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Spatial Distribution of Polycyclic Aromatic Hydrocarbons from Lake Taihu, China

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Abstract A total of 30 sediments, overlying water and porewater samples were collected from Lake Taihu, China for the analysis of PAHs. The total PAHs varied from 209 to 3,843 ng g^{-1} in sediments, from 238 to 7,422 ng L^{-1} in overlying water and from 2,012 to 19,899 ng L^{-1} in porewater, respectively. There are good correlations between sediment-porewater/sediment-overlying water partition coefficients and PAHs' logKow values, with correlation coefficient of 0.94 and 0.95, respectively. The sediment PAHs in Lake Taihu originated from both pyrolytic and petrogenic sources, showing a mixed input pattern. Based on the numerical effect-based sediment quality guidelines of the United States, the sediments from Lake Taihu causing adverse effects by PAHs should have potential biological impact, but should have no impairment.

Keywords Polycyclic aromatic hydrocarbons · Taihu · Sediment · Porewater · Overlying water · Partition

Lake Taihu is the third largest freshwater lake in China, with an average depth of 1.9 m. With the rapid urbanization around the Taihu Region, it receives large amounts of wastes from agricultural non-point sources, municipal sewage, industrial wastewater, aquaculture, etc., causing the pollution of the lake a great concern by both scientific and public communities (Zhao et al. 2009). Many contaminants have been detected in Lake Taihu, among which PAHs contamination has drawn much attention due to their toxicity, bioaccumulation and widespread environmental occurrence.

Several publications reported the PAHs occurrence in Lake Taihu. However, these researches either took samples from one region of the whole lake, or analyzed PAHs only in sediment and overlying water matrices. For instance, Qiao et al. (2006) and Liu et al. (2009) investigated PAHs occurrence in the sediments of Meiliang Bay and Xukou Bay in Lake Taihu. Wang et al. (2003) reported the occurrence of PAHs in both water and sediment samples in the lake. Owing to the hydrophobic nature, PAHs in the aquatic system tend to adsorb to sediment particles (Cornelissen et al. 2006). Yet they are still harmful to benthic organisms due to their possibility to release back into water column (Hawthorne et al. 2007). Partitioning of PAHs between sediment and porewater thus is important, which controls the transport, fate and ecotoxicological risk of the micro-levels of lipophilic contaminants in aquatic environment (Yu et al. 2009). To the best of our knowledge, no data are available on the distribution of PAHs around the whole lake and on the partition between sediment and porewater phases.

This study investigated the occurrence of PAHs in sediment and corresponding overlying water and porewater samples in Lake Taihu, interpreted the partition of PAHs between sediment-porewater and sediment-overlying water matrices, identified the probable sources, and assessed the potential toxicological impacts of PAHs in the sediments. The results will be helpful in better understanding the environmental bioavailability and fate of the PAHs in the sediment–water system.

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Materials and Methods

Individual PAHs standards, naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chry-sene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP), each at 200 g mL^{-1}, were purchased from J&K Chemical Co. Ltd. (Beijing, China). The recovery surrogate standard consisting of a mixture of deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12, each at 4,000 g mL^{-1}) was also obtained from J&K Chemical. All solvents and reagents (n-hexane, dichloromethane, methanol, ethyl acetate) used for sample processing were high performance liquid chromatography (HPLC) grade. Anhydrous sodium sulfate was baked at 450°C for 8 h and stored in sealed containers.

A total of 30 surface sediment and overlying water samples were collected in Lake Taihu in May 2010, with sampling locations shown in Fig. 1. Surface sediments were grab sampled, and placed in glass bottles with Teflon-lined caps. Overlying water was taken 1 m beneath the surface, and stored in 4-L glass amber bottles. Samples were transported to the laboratory on ice. Porewater from each sediment was obtained by high-speed centrifugation. Both overlying water and the isolated porewater samples were stored in the dark at 4°C, and the remainder of sediment samples was frozen at −20°C before treatment. All samples were analyzed within 1 week.

