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Current status and historical variations of phthalate ester (PAE) contamination in the sediments from a large Chinese lake (Lake Chaohu)

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Abstract The residual levels of phthalate esters (PAEs) in the surface and two core sediments from Lake Chaohu were measured with a gas chromatograph–mass spectrometer (GC–MS). The temporal–spatial distributions, compositions of PAEs, and their effecting factors were investigated. The results indicated that di-n-butyl phthalate (DnBP), diisobutyl phthalate (DIBP), and di(2-ethylhexyl) phthalate (DEHP) were three dominant PAE components in both the surface and core sediments. The residual level of total detected PAEs (∑PAEs) in the surface sediments (2.146±2.255 μg/g dw) was lower than that in the western core sediments (10.615 ±9.733 μg/g) and in the eastern core sediments (5.109± 4.741 μg/g). The average content of ∑PAEs in the surface sediments from the inflow rivers (4.128±1.738 μg/g dw) was an order of magnitude higher than those from the lake (0.323±0.093 μg/g dw), and there were similar PAE compositions between the lake and inflow rivers. This finding means that there were important effects of PAE input from the inflow rivers on the compositions and distributions of PAEs in the surface sediments. An increasing trend was found for the residual levels of ΣPAEs, DnBP, and DIBP from the bottom to the surface in both the western and eastern core sediments. Increasing PAE usage with the population growth, urbanization, and industrial and agricultural development in Lake Chaohu watershed would result in the increasing production of PAEs and their resulting presence in the sediments. The significant positive relationships were also found between the PAE contents and the percentage of sand particles, as well as TOC contents in the sediment cores.

Keywords Phthalate esters · Sediment · Residual level · Temporal–spatial distribution · Composition · Lake Chaohu

Introduction

Phthalate esters (PAEs) are widely used as raw chemical materials for producing pesticides, fuel, cosmetics, perfumes, and medical equipment (Staples et al. 1997). PAEs are also used as chemical additives in the manufacturing of PVC to improve the flexibility and workability of PVC (Gomez-Hens and Aguilar-Caballos 2003; Koniecki et al. 2011; Zheng et al. 2014). Furthermore, PAEs play a dominant role in the production and use of plasticizer, accounting for approximately 92 % of the total production of plasticizer (Rahman and Brazel 2004). Annually, several million tons of PAEs are produced and consumed worldwide (Xie et al. 2007; Guo et al. 2012). In China, over one million tons of PAEs are produced and consumed each year, accounting for one fifth of the global consumption (Zhang 2004; He et al. 2013a, b; Liu et al. 2014). China is a country with the largest amount of plasticizer use with an annual growth rate of over 10 %: this growth is observed particularly in such rapid economic development regions as Yangtze River Delta and Pearl River Delta regions (Xie et al. 2007; CPCIA 2009). Because of their worldwide mass production and use, PAE compounds are among the most widespread environmental pollutants on Earth because they are easily released into the environment during manufacture, usage, and disposal. PAEs can be detected in various environmental

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media, such as water (Shi et al. 2012), soil (Chen et al. 2012), sediment (Liu et al. 2010), air (Kang et al. 2012), and biota (Blair et al. 2009). With increased rates of PAE contamination, PAE toxicity to organisms and humans has been gradually confirmed: increased cases of reproductive toxicity (Foster et al. 1980; Li et al. 2013; Ventrice et al. 2013), neural toxicity (Testa et al. 2012; Ventrice et al. 2013), respiratory toxicity (Jaakkola et al. 1999; Jaakkola and Knight 2008), as well as carcinogenic, teratogenic, and mutagenic effects (Selenskass et al. 1995; Lopez-Carrillo et al. 2010) have been observed. Many countries have now limited the usage of PAEs and have created relevant policies and laws (EC 2003, 2005; PRC-NS 2008). For instance, six PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DnOP) were listed as priority pollutants by US EPA. In Japan, six PAEs including DnBP, DnOP, DEHP, diisobutyl phthalate (DIBP), di-iso-heptyl ester phthalate (DIHP), and diisodecyl phthalate (DIDP) types of PAEs were listed as the key pollutants in environmental surveys. Also, in China, three PAEs, including DMP, DEP, and DnOP, were listed as priority pollutants. Regulations for the contents of PAEs in toys and childcare articles were made in European Union (EU), Brazil, and Argentina.

Lake ecosystems are primary sinks for various contaminants from watersheds (Doong et al. 2002; Feng et al. 1998). PAEs can enter lake ecosystems through a variety of routes, such as the discharge of industrial and domestic wastewater, surface runoff input from agricultural and urban areas, and atmospheric wet and dry deposition (Fauser et al. 2009). Sediment plays a key role in the biogeochemical cycles of PAEs in aquatic ecosystems because it could serve as both a source and a sink of PAEs though the deposition of suspended solids and the resuspension of sediment. Many studies on PAE residues and distributions in the sediments of rivers and lakes have been reported in recent years in the Yangtze River (Wang et al. 2008), the Yellow River (Sha et al. 2007), the Pearl River (Liu et al. 2014), the Qiantangjiang River (Sun et al. 2013), the urban lakes in Guangzhou (Zeng et al. 2008), the lakes in Beijing area (Zheng et al. 2014), the Ogun River in Nigeria (Adeniyi et al. 2011), the Gomti River in India (Srivastava et al. 2010), the rivers and lakes in Berlin, Germany (Fromme et al. 2002), and the lakes in North Holland (Vethaak et al. 2005). Worldwide, DnBP and DEHP have been detected at very high levels in sediment. Compared with the extensive studies on PAEs in surface sediment, available information is limited on PAE distributions in sediment core that could show the PAE contamination history (Peterson and Freeman 1982; Pruell and Quinn 1985).

