33 contaminants ($p < 0.05$). In the PAH group, the binding coefficient ($\lg K_{\text{doc}}$) of chrysene (CHR: 6.63 ± 0.07) is out of the literature range, whereas $\lg K_{\text{doc}}$ values of the other four PAHs are within the range (Krop et al., 2001; Laor and Rebhun, 1997; Wang et al., 2011). Nevertheless, K_{doc} values determined using various DOMs were different as indicated by inconsistent K_{doc} values between HA in this study and Aldrich HA in Laor and Rebhun (1997) for fluoranthene and pyrene. For OCPs, the correlation coefficient (R^2) ranged from 0.47 to 0.94. Unlike PAHs, most OCPs have limited referenced binding coefficients, except for p, p'-DDT and lindane (γ -HCH). The $\lg K_{\text{doc}}$ values of p, p'-DDT and γ -HCH were higher than the reference medians (4.80 and 2.78, respectively). Moreover, the $\lg K_{\text{doc}}$ of γ -HCH using CF was over two times as large as the solubility enhancement (Chiou et al., 1986). The R^2 for PBDE congeners in this study varied from 0.38 to 0.84. Only several studies of the K_{doc} values for PBDE have previously been performed, primarily on BDE-47 and BDE-99, and K_{doc} values of four PBDEs (BDE-17, -71, -85, and -138) obtained in our study were not reported previously. For both BDE-47 and BDE-99, our results were lower than all results reported by Wang et al. (2011); that study employed SPME and sedimentary DOM. Our results were higher than those reported by Wei-Haas et al. (2014) and Kuivikko et al. (2010), whose studies utilized dialysis and solubility

enhancement with various aquatic DOMs. The K_{doc} values of all four PAEs are first reported in our study with R^2 range from 0.36 to 0.83, which exhibited the potential to be useful reference values in the future. In summary, the K_{doc} of specific HOCs were successfully measured by the CF method. However, we should note that different methods and DOMs with the various sources utilized may result in this discrepancy of K_{doc} for the same HOC.

3.2. Correlation between K_{doc} with K_{ow}

Many studies have determined that a linear relationship exists between K_{doc} and the octanol–water partition coefficient (K_{ow}) of various hydrophobic compounds (Krop et al., 2001; Mott, 2002) as follows:

$$\lg K_{\text{doc}} = a + b \cdot \lg K_{\text{ow}} \quad (2)$$

where a and b are fitting coefficients derived from regression of $\lg K_{\text{doc}}$ and $\lg K_{\text{ow}}$.

There were significant correlations ($R^2 > 0.70$, $p < 0.05$) between the $\lg K_{\text{doc}}$ and the $\lg K_{\text{ow}}$ (Table 1) for PAHs, OCPs, and PBDEs (Fig. 2a). However, the regression of PAH congeners was not as good as the OCPs and PBDEs, which may be caused by the relatively small sample size ($n = 5$). This linear curve was not adequate for the prediction of K_{doc} for other PAHs. Good linear relationships ($R^2 = 0.95$, $p < 0.00001$) were found in the PBDE groups, which were more reliable than results in Wang et al. (2011). In that study, the K_{doc} of 8 PBDE congeners using 4 sedimentary DOMs was investigated (average of R^2 values, 0.34; R^2 values for each DOM are 0.90, 0.26, 0.34 and -0.04). In addition, the K_{doc} of most PBDE congeners were not determined. Therefore, the fitting formula in our study can assist in predicting K_{doc} values of other congeners within the linearity range. Furthermore, the involved DOM should have similar properties as ours. For the OCP class, methoxychlor is not collinear with the other compounds (Fig. 2a), which is most likely observed because the methoxy moiety influences the binding site and mechanism of the different K_{ow} source. Care was taken to use the K_{ow} values from the same source to minimize regression error for each HOC class. For the OCP class, most K_{ow} values are the final adjusted values (FAV) from Xiao et al. (2004) and Shen and Wania (2005). In these studies, the literature-derived values (LDV, Table 1) are also provided. However, there were no significant differences between FAV and LDV when they were used to test for correlation between $\lg K_{\text{ow}}$ and $\lg K_{\text{doc}}$. Finally, we excluded methoxychlor from the linear regression, and the correlation was more favorable (FAV, $R^2 = 0.82$, $p < 0.0001$; LDV, $R^2 = 0.81$, $p < 0.0001$). However, the linear equation presented in this study should be employed cautiously when extrapolating other OCPs because OCPs do not have similar structures as PBDEs. Nevertheless, this formula does describe the studied OCPs successfully. Furthermore, the uncertainty of the potentially different binding mechanisms must be considered. This uncertainty will be addressed in future work.