Liquid samples were passed through 0.45 μm glass fibers to remove suspended particles, and concentrated by solid phase extraction (SPE). The HyperSep C18 cartridges (500 mg/6 mL, Thermo Electron Corporation) were preconditioned by 5 mL of ethyl acetate, 5 mL of methanol and 5 mL of distilled water sequentially. Filtered water samples were loaded onto cartridges at a flow rate of approximate 8 mL min^{-1}. After the sample loading, 10 mL of distilled water were used to wash the cartridges, followed with the vacuum on for about 1 h till the cartridges were all dry. The cartridges were eluted by 4 mL of 1:1 dichloromethane/n-hexanes and 4 mL of n-hexanes. The extract was concentrated to less than 1 mL with a gentle nitrogen stream, reconstituted with 8 mL of n-hexanes, and again concentrated to less than 1 mL. Anhydrous sodium sulfate was used to remove water residue. The extract was finally concentrated to 200 μL for analysis.

Sediments were extracted with an automated Dionex ASE 200 accelerated solvent extractor (Sunnyvale, CA, USA). Surface sediments were freeze-dried and ground in a mortar to pass through a sieve with 0.5 mm openings. Five grams of each sediment sample were weighed accurately, combined with 5 g of copper powder and 2 g of diatomite, and placed into the steel cells. A hexane-dichloromethane

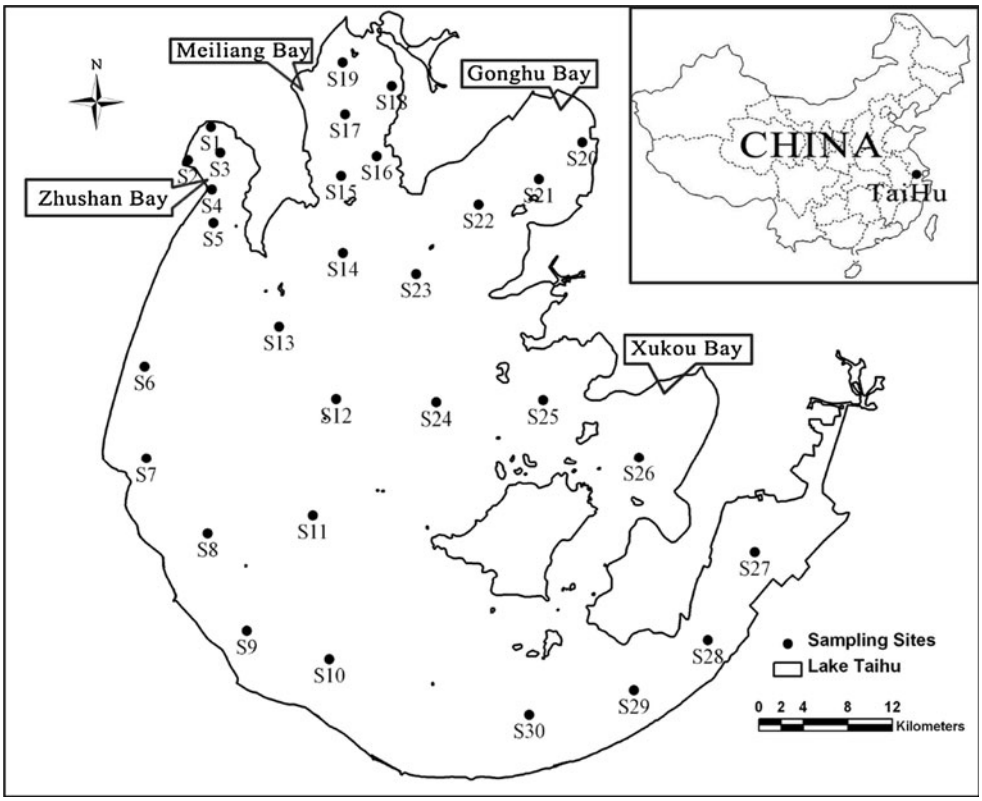

Fig. 1 The sampling sites in the study area

mixture (50/50, v/v) proved to be optimal as extraction solvent. Extraction temperature was 100°C and extraction pressure was 1,500 psi. Preheating time and static time were both set to 5 min. A total flush volume of 100% the cell volume and a purge time of 60 s with nitrogen was used. The final extraction volume was approximately 20 mL with two extraction cycles. The extracts were completely condensed to approximately 2 mL using rotary evaporation, followed by SPE for clean-up, and concentrated to 1 mL for analysis.

