

Bound PAHs in Sediment and Related Environmental Significance

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Abstract Extractable polycyclic aromatic hydrocarbons (EPAHs) and bound PAHs (BPAHs) were measured in a sediment core using conventional Soxhlet extraction and a more astringent extraction method, with the objectives of determining the influence of BPAHs on the historical reconstruction of PAHs and exploring the formation of BPAHs and long-term behaviors of PAHs in sediment. The results indicated that the formation of BPAHs was clearly sediment-depth and molecular-size dependent. BPAHs represents an important portion of PAHs in sediment and cannot be extracted by conventional Soxhlet extraction. This suggests that the previously developed vertical profile of PAHs is not the real chronology of PAHs and the plausible interpretation derived from the sedimentary records of PAHs needs reexamination. Based on the previous findings, a biphasic model was proposed and the formation of BPAHs was predicted. Due to the different nature of geosorbents in sediment, redistribution of PAHs among these geosorbents logically leads to the formation of BPAHs and is kinetically favorable for smaller molecular PAHs. This is consistent with the obtained results. Many factors may influence the formation of BPAHs, such as the physicochemical structure of sediment and environmental conditions. There is still a long way to reveal the

thermodynamical characteristics in action during the formation of BPAHs.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in environment and have long been concerned due to their adverse impacts on environment and human beings. Although assumed to be recalcitrant and persistent in sediment, PAHs can be released under certain conditions, thus could be harmful to aquatic ecosystem. To confirm the serious ecological risks of PAHs in aquatic ecosystem and to determine the related controlling parameters or conditions, great efforts have been focused on PAHs in sediment during the past several decades. However, PAHs in sediment must experience an aging process, resulting in the formation of bound PAHs, decreased bioavailability, and reduced extractability of PAHs, especially in deeper sediments (Northcott and Jones 2000). Due to the formation of bound PAHs in sediment, conventional extraction methods, such as Soxhlet extraction, microwave extraction, ultrasonic extraction, and accelerated solvent extraction (Itoh et al. 2008; Oukebdane et al. 2010; Wang et al. 2007), may not be able to extract all PAHs in sediment, not to mention the nonexhaustive methods, such as Tenax extraction and sequential extraction (Cornelissen et al. 2001; Macleod and Semple 2003). This indicated that the obtained “extractable” PAHs via conventional extraction cannot fully represent the whole PAHs in sediment.

In fact, “extractable” and “bound” residues are coined words that indicate the extractability of a chemical in complicated matrix and are usually operationally defined. Therefore, it is important to be clear which method was used and what information can be provided by the employed method (Gevao et al. 2000; Mordaunt et al. 2005). Bound residues in soils have attracted great interest

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and have been extensively investigated using radiolabelled compounds, isotopically labelled compounds, and spectroscopic methods (Northcott and Jones 2000, and the references therein). These efforts greatly improved our understanding on the fate, reduced bioavailability, detoxification mechanisms, and long-term behaviors of organic contaminants in soil (Gevao et al. 2000; Northcott and Jones 2000). As for bound residues in sediment, few investigations have confirmed that bound residues made up an important portion of total organic contaminants in sediment and can provide valuable information on the post-depositional behaviors of organic contaminants (Calderbank 1989; He et al. 2008). However, direct information on the bound PAHs in sediment is still limited, although many efforts associated with this issue have been made based on laboratory and field contaminated sediments (Ten Hulscher et al. 1999; Oen et al. 2006; Tuikka et al. 2016).

In the present work, we referred to the extractable PAHs (EPAHs) as those that can be extracted by conventional Soxhlet extraction—the most widely used method due to its easy-to-operation, economic benefits, and accepted extracting efficiency. As for the bound PAHs (BPAHs), it was defined as those that can be extracted by more astringent method developed by He et al. (2008)—a method with the potential to extract the bound/sequestered PAHs in sediment. EPAHs and BPAHs were analyzed in a sediment core from Dianchi Lake, Southwest China. The purpose of this work is to: (1) determine the influence of bound PAHs on the historical reconstruction of PAHs in sediment; and (2) explore the formation of BPAHs and long-term behaviors of PAHs in sediment based on the field survey and previous findings. This is essential for the development of meaningful quality criteria, regulatory limits, and risk assessment criteria for organic contaminants in aquatic ecosystem.