We also examined the regression of $\lg K_{\text{ow}}$ and $\lg K_{\text{doc}}$ for all of the HOCs selected in our study (line e, Fig. 2b). Although a significant positive correlation ($p = 0.0159 < 0.05$) was observed, equation e cannot be applied for accurate prediction because of the small R^2 (0.15). Two linear relationships can be observed in Fig. 2a: one primarily consists of the PAH data, and the other consists of PBDEs and OCPs (methoxychlor excluded). These differences indicate that the binding mechanism of PAHs differs from the mechanism of the organic halogenide (PBDEs and OCPs). The linear regression of line f in Fig. 2b (FAV, $R^2 = 0.90$, $p < 0.00001$) supports the hypothesis that PBDEs and OCPs display similar binding mechanisms or sites in this experimental multi-contaminant

Table 1
Observed binding coefficients ($\lg K_{\text{doc,obs}}$) of selected HOCs to HA in mixed system, reference K_{doc} ($\lg K_{\text{doc,ref}}$, median values in Table S1) and corresponding octanol–water partition coefficient (K_{ow}).

	$\lg K_{\text{doc,obs}}$	R^2	p -value	Reference range	$\lg K_{\text{doc,ref}}$	Detection limits (ng/mL)	$\lg K_{\text{ow}}$
PAHs							
FLU	5.35 ± 0.07	0.82	0.0001	3.50–5.60	4.90	0.02	5.16
PYR	5.53 ± 0.06	0.69	<0.0001	3.24–5.69	4.76	0.02	4.88
BAA	5.96 ± 0.03	0.88	<0.0001	4.14–6.28	5.36	0.03	5.76
CHR	6.63 ± 0.07	0.69	0.0123	3.50–5.60	4.67	0.03	5.81
BKF	6.62 ± 0.07	0.78	0.0001	4.43–6.80	5.16	0.06	6.11
PAEs							
DnHP	7.14 ± 0.09	0.45	0.0036	N.A.	7.14	0.05	6.30
HEHP	5.75 ± 0.08	0.44	0.0044	N.A.	5.75	0.07	N.A.
DCHP	4.92 ± 0.23	0.36	0.0400	N.A.	4.92	0.04	5.60
DPP	4.94 ± 0.08	0.83	0.001	N.A.	4.94	0.03	3.27
PBDEs							
PBDE-17	4.63 ± 0.06	0.76	<0.0001	N.A.	N.A.	0.03	5.74
PBDE-28	4.73 ± 0.08	0.64	0.0003	3.97–6.81	5.68	0.04	5.94
PBDE-47	5.11 ± 0.06	0.77	0.0004	4.04–6.19	4.75	0.05	6.81
PBDE-66	5.35 ± 0.06	0.77	<0.0001	6.05–6.78	6.48	0.07	6.77
PBDE-71	5.08 ± 0.06	0.77	<0.0001	N.A.	N.A.	0.04	6.77
PBDE-85	5.63 ± 0.05	0.84	<0.0001	N.A.	N.A.	0.09	7.66
PBDE-99	5.41 ± 0.06	0.79	<0.0001	4.47–6.35	5.1	0.08	7.31
PBDE-100	5.33 ± 0.05	0.81	<0.0001	6.08–6.99	6.70	0.08	7.24
PBDE-138	5.94 ± 0.10	0.56	0.0032	N.A.	N.A.	0.12	8.55
PBDE-153	5.64 ± 0.16	0.38	0.0143	5.00–7.24	6.43	0.07	7.90
PBDE-154	5.65 ± 0.07	0.7	0.0001	6.35–7.20	7.14	0.10	7.82
OCPs							
α -HCH	4.57 ± 0.04	0.94	0.0052	N.A.	N.A.	0.03	3.81/3.94
γ -HCH	4.16 ± 0.13	0.47	0.0171	1.5–4.41	2.78	0.03	3.70/3.83
δ -HCH	4.24 ± 0.11	0.51	0.0054	N.A.	N.A.	0.03	4.17
Aldrin	4.93 ± 0.07	0.78	0.0002	5.05	5.05	0.08	6.5/6.24
α -Chlordane	4.93 ± 0.08	0.74	0.0119	4.77	4.77	0.03	6.1/6.2
γ -Chlordane	4.91 ± 0.05	0.89	0.0022	4.64–6.98	5.30	0.04	6.23/6.27
α -Endosulfan	4.30 ± 0.12	0.52	0.0246	N.A.	N.A.	0.03	4.74/4.94
o, p' -DDE	4.95 ± 0.08	0.74	0.0036	N.A.	N.A.	0.06	6.00
p, p' -DDE	5.30 ± 0.08	0.73	0.0195	4.87–5.45	5.05	0.07	6.96/6.93
o, p' -DDD	4.91 ± 0.11	0.48	0.0076	N.A.	N.A.	0.04	5.87
p, p' -DDD	5.15 ± 0.08	0.69	0.0003	N.A.	N.A.	0.03	6.22/6.33
p, p' -DDT	5.30 ± 0.04	0.92	0.0008	3.79–5.88	4.80	0.05	6.28/6.39
Methoxychlor	6.00 ± 0.05	0.92	0.0176	N.A.	N.A.	0.14	5.08