The PAHs were analyzed using an Agilent 6890 N gas chromatograph with 5975C mass selective detector (GC/MSD) equipped with an Agilent 7683B automatic liquid sampler and a HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Helium was used as the carrier gas, with a column flow rate of 1.2 mL min^{-1} in constant-flow mode. Injector, ion source and transfer line temperatures were set at 250, 230 and 280°C, respectively. The GC oven temperature was programmed from 70°C (2 min) to 260°C (8 min) at 10°C min^{-1}, then to 300°C at 5°C min^{-1} and held for 5 min. The electron impact energy was set at 70 eV. 1 μL of samples was injected in splitless mode. PAHs were analyzed with the selected ion monitoring (SIM) mode. Quantification of samples was performed using an external standard method.

All analytical procedures were monitored with strict quality assurance and control measures. The instruments were calibrated daily with calibration standards and the relative percent differences between the seven-point calibration and the daily calibrations were less than 20% for all target analytes. Procedural blanks were analyzed concurrently with the water and sediment samples. The water blank, consisting of 1,000 mL of double distilled water, was extracted in the same manner as the water samples. The sediment blank was solvent-extracted sediment that had been baked in a muffle furnace at 450°C overnight and was extracted in the same manner as the sediment samples. The PAHs in the sediment and water blanks were not detected or much lower than the detection limits of the method, which were 1.0–6.0 ng g^{-1} for sediment and 8–60 ng L^{-1} for water. Mean recoveries and the relative standard deviation of surrogates in the sediment and water extracts were 70.2 ± 7.5% and 63.4 ± 6.8% (naphthalene-d8), 84.5 ± 5.6% and 78.4 ± 9.2% (acenaphthene-d10), 92.5 ± 5.6% and 94.1 ± 13.2% (phenanthrene-d10), 92.4 ± 10.2% and 90.5 ± 10.5% (chrysene-d12), 89.0 ± 9.4% and 84.7 ± 8.8% (perylene-d12), respectively. For statistical analysis, two-tailed *t* test was used to compare the average concentrations between samples in the present study.

Results and Discussion

The range and mean concentrations of individual PAHs in sediments, water and porewater matrices from Lake Taihu are shown in Table 1. In sediments, the total concentrations of PAHs ranged from 209 to 3,843 ng g^{-1} dry weight, with a mean value of 584 ng g^{-1} dry weight. The lowest level of 209 ng g^{-1} was at S11, locating in the middle part of the

Table 1 PAHs concentrations in different matrices from Lake Taihu (May 2010)

PAHs	Water, ng L^{-1} (n = 30)		Porewater, ng L^{-1} (n = 27)		Sediment, ng g^{-1} dw (n = 30)	
	Range	Mean	Range	Mean	Range	Mean
Nap	38–6,525	1,154	148–14,632	1,906	7–654	41
Ace	8–174	72	50–834	228	0–130	6
Flu	29–327	122	134–2,446	541	2–222	17
Phe	89–323	153	470–4,096	1,320	58–570	104
Ant	nd	nd	nd	nd	2–569	28
Flua	25–123	44	49–374	143	22–400	76
Pyr	16–79	30	44–306	103	19–341	56
BaA	0–23	5	0–36	6	5–170	26
Chr	0–37	12	0–55	10	12–199	43
BbF	nd	nd	nd	nd	20–189	63
BkF	nd	nd	nd	nd	4–48	15
BaP	nd	nd	nd	nd	5–120	27
IcdP	nd	nd	nd	nd	11–118	41
DahA	nd	nd	nd	nd	2–19	6
BghiP	nd	nd	nd	nd	11–93	35
∑PAH	238–7,422	1,592	2,012–19,899	4,247	209–3,843	584