Materials and Methods

Chemicals and Reagents

A standard solution of 16 priority PAHs proposed by U.S. EPA, including Naphthalene (NAP), Acenaphthene (ACE), Acenaphthylene (ACY), Fluorene (FLU), Phenanthrene (PHEN), Anthracene (ANT), Fluoranthene (FLUO), Pyrene (PYR), Benz[a]anthracene (BaA), Chrysene (CHRY), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benz[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (INP), Dibenz[ah]anthracene (DBA), and Benzo[ghi]perylene (BghiP), and internal standards (2-Fluorobiphenyl and Terphenyl-*d*₁₄) were purchased from Accustandards (New Haven, CT). A mixture solution of perdeuterated PAHs,

including NAP-*d*₈, ACE-*d*₁₀, PHEN-*d*₁₀, CHRY-*d*₁₂, and Perylene-*d*₁₂, were obtained from Ultra Scientific (North Kingstown, RI). All organic solvents used in extraction and cleanup procedures, including dichloromethane (DCM), hexane, acetone, and methanol (MeOH), were from Thermo Fisher Scientific (Wyman, MA). Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China) were extracted with a mixture of DCM and MeOH (1:1, v:v) for 72 h, and were baked for 12 h at 180 °C and 250 °C, respectively. Sodium sulfate from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) was extracted similar to that of neutral silica gel and was baked at 450 °C for 4 h and stored in a sealed container before use.

Sampling

Sediment core was taken from Dianchi Lake (DC), Southwest China. This core was 35-cm long and was sectioned in situ at 1-cm intervals. The sectioned samples were transported to the laboratory where they were stored at –20 °C until further treatment. The upper sediments (DC₂, DC₃, and DC₄, number after DC represents the depth (cm) of the sample), middle sediments (DC₁₁, DC₁₃, and DC₁₅), and deeper sediments (DC₂₇, DC₂₉, and DC₃₁) were selected for analysis. The selection of these sections is based on their depositional ages. The average sedimentation rate of this core was estimated as 0.28 cm/year (Guo et al. 2013). Thus, PAHs in DC₂, DC₃, and DC₄ represent the newly introduced PAHs within past 10 years. As for DC₁₁, DC₁₃, and DC₁₅, the corresponding depositional age is approximately 30–50 years. We postulate that PAHs in these sections are in the transition state between EPAHs and BPAHs. As regard to DC₂₇, DC₂₉, and DC₃₁, the corresponding depositional age is approximately 100 years. We postulate that PAHs in these sections are in the stable state between EPAHs and BPAHs.

Extraction and Instrumental Analyses

For EPAHs, extraction procedures followed the method described elsewhere (Guo et al. 2010). Briefly, approximately 5 g of freeze-dried sample, spiked with perdeuterated PAHs as recovery surrogates and added with 2 g of activated copper for desulfurization, was Soxhlet-extracted with 200-ml mixture of hexane and acetone (1:1, v:v) for 48 h. The extract was concentrated and solvent-exchanged to hexane. Cleanup and fractionation were performed on an alumina/silica gel chromatography. The aliphatic and aromatic fractions were successively eluted with 15 ml of hexane and 70 ml of DCM/hexane (3:7 v:v). The aromatic fraction (F1) was collected and concentrated under a gentle

nitrogen flow. The internal standards, 2-fluorobiphenyl and p-terphenyl- d_{14} , were added before instrumental analysis.

For BPAHs, extraction procedures were based on the method proposed by He et al. (2008). In brief, after being Soxhlet-extracted, the remaining solid sample was successively extracted with 50 ml of MeOH, 50 ml of DCM:MeOH (1:1 v:v), and 50 ml of DCM. For each step, the mixture was shaken for 30 min and loaded in an ultrasonic bath for 1 h at room temperature, then centrifuged at 4000 rpm for 15 min. All the extracts were combined, concentrated, and solvent-exchanged to hexane. Cleanup and fractionation were similar to the method mentioned above. This portion was defined as F2. After that, the residues were pretreated with 6 M HCl for 12 h and rinsed with 2 M HCl, then treated with HCl:HF (1:1 v:v) for 12 h to remove the mineral materials. The residue was further processed in the same way for F2. The obtained extract was defined as F3. F2 + F3 represented the BPAHs in sediment. For the extraction and instrumental analysis of BPAHs, the same surrogates and internal standards were used.

Analyses of PAHs were performed on an Agilent 6890 gas chromatograph system equipped with an Agilent 5975B mass selective detector operating in selective ion monitoring mode using a DB-5 capillary column (60 m length \times 0.25 mm i.d. \times 0.25- μ m film thickness). Splitless injection of 1.0 μ l of sample was conducted with an auto-sampler. The oven temperatures were programmed from 90 to 180 °C at a rate of 10 °C/min, to 220 °C at a rate of 2 °C/min, and then to 290 °C at a rate of 8 °C/min (hold for 30 min).