Lake Chaohu (117.18°–117.50° E, 31.25°–31.42° N), located in eastern China (Fig. 1), is the fifth largest freshwater lake in China with a water area of approximately 760 km^2 and a reservoir capacity of 1.72 to 3.23 billion cubic meters. This lake is a highly important water source for drinking for the 9.6 million residents in the surrounding areas and for the development of industry and agriculture in its catchments. During the last decades, with the rapid social and economic development, a large amount of pollutants have discharged into the lake. Lake Chaohu has been suffered from serious eutrophication (Xu 1997; Xu et al. 1999), as well as heavy contamination of toxic chemicals, such as organochlorine pesticides (OCPs) (He et al. 2012; Wang et al. 2012a, b; Liu et al. 2013; Ouyang et al. 2012, 2013, 2014), polycyclic aromatic hydrocarbons (PAHs) (Qin et al. 2014), polybrominated diphenyl ethers (PBDEs) (He et al. 2013a), and perfluoroalkyl acids (PFAAs) (Liu et al. 2015). The concentrations and distributions of PAEs in the Lake Chaohu surface water were also reported (Yang et al. 2009; He et al. 2013b). However, the current status and historical variations of PAE contaminations in the sediments remain unknown. The objectives of the present study are (1) to ascertain the residual levels, spatial distributions, and compositions of PAEs in the surface sediments of Lake Chaohu; (2) to investigate the PAE contamination history and its spatial variations in the sediment cores; and (3) to analyze the factors affecting the residues and distributions of PAEs in the sediments.

Materials and methods

Reagents and materials

Acetone (high-performance liquid chromatography grade, HPLCG), n-hexane (HEX, HPLCG) and dichloromethane (DCM, HPLCG) were purchased from Tedia Co. Inc., Fairfield, OH, USA. A PAE stock standard mixture was prepared by diluting HEX with a commercial 19 PAE standard mixture (Accustandard Inc., New Haven, CT, USA), which contained DMP, DEP, DIBP, DnBP, DEHP, DnOP, di-(2-methoxyethyl) phthalate (DMEP), bis(4-methyl-2-pentyl) phthalate (BMPP), di-(2-ethoxyethyl) phthalate (DEEP), diamyl phthalate (DAP), dihexyl phthalate (DHXP), benzyl butyl phthalate (BBP), hexyl-2-ethylhexyl phthalate (HEHP), di-(2-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), diphenyl phthalate (DPP), diphenyl isophthalate (DPIP), dibenzyl phthalate (DBZP), dinonyl phthalate (DNP) at 1000 μg/ml each. The working standard solution was prepared by diluting the stock standard with HEX. One hundred micrograms per milliliter each of surrogate standard (SS) (3,4,5,6,d4-DnBP) and internal standards (ISs) (3,4,5,6,d4-DEP and 3,4,5,6,d4-DnOP) were acquired from Accustandard Inc., New Haven, CT, USA. Granular anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and glass fiber membranes wrapped with aluminum foil were heated at 650 and

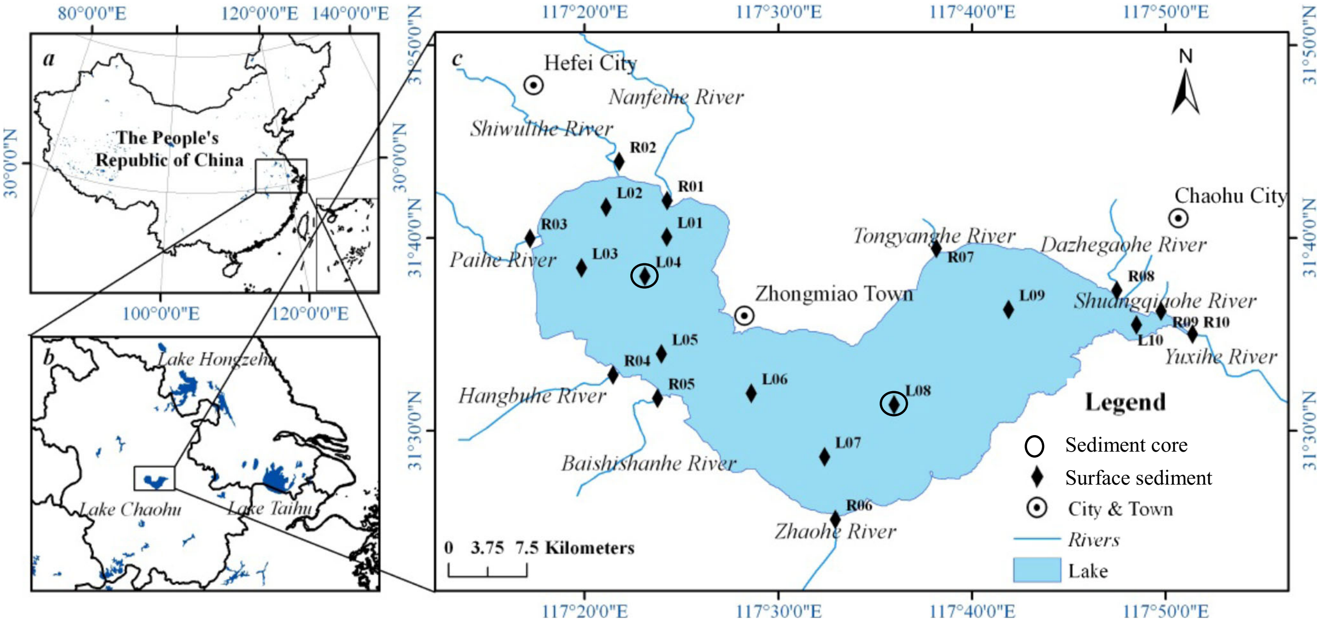


Fig. 1 Geographical localities of **a** Lake Chaohu, **b** Lake Chaohu in East China, and **c** the sediment sampling sites in Lake Chaohu

450 °C, respectively, in a furnace for 6 h and were stored in a sealed desiccator until they were used. All glassware was cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, Kunshan, China) and was heated at 450 °C for 6 h.