nd not detected

lake. The highest concentration of 3,843 ng g^{-1} was found at site S1. S1 located in Zhushan Bay, one of the most polluted areas in Lake Taihu, where there are two severely polluted rivers (Taige Canal and Caoqiao River) carrying contaminants directly into the lake. Along the water flow the concentrations of PAHs of S1, S2, S3 and S4 were decreasing gradually. The high PAHs levels in this area also partially originated from agriculture, domestic sewage and industry sources (Zhang et al. 2009; Luo et al. 2005). Meiliang Bay is also heavily contaminated by PAHs. Qiao et al. (2006) reported the total concentrations of PAHs in Meiliang Bay sediments in 2003 ranged from 1,207–4,754 ng g^{-1}. In this study, the total PAHs in Meiliang Bay (S15, S16, S17, S18, and S19) ranged from 354–765 ng g^{-1}, which were much lower than Qiao's results. This is probably ascribed to the application of "sediment-dredging project" since 2006 by the government, which is aiming to control and remediate the environmental pollution in Lake Taihu. The observed PAHs levels in this study are at the same magnitude with recent published data (Chen et al. 2009; Ji et al. 2010).

For aqueous phases, the total PAHs in the overlying water ranged from 238 to 7,422 ng L^{-1}, with mean value of 1,592 ng L^{-1}. S10 showed the highest concentration of 7,422 ng L^{-1}, and the lowest concentration occurred at S20. The total PAHs concentrations in porewater ranged from 2,012 to 19,899 ng L^{-1}, with a mean value of 4,247 ng L^{-1}.

There were 15 PAHs detected in sediments, and only 8 were detected in water and porewater samples. According to the number of the aromatic rings, PAHs can be divided into three groups, 2- and 3- ring, 4-ring, and 5-, 6-ring PAHs (Xu et al. 2007). Compositions of PAHs in different matrices from Lake Taihu are illustrated in Figs. 2, 3, 4. In sediment, 2- and 3-ring PAHs occupied 23%–66%, 4-ring occupied 25%–42%, and 5–6 ring occupied 9%–25% of the total PAHs, respectively in different areas. In overlying water and porewater, 2-and 3-ring PAHs dominated the PAHs distribution, with proportion up to 89%–99%.

PAHs belong to hydrophobic organic compounds, which have very low aqueous solubilities. The presence of dissolved organic colloids enhances the aqueous concentrations of PAHs beyond their solubilities significantly (Luthy et al. 1997; Nam and Alexander 1998), as shown in Table 1. To better understand the distribution of PAHs between different matrices, two partition coefficients, sediment-overlying water (K_{SW}) and sediment-porewater (K_{SP}) were calculated.

$$K_{SW} = C_S/C_W$$
$$K_{SP} = C_S/C_P$$

Organic carbon normalized coefficient (K_{OC}) values were also calculated with the following equations:

$$\log K_{SW,OC} = \log(K_{SW}/f_{OC})$$
$$\log K_{SP,OC} = \log(K_{SP}/f_{OC})$$