Quality Control and Quality Assurance

The surrogate recoveries in all samples were $58.6 \pm 8.3\%$ for NAP- d_8 , $83.6 \pm 8.1\%$ for ACE- d_{10} , $96.9 \pm 11.6\%$ for PHEN- d_{10} , $110 \pm 2.4\%$ for CHRY- d_{12} , and $99.2 \pm 4.4\%$ for Perylene- d_{12} . A procedural blank, triplicate spiked blank, and triplicate spiked matrices were analyzed. Mean recoveries of 16 PAHs ranged from 75.8 ± 4.9 to $114 \pm 8.2\%$ in triplicate spiked blanks and from 60.8 ± 1.1 to $121 \pm 9.1\%$ in triplicate spiked matrices. Only trace levels of targets were detected in blanks and were subtracted from those in samples, except that of NAP. The mean level of NAP in blanks was 28.3 ng/g, which is similar to NAP levels in some of the sediment samples. Therefore, NAP was excluded in data analysis. Detection limits were 0.5–2.0 ng/g dry weight for PAHs (defined as the lowest level of the standard curve). The results were expressed on a dry-weight basis, and surrogate recoveries corrected.

Results

EPAHs and BPAHs in Sediment

Concentrations of EPAHs and BPAHs in sediment are displayed in Table 1. For EPAHs, their concentrations (sum of 15 PAHs) in the upper, middle, and deeper sediments were in the range of 3408–3642, 1006–2240, and 229–241 ng/g, respectively. Small variation of EPAHs concentrations were found in the upper and deeper sediments, with the mean value of 3517 ± 117 and 236 ± 6 ng/g, respectively. As for concentrations of EPAHs in the middle sediments, they varied significantly, because the depositional time of these sediment samples was in the right period when PAHs concentrations rapidly increased in DC (Guo et al. 2013).

For BPAHs, their concentrations in the upper, middle and deeper sediments were in the range of 357–494, 1058–2335, and 518–647 ng/g, respectively (Table 1). Concentrations of BPAHs were much less than that of EPAHs in the upper sediments. On the contrary, concentrations of BPAHs were higher than that of EPAHs in the deeper sediments. While in the middle sediments, concentrations of EPAHs and BPAHs were comparable. This is clearly demonstrated by the variation of relative abundance of EPAHs and BPAHs against the sediment depth (Fig. 1). If adding BPAHs to EPAHs as the total PAHs (TPAHs) and define the ratio of EPAHs to TPAHs as the extractability of PAHs, the extractability of PAHs was evidently decreased as the sediment-depth increased, with mean value of 88.9 ± 1.44 , 49.9 ± 1.86 , and $29.6 \pm 2.40\%$ at the upper, middle, and deeper sediments, respectively.

Looking to the individual PAHs species, data were available for both EPAHs and BPAHs associated to the smaller molecular PAHs (SMPAHs). However, BPAHs for the larger molecular PAHs (LMPAHs) were seldom detected in the middle and deeper sediments (Table 1). This made it impossible to calculate the extractability of larger molecular PAHs in the middle and deeper sediments.

Relative Abundance of Each Grouped PAHs Against the Sediment Depth

If all analyzed PAHs are classified into three groups, i.e., 3 rings PAHs, 4 rings PAHs, and 5–6 rings PAHs, the relative abundance of each grouped PAHs also was intriguing and schematically is shown in Fig. 2. EPAHs in the upper sediments were composed of $37.5 \pm 1.3\%$ of 3 rings PAHs, $36.3 \pm 1.2\%$ of 4 rings PAHs, and $26.2 \pm 0.1\%$ of 5–6 rings PAHs, respectively (Fig. 2, left). In the middle sediments, composition of EPAHs was roughly similar to