Notes: FLU – Fluoranthene, PYR – Pyrene, BAA – Benz[a]anthracene, CHR – Chrysene, BKF – Benzo[k]fluoranthene; the reference range consists of the binding coefficients reported since the 1990s, regardless of the determination method and types of DOC; N.A. = not available; K_{ow} values of OCPs in various references are shown in FAV/LDV and their references are included in Table S1.

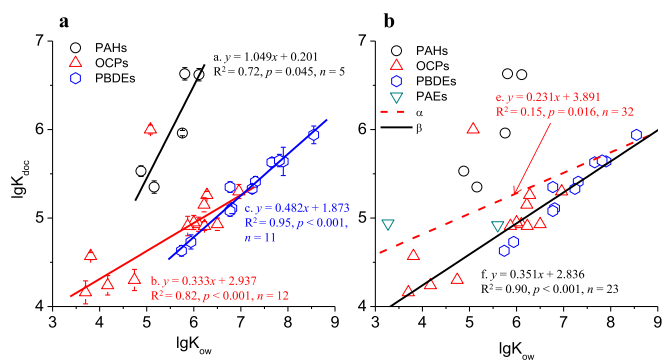


Fig. 2. Linear regression of the $\lg K_{\text{doc}}$ and $\lg K_{\text{ow}}$ of PAHs, PBDEs, OCPs, and all HOCs selected. Line a, b, and c in Chart a were linear curves of PAHs, PBDEs, and OCPs, respectively. Line e and f in Chart b were linear curves of all HOCs and halogen compounds (OCPs and PAHs) in our study, respectively.

system. Because both PBDEs and OCPs contain halogens, these halogens may be key in determining their binding sites for the HA DOM. Furthermore, the linearity range of line f (Fig. 2b) is larger than the equations for the PBDEs and OCPs (Fig. 2a), indicating that equation determined by line f can be utilized to expand the estimation range of organic halogenides. However, the uncertainty will increase due to being out of range. PAHs display higher K_{doc} values

than PBDEs and OCPs with similar K_{ow} values in Fig. 2b, suggesting that PAHs can more easily bind to DOM in the multi-contaminant system and potentially in the environment, which has also been observed in previous K_{doc} studies of solo-polluted systems (Akkanen et al., 2004; Cho et al., 2002). This affinity difference may result from the following: (1) halogenated compounds associate with a different fraction of DOM than PAHs (Akkanen et al., 2004), (2) the electron withdrawing ability of Br/Cl atoms influences interactions between the halogenated compounds and DOM (Nuerla et al., 2013) and (3) different steric configurations (Cho et al., 2002). However, due to limited studies of the binding of PBDEs to DOM, this mechanism remains largely unknown and needs to be explored in future studies.