Sample collection

The distributions of 20 sampling sites are presented in Fig. 1. Ten sites (L01–L10) were located inside the lake, and another ten sites (R01-R10) were in the estuaries of rivers. The detailed information on the geographical coordinates and locations for all sites are described in Table S1. In May 2011, the surface sediment samples were collected using a grab sampler from 20 sampling sites, and the sediment core samples were collected using a tube sampler from the sites L4 and L8 located at the center of the western and eastern regions of the lake, respectively. The sediment cores were sliced per 1 cm. The sediment samples were freeze-dried, ground, and sieved through a 70-mesh sieve before extraction.

Sample extraction and cleanup

Sediment samples were extracted with DCM for 48 h at a rate of 4–6 cycles/h in the Soxhlet extractor. Activated copper granules were added to the extraction flasks during the extraction to remove elemental sulfur. The extracts were concentrated to 1 ml by rotary evaporator. Concentrated extracts were cleaned and fractioned on a 10-mm i.d. 1:2 alumina/silica gel column packed, from the bottom to top, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). The initial solution eluted by 20 ml of hexane and 70 ml of DCM/HEX (3:7) mixture was discarded. Next, PAEs were eluted with 40 ml of acetone/HEX (2:8) mixture. The eluate was concentrated to 1 ml using a rotary evaporator. A known quantity of IS was added to the sample prior to instrumental analysis.

Sample analysis and quality assurance

The extracted compounds were analyzed using an Agilent 6890 gas chromatograph equipped with an HP-5 MS column (30 m× 0.25 mm internal diameter and 0.25 μm film thickness) and an Agilent 5973 mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA, USA) operating in electron impact (EI) and selective ion monitoring (SIM) modes. The extracts were injected by autosampling at 60 °C in splitless mode with a venting time of 0.75 min. The oven temperature was programmed to an initial temperature of 60 °C for 2 min and then increased at a rate of 8 °C/min from 60 to 300 °C, where the temperature was maintained for 15 min. Helium was used as both the carrier (1 ml/min) and the makeup gas (50 ml/min). The temperatures of the inlet, quadrupole, and ion source were 280, 150, and 246 °C, respectively. Quantitation was performed using the internal calibration method based on a six-point calibration curve for individual PAEs. 3,4,5,6,d4-DEP and 3,4,5,6,d4-DnOP were used as internal standards for the quantification of PAEs.

The analysis quality assurance method proposed by US EPA was applied in the present study. Two and three parallel samples were collected for the sediment core and surface sediment samples, respectively. The SS were added to 40 % of the samples to investigate matrix effects and extraction efficiency, considering the good reproducibility of the method and economic cost for large number of samples. The instruments were recalibrated using the calibration standard for each of the samples. The solvent blank was performed by using n-hexane. The procedure blank was prepared by using glass fiber filter (ashed at 450 °C for 6 h) and extracted as sediment samples. The procedure recovery test was also performed. Five-hundred-nanogram mixtures of 19 PAE standards, which contained DMP, DEP, DIBP, DnBP, DMEP, BMPP, DEEP, DAP, DHXP, BBP, HEHP, DBEP, DCHP, DEHP, DPP, DPIP, DnOP, DBZP, and DNP were spiked into the ashed glass fiber filter and extracted as sediment samples. The recoveries of 19 PAEs were calculated using the following equation: recovery=(procedure standards−procedure blank)/(500−solvent blank). The detailed information on the recoveries and detection limits of the analysis method for the 19 study PAEs is presented in Table S2 in the Supplementary Materials. Except for DBIP and DEEP with the detection limit of 5 ng/g, the detection limits for other 17 PAE components varied from 0.1 to 2 ng/g. Except for DBEP with the recovery of 68.2 %, the recoveries for other 18 PAE components were between 70 to 106 %.

Dating of the sediment cores

The chronologies of the sediment were determined from ^{210}Pb and ^{137}Cs radionuclide activities. Measurements of ^{210}Pb, ^{226}Ra, and ^{137}Cs radionuclide activities for each sample were conducted by using Ortec HPGe GWL series of well-type, coaxial, low background, intrinsic germanium detectors (GCW3022 H-P Ge) at the State Key Laboratory of Lake Science and Environment of Chinese Academic of Science (CAS), Nanjing, China. The activities of excess ^{210}Pb in each sample, which was used for dating, were obtained by subtracting ^{226}Ra from the total ^{210}Pb activities. Sediment age determined by excess ^{210}Pb was based on constant initial concentration (CIC) and constant rate of supply (CRS) dating model (Appleby 2001). CIC model assumes a constant rate of sediment accumulation, i.e., the initial unsupported ^{210}Pb activity in each layer of the sediment are the same. On the other hand, when CRS model is applied, changes in the sedimentation rate are considered, which results in changes in the initial unsupported ^{210}Pb concentrations. CIC model showed that the sedimentation rates in west and east part of Lake Chaohu were 0.36 and 0.30/cm/year, respectively, while sediment accumulation rates in west and east part of Lake Chaohu were 0.24 and 0.20 g/cm^2/year, respectively. ^{137}Cs peak activities provided an independent age marker at depth of 19 cm in WL1 and 14 cm in EL1, which corresponds to the global nuclear tests dated to 1963 AD and can be considered as a verification of the ^{210}Pb-based age results (Wang et al. 2012a, b). Based on ^{137}Cs activities, sedimentation rates since 1963 in west and east part of Lake Chaohu were 0.38 and 0.28/cm/year, respectively, while sediment accumulation rates in west and east part of Lake Chaohu were 0.21 and 0.15 g/cm^2/year, respectively.