Table 1 EPAHs (F1) and BPAHs (F2 + F3) (ng/g dw) in cored sediments

Compound	DC2		DC3		DC4		DC11		DC13	
	F1	F2 + F3	F1	F2 + F3	F1	F2 + F3	F1	F2 + F3	F1	F2 + F3
ACE	20.4	1.30	24.4	2.70	21.1	2.20	11.9	86.2	6.20	25.7
ACY	31.2	3.80	46.7	8.50	42.5	6.60	34.1	157	9.20	90.2
FLU	179	61.0	232	78.4	225	73.4	197	560	68.9	330
PHEN	969	144	881	239	1049	249	535	1245	305	766
ANT	74.7	6.10	86.1	9.10	80.9	11.7	57.2	59.3	32.0	34.6
FLUO	419	31.8	444	40.5	439	37.5	361	101	270	75.0
PYR	314	34.7	343	26.7	332	36.4	218	71.1	166	44.8
BaA	156	20.5	164	20.0	158	21.1	113	19.1	89.6	19.2
CHRY	221	28.1	222	28.3	210	30.1	123	30.6	109	24.6
BbF	433	10.7	455	10.6	464	10.9	261	6.10	216	8.70
BkF	132	3.40	138	3.90	135	3.00	77.4	ND	64.9	2.90
BaP	138	3.10	141	2.70	147	3.6	86.4	ND	75.2	2.30
INP	93.1	4.20	94.3	2.7	97.0	4.0	47.1	ND	40.8	2.60
DBA	24.8	ND	23.5	ND	27.0	ND	14.5	ND	10.8	ND
BghiP	203	4.10	206	4.00	214	4.30	104	ND	85.3	ND
\sum PAHs	3408	357	3499	477	3642	494	2240	2335	1548	1427
Compound	DC15		DC27		DC29		DC31			
	F1	F2 + F3	F1	F2 + F3	F1	F2 + F3	F1	F2 + F3		
ACE	4.70	23.2	1.30	37.9	1.20	21.0	1.10	22.5		
ACY	17.8	78.0	4.80	67.9	3.90	49.6	4.10	44.8		
FLU	99.6	283	44.5	176	35.0	169	38.4	146		
PHEN	288	514	116	188	113	319	114	229		
ANT	19.6	36.1	3.80	12.9	3.60	20.0	3.60	17.2		
FLUO	156	52.4	25.4	20.4	28.6	31.5	25.1	22.9		
PYR	86.3	32.9	10.5	10.7	11.0	16.1	9.20	12.0		
BaA	39.1	9.60	3.20	7.40	3.80	7.40	3.10	10.9		
CHRY	56.9	21.5	5.00	7.30	6.10	13.8	4.90	13.0		
BbF	102	5.30	12.0	ND	14.0	ND	11.5	ND		
BkF	31.7	2.20	3.60	ND	4.40	ND	3.50	ND		
BaP	35.2	ND	2.90	ND	3.70	ND	2.70	ND		
INP	21.1	ND	3.20	ND	3.60	ND	2.90	ND		
DBA	5.10	ND	ND	ND	ND	ND	ND	ND		
BghiP	42.5	ND	5.20	ND	6.20	ND	5.10	ND		
\sum PAHs	1006	1058	241	528	238	647	229	518		

ND not detectable

that of EPAHs in the upper sediments, with slightly higher abundance of 4 rings PAHs ($40.6 \pm 4.2\%$), and slightly less abundance of 3 rings PAHs and 5–6 rings PAHs (35.7 ± 7.9 and $23.7 \pm 3.6\%$). While in the deeper sediments, this was totally different. EPAHs in the deeper sediments were dominated by 3 rings PAHs ($68.9 \pm 2.7\%$), followed by 4 rings PAHs ($20.8 \pm 1.6\%$), and 5–6 rings PAHs ($10.3 \pm 1.1\%$). This is consistent well with our previous reported data and is probably a reflection

of the source change of PAHs in Dianchi Lake (Guo et al. 2013).

As for BPAHs (Fig. 2, right), 3 rings PAHs dominated in all the analyzed samples. In the middle and deeper sediments, 3 rings PAHs contribute almost 90% of the corresponding BPAHs, followed by 4 rings PAHs (approximate 10%). Contribution of 5–6 rings PAHs to BPAHs was very limited in the middle and deeper sediments (<1%). In fact, 5–6 rings BPAHs were seldom