3.3. Bioconcentration factor influenced by DOM

The bioconcentration factor (BCF) expresses the degree to which bioconcentration occurs (Arnot and Gobas, 2006). The BCF is calculated as the ratio of the concentration of a chemical in an organism to its concentration in water (Eq. (3)). Arnot and Gobas (2006) summarized the BCF of 842 organic chemicals in 219 aquatic species, including a large number of the HOCs selected for this study. Therefore, we adopted these researchers' summarized data for this report. However, this study did not report BCF values of PBDEs. Therefore, we also used data from Mansouri et al. (2012) for

Table 2
The $\lg K_{\text{doc}}$ - $\lg \text{BCF}$ relationship of HOC groups.

HOCs		<i>p</i>	<i>r</i>	HOCs		<i>p</i>	<i>r</i>
PAHs	Median	0.625	-0.214	PAHs (BKF excluded)	Median	0.009	0.974
	Mean	0.741	-0.277		Mean	0.033	0.903
	Geomean	0.838	-0.312		Geomean	0.053	0.845
PBDEs		0.243	0.053	PBDEs (6-brominated excluded)		0.001	0.834
OCPs	Median	0.517	-0.058	OCPs (α -endosulfan and methoxychlor excluded)	Median	0.001	0.777
	Mean	0.507	-0.055		Mean	0.002	0.749
	Geomean	0.781	-0.101		Geomean	0.003	0.701

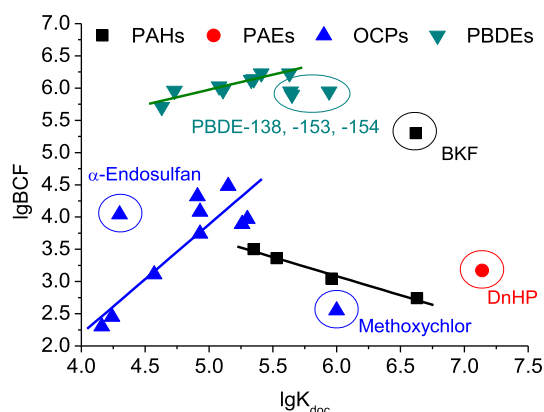


Fig. 3. Correlation between the $\lg K_{\text{doc}}$ and $\lg \text{BCF}$. Linear curves were fitted for PAHs (excluding BKF), OCPs (excluding α -endosulfan and methoxychlor), and PBDEs (PBDE-138, -153, and -154).

PBDEs (both experimental and predicted data). For the other selected HOCs, BCF data were obtained from the U.S. EPA dataset (www.epa.gov/ecotox/). For each HOC, the arithmetic mean, geometric mean and median BCF values of different species and conditions were calculated to examine the relationship between the $\lg K_{\text{doc}}$ and $\lg \text{BCF}$ (Table S2 and Table 2). The soil sorption coefficient (K_{oc}) has often been used to evaluate BCF (Kenaga, 1980); therefore, correlations between K_{doc} and BCF in the aquatic ecosystems may exist.

In our studies, there exists no evident correlation between the two parameters for all of the selected HOCs (Fig. 3 and Table 2, $p > 0.05$). However, for a specific HOC class, such as PAHs, the $\lg K_{\text{doc}}$ and $\lg \text{BCF}$ of FLU, PYR, BAA, and CHR exhibits good negative correlation ($p < 0.05$, Table 2) after excluding BKF, indicating that the binding mechanisms of these compounds to DOM in the multi-contaminant system differs from the binding mechanisms to organisms. This result is similar to previous findings (Kipopoulou et al., 1999; Oleszczuk and Baran, 2005). The deviation for BKF may be caused by the limited number of BCF studies or by a different occurring mechanism. Further studies of the K_{doc} and BCF that include a larger number of PAH congeners will be beneficial in testing this correlation, and studies on the binding site/mechanism are warranted to explain this relationship. Positive correlations between the two parameters can be observed in selected PBDEs and OCPs. We find a significant $\lg K_{\text{doc}}$ - $\lg \text{BCF}$ correlation in PBDE congeners with 3–5 bromines ($p = 0.001 < 0.05$), indicating similar potential partition mechanisms of these PBDEs to DOM and organism tissues. Furthermore, competition partition of PBDEs between DOM and organisms might occur when the organisms are in the water bodies with high levels of organic matter. In the sediment, the PBDEs bound to OM are typically immobile, which reduces the bioavailability and further reduces the partition of PBDEs into biota phases (You et al., 2011). The BCF values of hexa-BDEs (BDE-138, -153, and -154) are excluded due to the general