The analyses of organic carbon and granularity

The sediment samples were divided into two parts to determine total carbon (TC) and inorganic carbon (IC) using a total organic carbon (TOC) analyzer (TOC-5000A; Shimadzu Corp., Japan) with a solid sampler (SSM-5000A) to obtain TOC levels. Analytically pure glucose was used to measure the TC standard curve and analytically pure sodium carbonate was used to measure the IC standard curve. Sediment granularity was determined by laser particle size analyzer (A22 FRITSCH) after 5 % HCl and 5 % H_2O_2 treatment.

Results and discussion

Current status of PAE contamination in the surface sediments

Residue levels of PAEs in the surface sediments

The statistical features, the results of the normal distribution test, and the frequency distribution histogram before/after logarithmic transformation of residue level of PAEs in the surface sediments are presented in Tables 1 and 2 and Figs. 2 and 3, respectively. The current research on the six priority PAEs set by US EPA is compared with other studies in Table 3.

Among the 19 studied PAEs, 16 individual PAE components were detected while DMEP, DPP, and DPIP were absent. The contents of total PAEs ($\sum_{16}$PAEs) ranged from 0.244 to 5.922 μg/g dw with a mean value of 2.146±2.255 μg/g dw in the surface sediments. The contents of total six priority PAEs ($\sum_6$PAEs) ranged from 0.130 to 4.245 μg/g dw with a mean value of 1.393±1.502 μg/g dw. DnBP had the highest concentrations (0.790±0.881 μg/g dw), followed by DIBP (0.601±0.651 μg/g dw), DEHP (0.299±0.417 μg/g dw), and DMP (0.252±0.407 μg/g dw). The detection rates for DMP, DEP, DIBP, DnBP, DEEP, BBP, DEHP, and DnOP were 100 % in all sampling sites while the detection rates for DBEP and DHXP were 89.5 and 63.2 % and less than 50 % for other PAEs. DnBP, DIBP, and DEHP and DMP could be considered primary contaminants in the surface sediments, according to their residue levels and detection rates in Lake Chaohu. This finding was in accordance with the results of surface waters and suspended solids (Wang 2014). All the detected PAE components in the surface sediments followed normal distributions (Table 2, Figs. 2 and 3).

Table 3 shows that as the main PAE components, the contents of DMP and DnBP in the surface sediments from Lake Chaohu were at high levels, which were higher than those of the urban lakes in Guangzhou (Zeng et al. 2008), the lakes in Beijing (Zheng et al. 2014), River Qiantang (Sun et al. 2013), the Pearl River (Liu et al. 2014), the Ogun River in Nigeria (Adeniyi et al. 2011), Gomti River in India (Srivastava et al.

Table 1 Statistical features of PAEs contents in the surface sediments from Lake Chaohu (μg/g dw)

PAEs	Mean	SD	Min	Max	Detection rate%
DMP	0.252	0.407	0.006	1.336	100.0
DEP	0.015	0.016	0.001	0.042	100.0
DIBP	0.601	0.651	0.071	1.797	100.0
DnBP	0.790	0.881	0.080	2.627	100.0
DMEP	ND	ND	ND	ND	0
BMPP	0.0006	0.0015	ND	0.0061	42.1
DEEP	0.145	0.186	0.013	0.662	100.0
DAP	0.001	0.003	ND	0.008	47.4
DHXP	0.0002	0.0004	ND	0.0016	63.2
BBP	0.033	0.066	0.0004	0.286	100.0
HEHP	0.0006	0.0013	ND	0.005	31.6
DBEP	0.002	0.003	ND	0.014	89.5
DCHP	0.0003	0.0008	ND	0.003	26.3
DEHP	0.299	0.417	0.031	1.820	100.0
DPP	ND	ND	ND	ND	0
DPIP	ND	ND	ND	ND	0
DnOP	0.004	0.007	0.0002	0.029	100.0
DBZP	0.002	0.004	ND	0.016	15.8
DNP	0.001	0.003	ND	0.013	42.1
$\sum_6$PAEs	5.059	3.079	2.005	14.752	100.0
$\sum_{16}$PAEs	2.146	2.255	0.244	5.922	100.0

ND not determined

Table 2 Skewness, kurtosis, and the result of Shapiro-Wilk normal distribution test of the contents of PAEs in the surface sediments before/after logarithm transformation

PAEs	Before transformation			After transformation		
	Skewness	Kurtosis	*P*	Skewness	Kurtosis	*P*
DMP	1.706	1.775	0.028	0.537	−1.379	0.160
DEP	0.595	−1.510	0.019	0.325	−1.996	0.086
DIBP	0.652	−1.349	0.031	0.345	−1.990	0.061
DnBP	0.969	−0.419	0.075	0.302	−1.833	0.109
BMPP	1.978	3.701	0.413	0.756	−0.778	0.732
DEEP	1.807	2.730	0.048	0.465	−0.932	0.453
DAP	0.779	−0.846	0.922	−0.533	−1.382	0.914
DHXP	2.184	4.724	0.078	0.933	−0.524	0.533
BBP	3.525	13.411	0.026	−0.088	−0.417	0.907
HEHP	1.021	0.217	0.743	0.083	−2.717	0.787
DBEP	2.971	9.544	0.099	0.734	−0.105	0.894
DCHP	1.658	2.422	0.712	0.643	−1.478	0.878
DEHP	2.905	10.302	0.153	0.306	−1.403	0.275
DnOP	2.788	8.826	0.105	0.353	−1.309	0.527
DBZP	1.052		0.984	0.390		1.000
DNP	2.604	7.017	0.231	−0.105	−1.315	0.793

2010), and the North Sea around Netherlands (Vethaak et al. 2005) but lower than the levels observed in the Yellow River (Sha et al. 2007). The DEP content in the surface sediments from Lake Chaohu was lower than that in the River Ogun in Nigeria and in the North Sea around Netherlands but was comparable to other studies. The contents of BBP, DEHP, and DnOP were lower than the most results of other studies. Additionally, in the surface sediments from Lake Chaohu, the concentration of DnBP was higher than that of DEHP, while the relationship was the opposite in most of the other studies. The variations in the residual levels and interrelationships of PAE components in different studies might be attributed to the difference in the use of domestic and agricultural plasticizers.