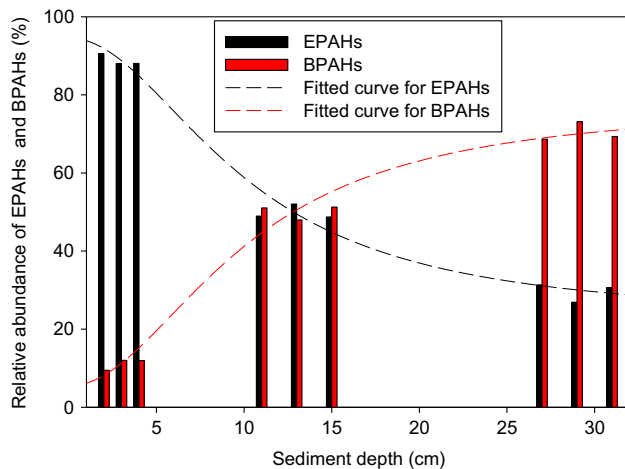


Fig. 1 Relative abundance of EPAHs and BPAHs against the sediment depth

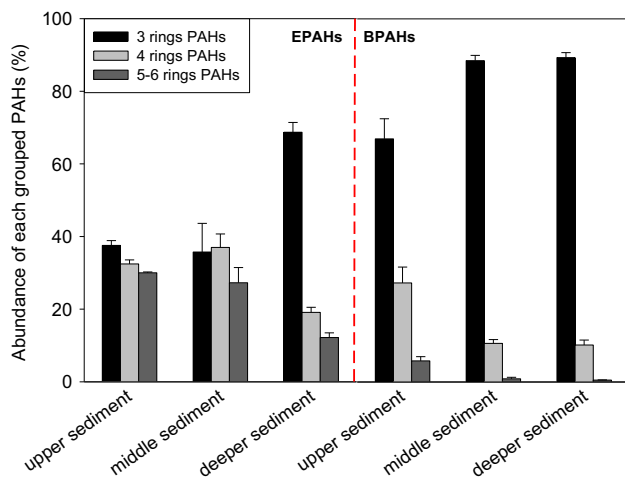


Fig. 2 Relative abundance of each grouped PAHs in EPAHs and BPAHs

detected in the deeper sediments (Table 1). The difference in composition between EPAHs and BPAHs suggested that the extractability of PAHs is not only sediment–depth-dependent but also molecular–size-dependent. It seems that the extractability of LMPAHs was much higher than that of smaller molecular ones, because more PAHs with smaller molecular size were left as BPAHs.

Fitted Curves of the Extractability of PAHs Against Sediment Depth

To further clarify the extractability of PAHs against the sediment depth, fitted curves of the extractability of sum of PAHs and the selected individual PAHs against the sediment depth are demonstrated in Fig. 3. It should be pointed out that the curve of BbF is a conceptual simulated curve, other than the real curve fitted from the extractability of

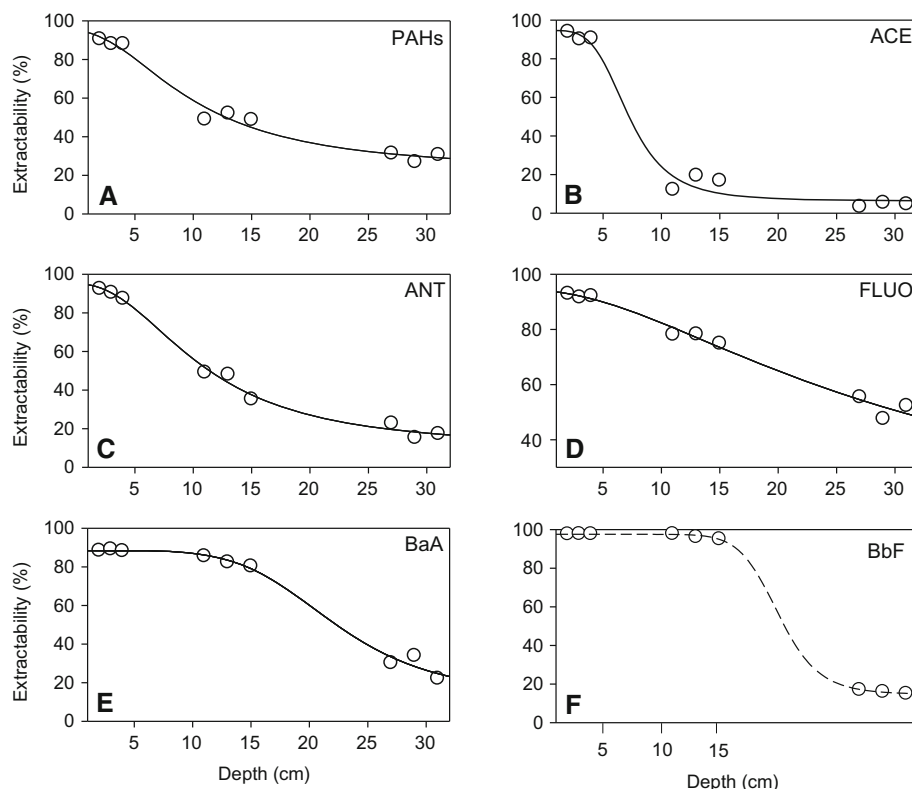
BbF due to the lack of related BPAHs in deeper sediments (Fig. 3f). The extractability of sum of 15 PAHs was approximate 90% in the upper sediments and then smoothly decreased to approximately 50% in the middle sediments and to nearly 30% in the deeper sediments (Fig. 3a). Similar to that of sum of 15 PAHs, extractability of individual PAHs also were close to 90% in the upper sediments and were decreased as the sediment depth increased, indicating that most newly introduced PAHs were extractable and the decreased extractability in the deeper sediments (Fig. 3b–f). However, the decreasing patterns were totally different among different PAHs species. From the upper sediments to the middle sediments, the extractability of ACE sharply decreased from ~91% to nearly 20% (Fig. 3b). On the contrary, the extractability of BbF only decreased by 1% from the upper sediments to the middle sediments (Fig. 3f). As for the fitted curves of ANT, FLUO, and BaA, they were the transition states between ACE and BbF (Fig. 3c–e). It seems that the formation of bound PAHs in sediment was kinetically favorable for smaller molecular ones. In fact, different geosorbents coexisted in sediment, and both linear sorption and nonlinear sorption of PAHs to different geosorbents can happen simultaneously. These fitted curves should be the reflection of accumulative results of several sorption processes, other than an individual sorption process (Cornelissen and Gustafsson 2005). Thus, these curves could provide valuable information on the formation of BPAHs in sediment.