bilinear correlation pattern for the BCF of PBDEs with the number of halogens in the molecule (Mansouri et al., 2012). Furthermore, PBDEs with 1–5 and 6–10 bromine atoms obey positive and negative linear correlation with the number of bromines or K_{ow} , respectively. The α -endosulfan and methoxychlor does not display collinearity with other contaminants, implying a different molecular binding mechanism. Because only one study reports the BCF value for α -endosulfan, the non-collinear relationship may result from the uncertainty in the BCF values. After excluding those two chemicals, the significant positive correlation between $\lg K_{\text{doc}}$ and $\lg \text{BCF}$ of OCPs also suggests that these compounds have similar binding sites to DOM and organism tissues.

Many studies have shown that the bioconcentration of HOCs generally decreases with increasing DOM concentrations. Nevertheless, one fourth of these studies demonstrate that DOM enhances the bioconcentration of organic chemicals (Haitzer et al., 1998). The influencing mechanism of DOM remains controversial. The generally accepted assumption in the field is that only the free fraction of contaminants is bioavailable (Gourlay et al., 2003; Wang et al., 2014), while the bound fraction is overly large and/or polar to be taken up by aquatic organisms (Landrum et al., 1987; McCarthy and Zachara, 1989). Therefore, we deduced that relationship of BCF and [DOC] as follows:

$$\text{BCF} = C_{\text{bio}}/C_{\text{water}} \quad (3)$$

$$\begin{aligned} C_{\text{free+bound}}/C_{\text{free}} &= (C_{\text{bio}}/C_{\text{free}})/(C_{\text{bio}}/C_{\text{free+bound}}) \\ &= \text{BCF}_{\text{free}}/\text{BCF}_{\text{free+bound}} \end{aligned} \quad (4)$$

$$\text{BCF}_{\text{free}}/\text{BCF}_{\text{free+bound}} = 1 + K_{\text{doc}}[\text{DOC}] \quad (5)$$

$$\text{BCF}_0/\text{BCF}_{\text{DOM}} = 1 + K_{\text{doc}}[\text{DOC}] \quad (6)$$

$$\text{BCF}_{\text{DOM}} = \text{BCF}_0/(1 + K_{\text{doc}}[\text{DOC}]) \quad (7)$$

where BCF_{DOM} is the bioconcentration factor for an HOC in water containing DOM, and BCF_0 is the bioconcentration factor for a chemical in water containing no DOM (Haitzer et al., 1999). As shown in Eq. (4), a relationship exists between $C_{\text{free+bound}}/C_{\text{free}}$ and $\text{BCF}_{\text{free}}/\text{BCF}_{\text{free+bound}}$ ($=\text{BCF}_0/\text{BCF}_{\text{DOM}}$), which further describes the relationship between $\text{BCF}_0/\text{BCF}_{\text{DOM}}$ and [DOC] in Eq. (6). The DOM-influenced BCF (BCF_{DOM}) can be calculated using Eq. (7). In this manner, we succeeded in constructing a quantitative relationship between BCF_{DOM} and BCF_0 . We were also able to correlate K_{doc} and [DOC], which will be useful in predicting the BCF_{DOM} in aquatic ecosystems with high levels of DOC, especially considering that global organic carbon is currently increasing (Monteith et al., 2007). We compared the DOM-influenced BCF of different HOCs in the environment in two scenarios with different DOC concentrations (low: 20 $\text{mg}\cdot\text{C}\cdot\text{L}^{-1}$, high: 50 $\text{mg}\cdot\text{C}\cdot\text{L}^{-1}$) and applied the arithmetic mean BCF values of the dataset (Table S2) as the BCF_0 because the