Spatial distribution of PAEs in the surface sediments

The spatial distributions of PAEs in the surface sediments from Lake Chaohu are presented in Fig. 4. The PAE contents in the surface sediments from the inflow rivers were an order of magnitude higher than those from the lake. The average contents of $\sum_{16}$PAEs and $\sum_6$PAEs in the surface sediments from the inflow rivers were 4.128±1.738 μg/g dw (0.807~5.922 μg/g dw) and 2.634±1.229 μg/g dw (0.568~4.245 μg g dw), respectively, while those from the lake were 0.323±0.093 μg/g dw (0.244~0.540 μg/g dw) and 0.209±0.093 μg/g dw (0.130~0.441 μg/g dw). This means that the PAEs in Lake Chaohu might be from the inflow rivers. There were no significant differences in the PAEs contents of the surface sediments from the lake. However, significant differences were found for the PAE contents of the surface sediments from the inflow rivers. For the river samples, the lowest and highest contents of PAEs in the surface sediments were found for R1 (Nafeihe River) and R9 (Shuangqiaohe River), respectively. The highest contents of PAEs in the surface sediments from R9 might be attributed to the discharge of industrial wastewater from power plant and domestic sewage from the nearby villages, as well as the input of rainfall runoff from nearby farmland were vegetables and other crops are cultivated. The contents of PAEs in the surface sediments form the Nanfeihe River in the northwest region of the lake (R1) should have been highest, since the river flowed through the urban area of Hefei City, the Anhui Province capital, which is home to 5.7 million citizens, and carried large amounts of sewage and solid waste. However, the dredging engineering in the mouth of the Nanfeihe River (R1) might be resulted in the lowest contents of PAEs in its surface sediments.

Compositions and spatial variations of PAEs in the surface sediments

The spatial distributions of PAE compositions in the surface sediments from Lake Chaohu are presented in Figs. 5 and 6. The average percentages for three dominant components, DnBP, DIBP, and DEHP in all surface sediment samples and

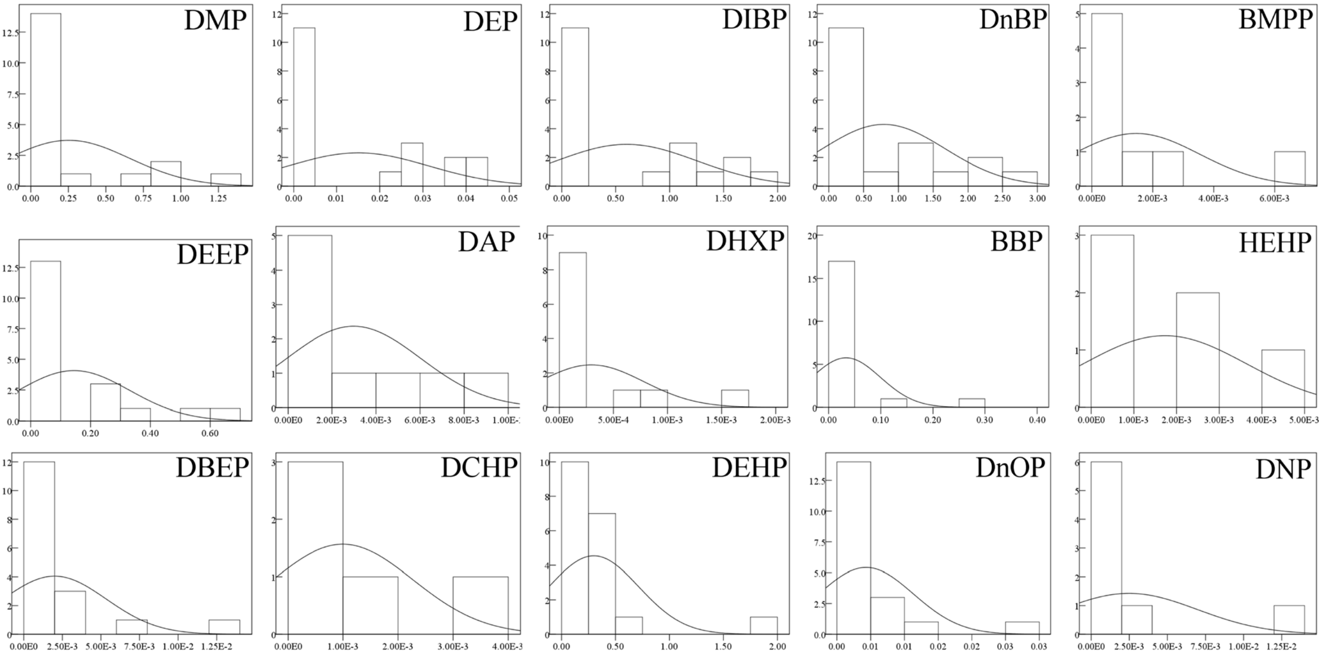


Fig. 2 Histogram for the contents of PAEs (μg/g dw) in the surface sediments

were 37.8, 27.2, and 15.8 %, and those for other PAE components were less than 8.0 %. DnBP, DIBP, and DEHP were also found as dominant PAE components in the sediments due to their large amount of production and use around the world (Peterson and Freeman 1982; Pruell and Quinn 1985). The average percentage for DnBP in the surface sediments from the lake sites (41.0 %) was higher than that from the inflow river sites (31.2%) while the average percentages for DIBP, DEHP, and DMP in the surface sediments from the lake sites (26.4, 14.7, and 3.9 %) were lower than those from the inflow river sites (28.6, 18.0, and 12.2 %).