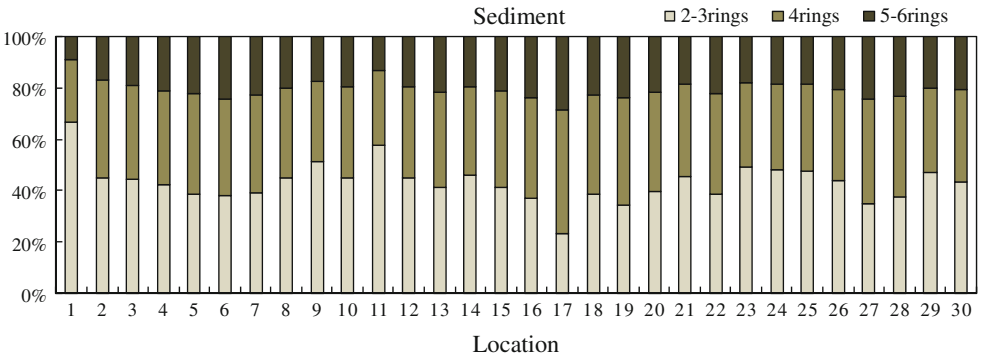

Fig. 2 Composition of parent PAHs in sediment from Lake Taihu

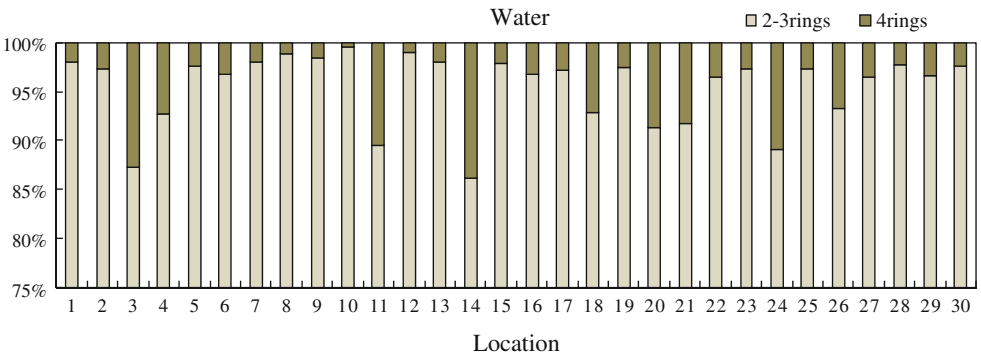

Fig. 3 Composition of parent PAHs in overlying water from Lake Taihu

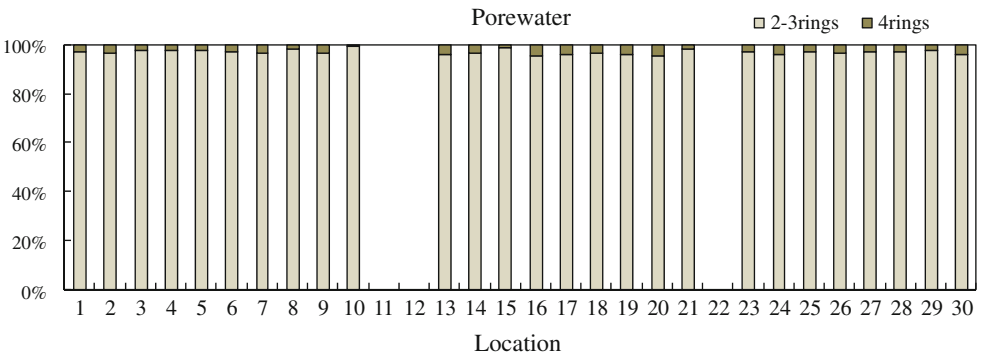

Fig. 4 Composition of parent PAHs in porewater from Lake Taihu

Table 2 The organic carbon normalized partition coefficients of PAHs in this study

PAHs	$\log K_{OW}$	$\log K_{SW,\ OC}$	$\log K_{SP,\ OC}$
Nap	3.37	2.86	2.59
Ace	3.92	2.83	2.35
Flu	4.18	3.31	2.73
Phe	4.57	4.16	3.26
Flua	5.22	4.55	4.18
Pyr	5.18	4.59	4.05
BaA	5.91	5.16	4.83
Chr	5.86	5.01	4.86

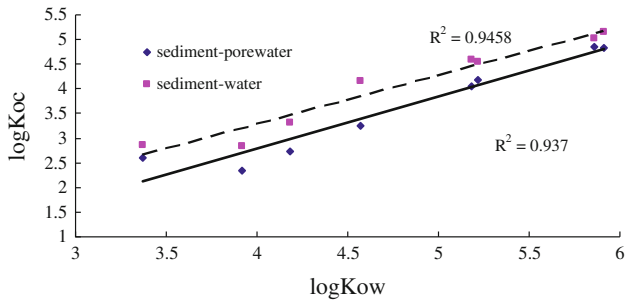

Fig. 5 Correlation between partition coefficients and octanol–water coefficients of PAHs

where Cs is the sediment concentration, Cw is the water concentration, Cp is the porewater concentration, and foc is the sediment organic carbon content. The results are shown in Table 2. The obtained $\log K_{SW,OC}$ and $\log K_{SP,OC}$ values were all lower than their corresponding octanol–water partition coefficients ($\log K_{OW}$), despite of their range of solubilities. It is notable that there are good correlations between $\log K_{SW,OC}$/$\log K_{SP,OC}$ and $\log K_{OW}$ in this study, with correlation coefficients of 0.95 and 0.94, respectively (Fig. 5). $\log K_{OC}$ was reported to be strongly correlated to $\log K_{OW}$, with slopes typically around 1 (Karickhoff 1981). The same trend was also observed by some other studies (Yu et al. 2009; Booij et al. 2003).