Environmental Significance of Bound PAHs

Influence on the Historical Reconstruction of PAHs in Sediment

Based on the information mentioned above, three basic conclusions can be derived: (1) there exists a portion of PAHs in sediment that cannot be extracted by Soxhlet extraction due to the formation of BPAHs; (2) more and more PAHs were left as BPAHs in sediment as the sediment–depth increased (Fig. 1); and (3) formation of BPAHs was molecular size dependent and more PAHs with smaller molecular size were left as BPAHs at the early stage of aging process (Fig. 3). All these findings may considerably change our understanding on the historical records of PAHs. Though believed to be an exhaustive method and usually used in the historical reconstruction of PAHs in sediment (Guo et al. 2010.; Lin et al. 2012), sedimentary PAHs derived from the Soxhlet extraction cannot represent the total PAHs introduced into the sediment due to the existence of BPAHs. Accordingly, the historical records of PAHs in DC, based on the Soxhlet extraction that we

Fig. 3 Fitted curves of the extractability of PAHs against the depth (*note: curve of BbF is not a real fitted curve and the dashed line was used*)



reported previously (Guo et al. 2013), may not represent the real chronology of PAHs in DC.

In fact, even in the upper sediments from DC, there still a small portion of PAHs existed as BPAHs (Fig. 1). Because the sediment-depth increased, the real chronology of PAHs can be seriously biased. To explain how the vertical profile of PAHs was developed, many people have linked the vertical profile of PAHs to the variation of local or regional energy consumption, gross domestic product and/or population, and good relationship have been established between them (Guan et al. 2012; Liu et al. 2012; Simcik et al. 1996). This implied that energy consumption or other mentioned factors could be the major causes for the vertical profile of PAHs developed in sediment and sounds reasonable (Guan et al. 2012; Simcik et al. 1996). However, this relationship is not quite well in some cases (Guo et al. 2013; Li et al. 2013). Although many factors can influence this relationship, the most possibility for the lack of a direct correlation between the increase in energy consumption and the increase in PAHs emission is stemmed from the changes in burning techniques. Additionally, the occurrence of BPAHs in sediments could be partly responsible for this.

In addition to the vertical profile of PAHs, information on the sedimentary records of PAHs were used for the source identification and apportionment of PAHs in sediment (Christensen and Arora 2007; Gu et al. 2003; Xu et al.

2014). Due to the formation of BPAHs in sediment, the real source information extracted by Soxhlet extraction must be incomplete and some important details may be lost. Consequently, information on the sedimentary records of PAHs are likely to be misrepresented and the reliability of deduction is questionable. We do not know what extent can BPAHs influence the chronology of PAHs and the source identification and apportionment of PAHs. One thing is certain: the formation of BPAHs is associated with many factors, including the source of PAHs, physicochemical properties of sediment, and the in situ environmental conditions, etc. Further efforts are clearly needed to clarify this.

Clues for the Formation of BPAHs in Sediment

Predicting the Formation of BPAHs in Sediment

Sediment is a highly heterogeneous matrix containing various geosorbents (Ghosh et al. 2000). Among them, organic materials (OMs) plays an important role on the environmental behaviors of PAHs (Chiou et al. 1979; Lambert 1968), which was assumed to be composed of two domains (Huang et al. 1997; Xing and Pignatello 1997). One was proposed to consist of amorphous OMs (AOM), such as biopolymers and humic substances. The other was composed of condensed OMs (COM), including unburned

coal, coke, soot, charcoal, and kerogen, which were collectively named as “carbonaceous geosorbents” (CG) (Cornelissen and Gustafsson 2005). PAHs can be absorbed to geosorbents via van der Waals forces, hydrophobic bonding, and π bonding, or the combined forces between them. Due to the different nature of geosorbents, sorption of PAHs to these geosorbents may vary from complete reversibility to total irreversibility (Gevao et al. 2000). Generally, PAHs bound to AOM shows a fast, linear, noncompetitive, and reversible properties, whereas PAHs bound to COM displays a slow, nonlinear, competitive, and at least partly irreversible properties (Cornelissen and Gustafsson 2005). Operationally, the former can be easily extracted from sediment by various organic solvents or solid sorbents, and the latter are difficult to be extracted by conventional extraction methods.