Our previous study on the spatial distribution of PAEs in the surface water from 3 to 4 lake sampling sites monthly during May 2010 to April 2011 found also that the annual concentrations of PAE components in the western region of the lake were higher than those in the eastern region of the lake (He et al. 2013b). This spatial distribution of PAEs in both the sediment and the water might be attributed to input sources of PAEs. The western area of the lake receives more than 80 % of the total water from the inflow rivers including Nanfeihe River (NFHR) and Hangpuhe-Fenglehe River (HP-FLR). The NFHR located in the northwest region of the lake flows through the urban area of

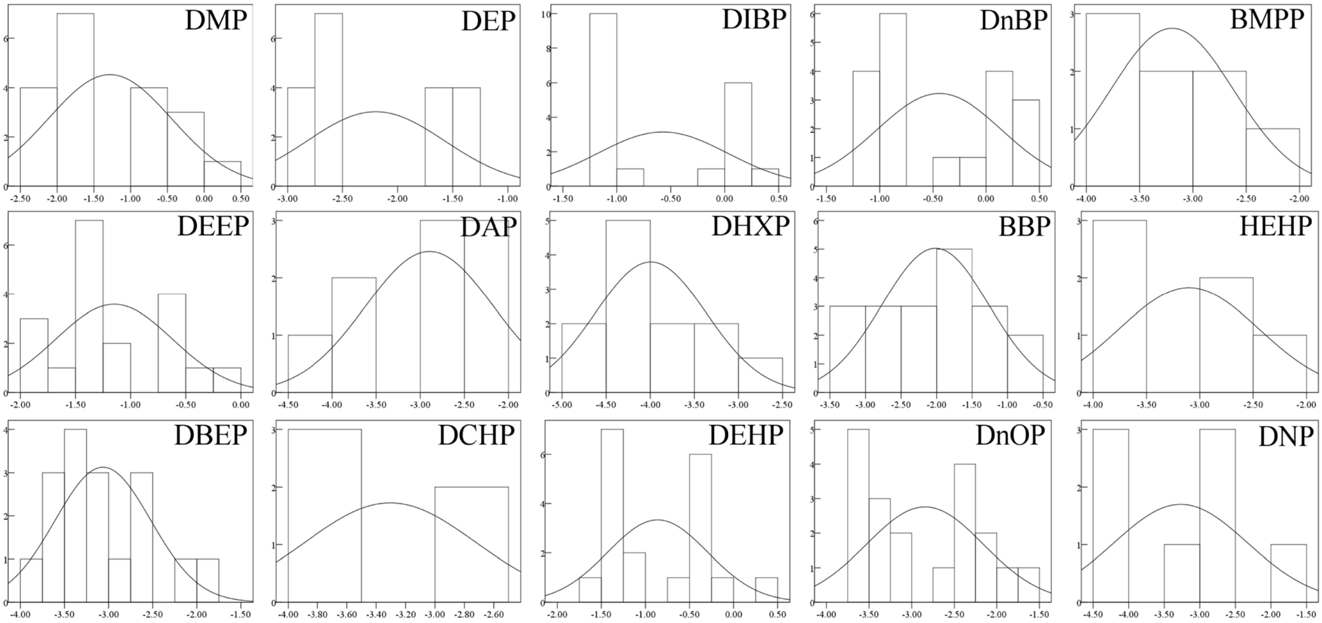


Fig. 3 Histogram for the contents of log(PAEs) (μg/g dw) in the surface sediments

Table 3 Comparison of the residue levels of PAEs in surface sediments in Lake Chaohu and other regions (μg/g dw)

Place		DMP	DEP	DnBP	BBP	DEHP	DnOP	Reference
Lake Chaohu		0.252	0.015	0.790	0.033	0.299	0.004	This study
The urban lakes in Guangzhou		0.039	0.13	0.28	0.034	1.30	0.020	Zeng et al. (2008)
Beijing	Shichahai	0.084	0.011	0.502	0.090	2.532	0.823	Zheng et al. (2014)
	Lake Kunminghu	0.047	0.008	0.132	0.116	0.998	0.300	
	Guanting Reservoir	0.040	0.014	0.130	0.052	0.055	0.080	
Qiantang River		0.053	0.018	0.113	0.0018	1.555	0.0049	Sun et al. (2013)
The Yellow River		0.276	0.006	2.88	–[a]	4.57	ND	Sha et al. (2007)
The Pearl River		0.002	0.012	0.148	0.009	1.46	0.013	Liu et al. (2014)
Kaohsiung Harbor, Taiwan		ND	ND	0.29	ND	4.90	0.14	Chen et al. (2013)
The Ogun River, Nigeria		0.212	0.185	0.412	–	0.050	–	Adeniyi et al. (2011)
Gomti River, India		0.011	0.005	0.011	–	0.032	0.005	Srivastava et al. (2010)
Berlin, Germany		–	–	0.45	–	0.70	–	Fromme et al. (2002)
The North Sea, Netherlands		0.014	0.133	0.390	0.014	0.600	0.011	Vethaak et al. (2005)

ND not determined

[a] Not analyzed

Hefei City, the Anhui Province capital. The HP-FLR located in the southwest region of the lake runs through the agricultural area that contributes approximately 60 % of total surface runoff to the lake. Generally, water flows from the western area of the lake to the eastern area, resulting in a decreasing trend of PAEs from the western to eastern areas of Lake Chaohu (He et al. 2013b).