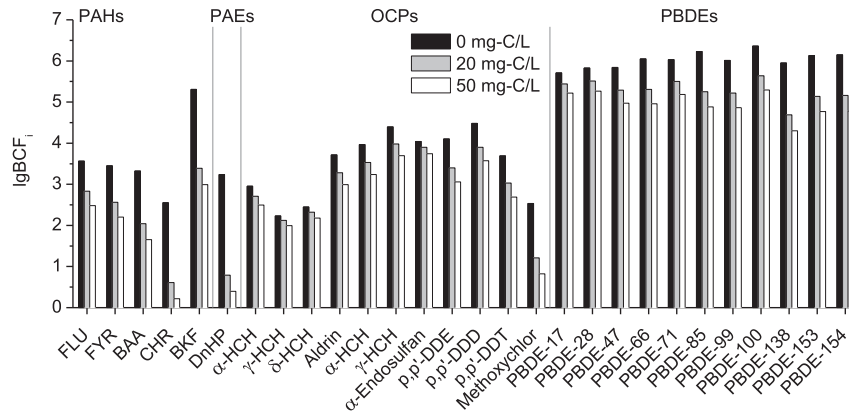


Fig. 4. BCF values of HOCs under different DOM concentrations (0, 20, 50 mg-C/L⁻¹).

majority of the studies have neglected the effect of DOM. Calculated BCF_{DOM} values are provided in Table S3 and Fig. 4.

Although all BCF values decrease with increases of DOM concentration, the extent of the decline is varied. For instance, in scenario I (20 mg-C/L of DOM), the BCF values of CHR, DnHP and methoxychlor decreased by over 50% (75%, 76%, 52%, respectively), whereas γ -HCH, δ -HCH, α -endosulfan, PBDE-17 and PBDE-28 decreased by only approximately 5% of the BCF value. Haitzer et al. (2001) have reported that certain DOMs decrease effects on bioconcentration for different HOCs were not equipotent. However, these studies did not provide a qualitative comparison. The BCF_{DOM} in the present multi-contaminant system, obtained in a qualitative manner, helps to elucidate the evaluation of DOM-affected BCF using a modeling approach. Notably, the calculated results in our study agree with their qualitative description.

3.4. Ecotoxicity influenced by DOM

Considering that the detoxification effect of DOM is not observed in all situations and that most toxicity data is determined without considering the influence of DOM, we assumed that only the freely dissolved form of HOCs are believed to cross membranes by passive diffusion and subsequently become toxicology active after reaching the target site (Chen et al., 2008). As mentioned previously, DOM will decrease the free HOCs concentrations by binding interaction in aquatic ecosystems. This finding indicates that toxicity decreases and is supported by previous research (Bejarano et al., 2005; Yang et al., 2006; Zhang et al., 2011). Therefore, the toxicity parameter of an HOC with regards to DOM

concentration was deduced from Eq. (1) as follows:

$$\text{LOEL}_{\text{DOM}} = \text{LOEL}_0 \times (1 + K_{\text{doc}}[\text{DOC}]) \quad (8)$$

where LOEL_{DOM} is the lowest observed effect level for an HOC in a water environment containing DOM, and LOEL₀ is for a DOM-free environment. Many parameters have been developed to quantify the toxicity of an organic pollutant to organisms, including the half maximal effective concentration (EC₅₀), median effective dose (ED₅₀), lethal concentration to 50% of organisms (LC₅₀), median lethal dose (LD₅₀), no observed effect concentration/level (NOEC/NOEL) and lowest observed effect concentration/level (LOEC/LOEL). To include as many HOCs as possible in this study, LOEC/LOEL values ($\mu\text{g/L}$) were selected from U.S. EPA ECOTOX (www.epa.gov/ecotox/). All values are shown in lgLOEL, and the arithmetic mean, geometric mean and median were calculated in Table S2. Two scenarios (DOM: 20 and 50 mg-C/L) were established to compare the toxicity changes of HOCs in Table S4 and Fig. 5. The arithmetic mean of LOEL values (Table S2) were used as the LOEL.

Although all LOEL values increase DOM concentration, the extents are different. In scenario I (20 mg-C/L of DOM), the LOEL values of CHR, BKF, DnHP and methoxychlor was 10 more times larger than LOEL₀ (87, 84, 278, and 21, respectively), whereas LOEL of γ -HCH, δ -HCH, and α -endosulfan changed only slightly (less than 2 times of LOEL₀). When DOM concentration was increased, the LOEL increased significantly for the HOCs with higher K_{doc} , indicating that DOM should be considered when evaluating the ecological risk of HOCs in natural ecosystems.