Once introduced into sediment, PAHs can be absorbed by AOM and COM simultaneously, resulting in the redistribution of PAHs among different geosorbents, or operationally resulting in the redistribution of PAHs between EPAHs and BPAHs. Intra-organic matter diffusion and intra-particulate diffusion are thought to be the main mechanisms contributing to the formation of BPAHs in sediment (Luthy et al. 1997). In fact, the conversion of EPAHs to BPAHs is the shift of PAHs from weak sorption sites to strong sorption sites and is thermodynamically favorable for the formation of BPAHs (Fig. 4, left). This process logically leads to the decreasing extractability of PAHs as the aging time increased (Fig. 4, right). If the molecular size is taken into account, slight differences in conversing characteristics between SMPAHs and LMPAHs can be expected. First, a quicker attainment of equilibrium between EPAHs and BPAHs is favorable for SMPAHs, because the diffusion rate of a specific compound is inversely proportional to its molecular size. Second,

compound with a larger molecular size have a stronger sorption to OMs, because a higher contact area between compound and geosorbent is beneficial for a stronger Van der Waals interaction (Jonker and Koelmans 2002; Van Noort et al. 2004). The stronger interaction between the LMPAHs and geosorbents can lead to two direct consequences: (1) more activity energy ($E_2 > E_1$) are needed to overcome for LMPAHs during the shift of PAHs from weak sorption sites to strong sorption sites (Fig. 4, left); and (2) more free energy ($\Delta G_2 > \Delta G_1$) is released for LMPAHs during the shift of PAHs from weak sorption sites to strong sorption sites (Fig. 4, left). This made the conversion of EPAHs to BPAHs kinetically favorable for SMPAHs and thermodynamically favorable for LMPAHs. If these differences were expressed as the extractability of PAHs, the decreasing rate of the extractability of SMPAHs is expected to be quicker than that of LMPAHs ($t_1 < t_2$ and $t_1' < t_2'$), and the extractability of LMPAHs is expected to be lower than that of SMPAHs provided that the environmental conditions are advantageous and the aging time is long enough (Fig. 4, right).

Based on these understandings, a biphasic model on the formation of BPAHs was proposed:

1. PAHs in sediment can be classified into two phases in light of their extractability, i.e., EPAHs, and BPAHs. Definition of EPAHs and BPAHs have been operationally defined above;
2. Due to the difference in sorption potential of different geosorbents, PAHs in sediment can redistribute among different geosorbents, resulting the conversion of EPAHs to BPAHs;
3. Theoretically, formation of BPAHs is kinetically favorable for SMPAHs and is thermodynamically favorable for larger molecular ones during the aging processes;

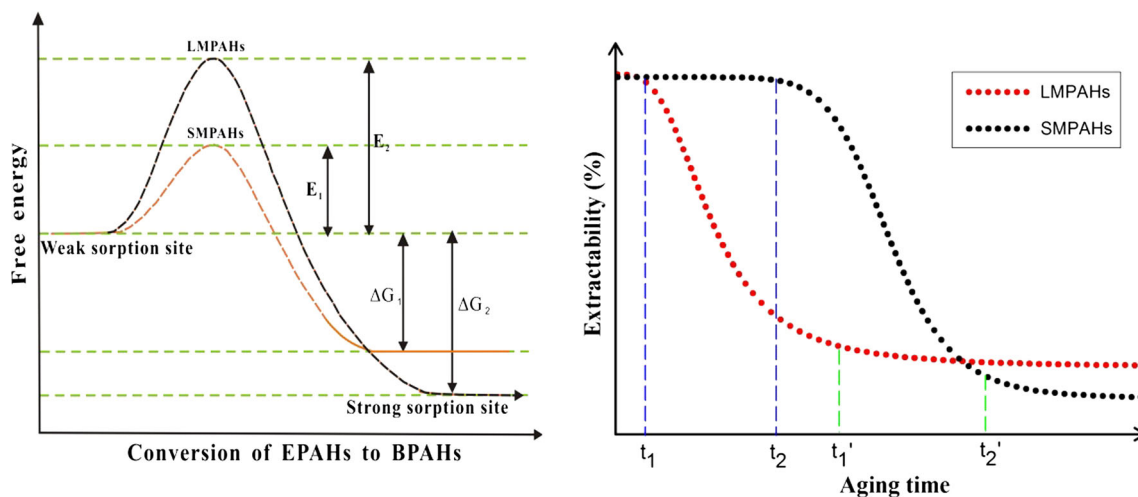


Fig. 4 Predicting the molecular-specific behaviors of PAHs in sediments

4. In the field survey, whether the formation of BPAHs is kinetically controlled or is thermodynamically controlled, largely depending on the physicochemical properties of sediment and the environmental conditions.