The relationships among the components of PAEs in the surface sediments

Ten individual PAE components were detected in all surface sediment samples, and they followed a log-normal distribution. The log-transformations were thus needed for the PAE contents before the Pearson correlation analysis could be performed. The relationships among ten detected PAE components in the surface sediments are presented in Table 4. There were significant positive correlations ($p<0.01$) among different PAE components with the correlation coefficient between 0.622 and 0.989. This implies that these components might have the same sources.

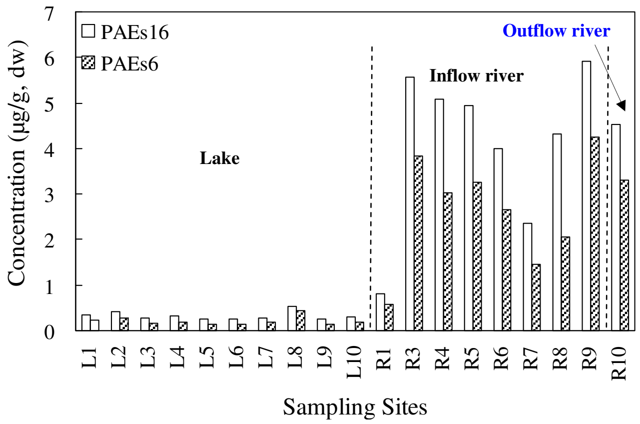


Fig. 4 The spatial distributions of PAE contents in the surface sediment sites from Lake Chaohu and its surrounding rivers

Historical variations of PAE contamination in the sediment cores

Residue levels of PAEs in the sediment cores

The general characteristics of PAE residual levels in two sediment cores L4 and L8 from the western and eastern regions of the lake are tabulated in Table 5. The comparisons of mean PAE contents in the two sediment cores are presented in Fig. 4. Among the 19 individual PAE components studied, 14 and 12 congeners were detected for the L4 and L8 sediment cores, respectively. A detection rate of 100 % was found for five congeners (DMP, DEP, DIBP, DnBP, and DnOP), and a 97–100 % detection rate was found for DEEP, DHXP, BBP, and DEHP while four congeners (DMEP, BMPP, DPP, and DPIP) were not detected in any of the samples of the two sediment cores. The contents of Σ_6PAEs, ΣPAEs, and all detected PAE components in the L4 sediment core were higher than those in the L8 sediment core. The average contents of $\sum_{16}$PAEs in the L4 and L8 sediment cores were 10.615±9.733 and 5.109±4.741 μg/g, respectively. DnBP, DIBP, and DEHP were three dominant PAE components in both the L4 and L8 sediment cores from the center of western and eastern areas of the lake. The average contents of DnBP, DIBP, and DEHP in the L4 sediment core (9.024±8.791, 1.015±0.555, and 0.490 ±0.734 μg/g) were higher than those in the L8 sediment core (4.435±4.456, 0.543±0.279, and 0.093±0.072 μg/g). The distribution patterns of PAEs in the two sediment cores were

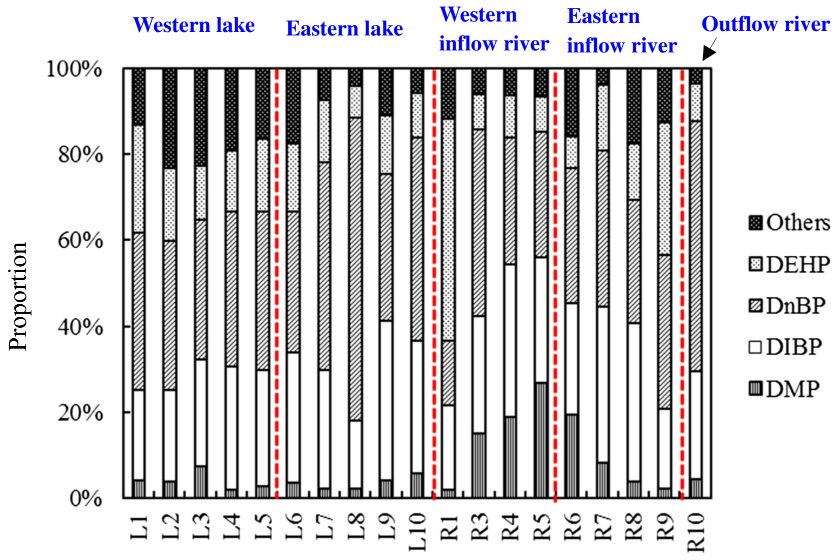


Fig. 5 Spatial variations of PAE compositions in the surface sediments sites from Lake Chaohu and its surrounding rivers

very similar, illustrating the dominance of DnBP, DIBP, and DEHP (Fig. 7). These three PAE compounds were also dominant in the tributaries (Wang 2014).