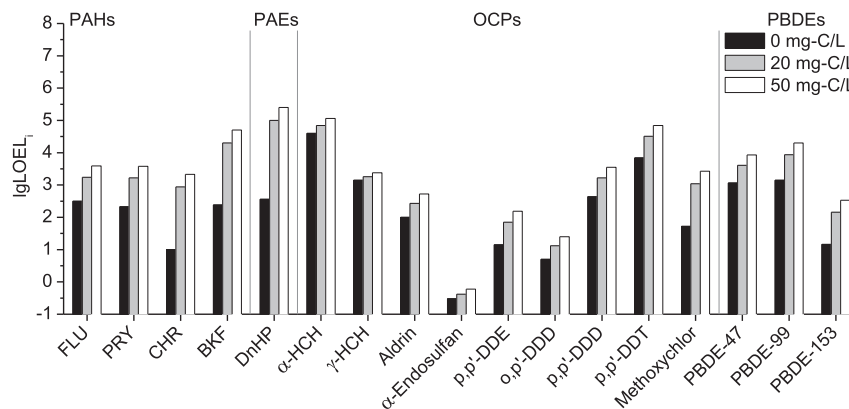


Fig. 5. LOEL values of HOCs under different DOM concentrations (0, 20, 50 mg-C/L⁻¹).

3.5. Implication of K_{doc} in multi-contaminant aquatic ecosystem and future work

K_{doc} can be used to determine the distribution of contaminants between different environmental media and therefore predict their fates and transmission. A theoretical prediction is rather valuable because there are a large number of HOCs, and it is not feasible to test every indicator of HOC properties that are affected by DOM, especially when new chemicals are considered. Importantly, the uncertainty of predictions and the sensitivity of each parameter should be an important consideration in future work. Additionally, the present study does not reflect conditions as accurately as using natural water that contains DOM in its naturally occurring composition. Therefore, we plan to conduct studies that take these factors into account. The parameters BCF and LOEL, which are often used for risk assessment of HOCs in aquatic ecosystem, were employed to test the influence of DOM. To the best of our knowledge, most K_{doc} s are determined in relatively simple systems. However, HOCs exist in a complex composition in natural ecosystems. The apparent K_{doc} s measured in our multi-contaminant system may be considerably closer to the true K_{doc} in the real environment. BCFs were smaller, and LOELs were larger, at higher levels of DOM, indicating that the ecological risk of HOCs are decreased by DOM. Therefore, K_{doc} values should be considered in environmental-like multi-contaminant systems to estimate ecological risks more credibly and to provide potential solutions for contaminant control and remediation (He et al., 2014). The properties and sources of DOM also play a significant role in the binding effect of HOCs (Laor and Rebhun, 1997). In this regard, we have also extracted DOM from a Chinese eutrophic lake (Lake Chaohu) and are preparing to measure the apparent binding effect of more chemicals to DOM from this source, which will further elucidate these effects. Currently, the concentration of DOM is increasing due to acidification and climate change caused by anthropogenic activities, including land use and pollution discharge (Evans et al., 2005; Oulehle and Hruška, 2009; Roulet and Moore, 2006). However, detoxification effects of DOM may reduce the ecological risks of HOCs discharged by humans.

4. Conclusions

This study successfully measured K_{doc} values of several HOCs in a multi-contaminant system by CF methods. Fifteen of the 33 K_{doc} values calculated in this study have not previously been reported. Significant positive correlations between the $\lg K_{doc}$ and $\lg K_{ow}$ were found for organic halogen HOCs (i.e., PBDEs and OCPs) and PAHs. However, the trends for PAHs are considerably larger than organic halogen HOCs, indicating that PAHs can more easily bind to DOM in a multi-contaminant system and, potentially, in the real environment. The different $\lg K_{doc}$ - $\lg BCF$ correlations between PAHs and organic halogen HOCs may be caused by various partitions or binding mechanisms and may result in discriminative competition partitions of HOCs between DOM and organisms. Estimates of BCF_{DOM} and $LOEL_{DOM}$ based on the multi-pollutant system K_{doc} values indicated a DOM detoxification effect on HOCs. Therefore, DOM should be considered when regulating HOCs in natural water bodies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.07.047>.

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