Results of the Present Work, a Comparison to the Prediction

According to the results from the present work, two key points can be derived: (1) extractability of PAHs was gradually decreased as the sediment-depth increased; and (2) extractability of PAHs with smaller molecular size has a faster decreasing rate during the early stage of the conversion from EPAHs to BPAHs. The first point is easy to understand and can be explained by the redistribution of PAHs among different geosorbents in sediment. Once entered sediment and contacted with geosorbents, PAHs are redistributed among different geosorbents via intra-organic matter diffusion and/or intra-particulate diffusion, due to the difference in sorption potential of different geosorbents. As the contact-time increased (along with the increase in sediment-depth), more and more PAHs were converted from free or loosely bound sites to tightly bound sites, causing the formation of BPAHs and the declined extractability. This is consistent with the prediction. The second point can be explained by the diffusion rate and activation energy during the redistribution of PAHs. As mentioned, intra-organic matter diffusion and intra-particulate diffusion are thought to be the main mechanisms for the formation of BPAHs (Luthy et al. 1997), suggesting diffusion rate being of great importance during the formation of BPAHs. Because the diffusion rate of a specific compound is inversely proportional to its molecular size, PAHs with smaller molecular size must have the higher diffusion rate during the formation of BPAHs. From the perspective of activation energy, as schematically showed in Fig. 4 (left), formation of BPAHs is also favorable for PAHs with smaller molecular size, because the smaller the PAHs compound is, the activation energy needed to be overcome is less. Thus, it is reasonable that PAHs with smaller molecular size have the faster conversion rate from EPAHs to BPAHs. This also coincides well with the prediction.

In the proposed model, thermodynamical characteristic of the formation of BPAHs also is predicted (Fig. 4). However, available data cannot support this. According to the prediction, the extractability of FLUO (or BaA) in the deeper sediments should be less than that of ACE (or ANT), because PAHs with larger molecular size must be more tightly bound to sediment and more difficult to be extracted from sediment. However, the opposite was true

(Fig. 3c–e). In fact, redistribution of PAHs in sediment is far from fully understood, and many possibilities exist. First, EPAHs and BPAHs of FLUO (or BaA) were far from equilibrium, and the extractability of FLUO (or BaA) is less than that of ACE (or ANT) provided that the contact-time is not long enough ($t > t_2'$) (Fig. 4, right). Second, PAHs with smaller molecular size preferentially occupied the stronger sorption sites, due their higher diffusion rate and less activation energy needed during the formation of BPAHs (Fig. 4, left), resulting in less extractability even in the deeper sediments. These two possibilities are kinetically controlled.

Another possibility is associated with the nonextractable PAHs (NEPAHs), a portion of PAHs that cannot be extracted from sediment using any methods developed presently. Main mechanisms on the formation of NEPAHs include bound molecules moving from reversible sorption sites to irreversible sites and diffusing of PAHs through and along meso-, micro-, and nanopores abundant in CG, where they entrapped irreversibly (Nam and Alexander 1998). PAHs with larger molecular size are more likely to exist as NEPAHs in sediment and the significance of NEPAHs must be elevated as sediment-depth increased (Macleod and Semple 2003, and the references therein). Nevertheless, in the present work, NEPAHs was excluded from the calculation of extractability and the obtained extractability of PAHs was merely an apparent value, other than the real value. The obtained apparent extractability of PAHs could partly responsible for the difference between the results of the present work and the prediction.

We are not sure which possibility is most likely close to reality and/or which possibility is dominant at the different stage of aging process. Certainly, the complexity of the formation of BPAHs is beyond our imagination. Many factors may influence the formation of BPAHs, such as the physicochemical structure of sediment and the environmental conditions. There is still a long way to clarify it.

Conclusions

The pervious developed vertical profiles of PAHs in sediment cannot fully represent the real chronology of PAHs and the plausible interpretation derived from the sedimentary records of PAHs needs reexamination, due to the formation of BPAHs in sediment. Redistribution of PAHs among different geosorbents in sediment results in the formation of BPAHs, which is sediment-depth dependent and is kinetically favorable for smaller molecular PAHs. The lack of data associated to NEPAHs prevents gaining deeper insight into the formation of BPAHs in sediment. Further investigations on the forming mechanism of BPAHs and NEPAHs are needed.

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