The characteristics of PAHs compositions can be used to indentify their sources, since different sources produce PAHs with different compositions. Generally, anthropogenic PAHs are formed mainly by two mechanisms: combustion of fossil fuels (pyrogenic) and discharge of petroleum-derived materials (petrogenic) (Xu et al. 2007). The petroleum-derived residues contain relatively higher concentrations of low-molecular-weight (LMW) PAHs, while high-molecular-weight (HMW) PAHs are formed in the high temperature combustion processes. The ratios of Phe/Ant, Flu/Pyr, Chr/BaA and Flu/(Flu+Pyr) are often used to identify the source of PAHs (Fu et al. 2009; Xu et al. 2007). In the present study, the calculated molecular ratios of PAHs are shown in Table 3. The ratios reflected a mixed pattern of both pyrolytic and petrogenic inputs of PAHs in Lake Taihu. For instance, Phe/Ant ratio was <10 in S1, S2, S3, S4, S5, S16, S17, S18, S19, S27 and S28, indicating a pyrolytic origin, while the other indices displayed a petrogenic origin in these sites. LMW/HMW ratios also ranged from low (0.8) to high (7.3). Liu et al. (2004) reported the ratio of HMW PAHs has increased after 1970s, indicating that origin has shifted from petrogenic to pyrolytic in Meiliang Bay. For most individual site, the molecular ratios showed different results, which was probably correlated with the specific pollution conditions in Lake Taihu. Taihu Region is highly industrialized and surrounded by many industrial factories, agricultural fields, livestock and aquaculture farming, and high-density populations, which may discharge contaminants directly into the lake. In addition, many other sources may contribute to the sediment PAHs, such as the deposition of atmospheric particles from factories, the leakage of crude oil, the runoff containing street dust, and municipal wastewater, resulting in the mixed pattern of PAHs inputs in sediments.

The pollution risk of PAHs in Lake Taihu sediments was evaluated by comparing obtained PAHs values with the effects range low (ERL) and effects range median (ERM) values. ERL and ERM were proposed by Long et al. (1995) to assess the sediment quality. The ERL and ERM values are intended to define chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biological effects. Results in this study (shown in Table 4) showed that the total PAH concentrations at all

Table 3 Characteristic values of selected molecular ratios of PAHs

	Pyrolytic origin	Petrogenic origin	This study
Phe/Ant	<10	>10	1.0–41.6
Chr/BaA	<1	>1	1.2–2.7
Flu/Pyr	>1	<1	0.1–0.6
Flu/(Flu + Pyr)	>0.5	<0.5	0.1–0.4
LMW/HMW	Low	High	0.8–7.3

Table 4 Standard pollution criteria of PAH components for sediment matrix (ng g^{-1})

PAHs	ERL	ERM	This research	
			Max	Average
Nap	160	2,100	654	41
Ace	44	640	130	6
Flu	19	500	222	17
Phe	240	1,500	570	104
Ant	853	1,100	569	28
Fla	600	5,100	400	76
Pyr	665	2,600	341	56
BaA	261	1,600	170	26
Chr	384	2,800	199	43
BbF	NA	NA	189	63
BkF	NA	NA	48	15
BaP	430	1,600	120	27
IcdP	NA	NA	118	41
DahA	63	260	19	6
BghiP	NA	NA	93	35
∑PAH	4,000	44,792	3,843	584

sites were below the ERL. At some sites, concentrations of Nap, Ace, Flu and Phe were higher than their ERL values, suggesting they may occasionally pose biological impairment, however all of them were below the ERM value. These findings indicated that in some samples there may be individual PAH that occasionally pose biological impairment, but no samples had constituents that may frequently pose biological impairment (with concentration greater than ERM). It is concluded that PAHs in sediments from Lake Taihu should have potential biological impact, but should have no impairment.

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