Historical variations of PAE residual levels in the sediment cores

The historical variations of the residual levels of total PAEs (ΣPAEs) and three dominant components (DnBP, DIBP, and DEHP) in the L4 and L8 sediment cores are shown in Fig. 8. The 30-cm sediment cores at the L4 and L8 sample sites reflect the pollution history of PAEs from 1865 to 2010 and from 1849 to 2010, respectively. An increasing trend was found for the residual levels of ΣPAEs, DnBP, and DIBP at both the L4 and L8 sites. The contents of ΣPAEs, DnBP, DIBP, and DEHP in the L4 site in the western lake were higher than those in the L8 site in the eastern lake. Such spatial and temporal trends in PAEs change in the sediment cores with different urbanization/industrialization histories in the present study were compared with the study in the Narragansett Bay (Pruell and Quinn 1985) and the Chesapeake Bay (Peterson and Freeman 1982) in the USA. For the L4 sediment core, there had been a significant increase of ΣPAEs, DnBP, and DIBP since the mid-1980s, which showed that the average contents of ΣPAEs, DnBP, and DIBP during the period of the mid-1980s to 2010 were 5.2±3.4, 4.1±3.0, and 0.7±0.3 μg/g, respectively, while those during the period of 1865 to the mid-1980s were 23.1±7.9, 20.4±7.0, and 1.7±0.4 μg/g, respectively (Fig. 8). Such an increasing trend for ΣPAEs, DnBP, and DIBP might be primarily attributed to the increasing usage of PAEs associated with the rapid socioeconomic development in the Lake Chaohu Basin (please see next paragraph for the details). It should be noticed that the vertical distribution of such environmentally stable contaminants with low water solubilities as PAEs can provide information on their input histories; however, such depositional sequences are often hard to interpret due to the complex nature of sedimentary processes (Pruell and Quinn 1985).

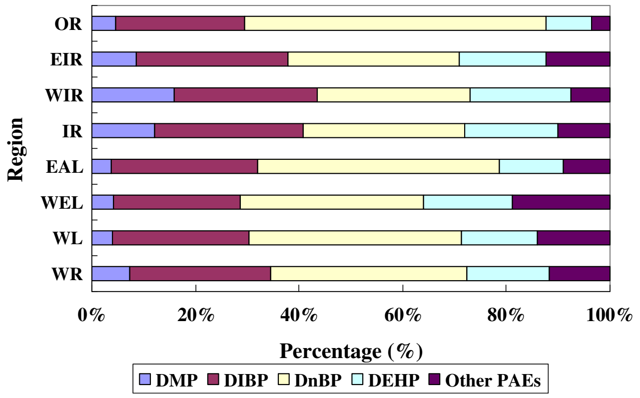


Fig. 6 PAE percentages in the surface sediments from Lake Chaohu and their spatial variations in different regions

Population growth, urbanization, and industrial and agricultural development would result in the increasing production and use of PAEs, thereby causing an increased discharge of sewage, wastewater, and garbage into the environment, exacerbating contamination by PAEs (Sun et al. 2013). The population in the Lake Chaohu Basin has been growing steadily from 5.88 million in 1949 to 12.3 million in 2009 with an average annual increase of 10.6 million (Fig. S1a). Levels of nonagricultural population have gradually increased as well (Fig. S1b). The urbanization in the Lake Chaohu Basin has also experienced significant growth since the 1980s. For instance, the downtown area of Hefei city (the capital of Anhui Province) increased 4.8 times from 59 km^2 in 1984 to 280 km^2 in 2009 while that of Chaohu City increased 7.6 times from 8 km^2 in 1984 to 61 km^2 in 2009 (Fig. S1c). The industrial development in the Lake Chaohu Basin has exponentially grown since 1949. For instance, the average annual growth rates of industrial

Table 4 Pearson correlation analysis among the log-transformed contents of ten detected PAE components in the surface sediments from Lake Chaohu (*N*=11~19)

	DMP	DEP	DIBP	DBP	DEEP	DHXP	BBP	DBEP	DEHP	DnOP
DMP	1									
DEP	0.958*	1								
DIBP	0.947*	0.989*	1							
DnBP	0.905*	0.954*	0.951*	1						
DEEP	0.787*	0.841*	0.847*	0.757*	1					
DHXP	0.795*	0.891*	0.905*	0.866*	0.967*	1				
BBP	0.666*	0.675*	0.638*	0.681*	0.676*	0.574	1			
DBEP	0.722*	0.825*	0.830*	0.842*	0.884*	0.902*	0.672*	1		
DEHP	0.794*	0.874*	0.893*	0.846*	0.862*	0.887*	0.622*	0.878*	1	
DnOP	0.776*	0.838*	0.854*	0.809*	0.872*	0.868*	0.638*	0.844*	0.976*	1

*The correlation is significant at the 0.01 level (two-tailed)

output for Hefei and Chaohu City in the 1990s were as high as 14 and 17 %, respectively (Fig. S2). As one of the important commodity grain bases in China, the agricultural output in the Lake Chaohu Basin has grown rapidly since the 1980s, especially in the development of industrial agriculture since the 1990s, which has lead to an increasing amount of plastic film usage from 4.35 kg/ha in 1990 to 15.15 kg/ha in 2009 (Fig. S3).

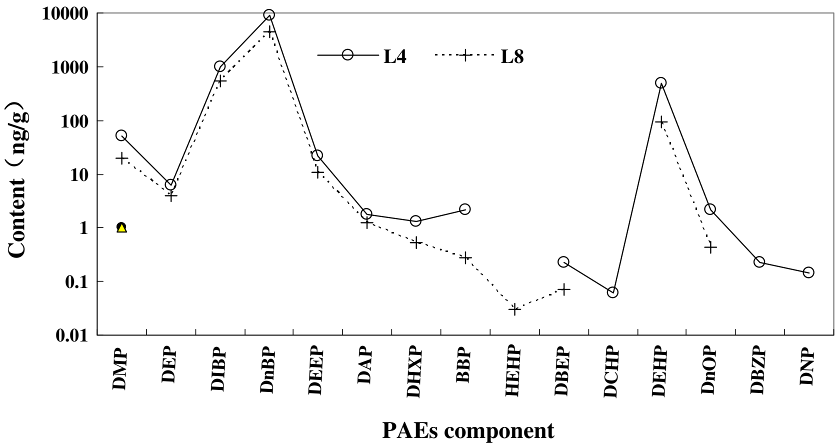
Sediment characteristics, such as granularity and TOC, might have the significant effects on the historical variations of PAE residual levels in the sediment cores. The relationships between PAEs and granularity as well as TOC in the sediment cores are presented in Tables 6 and 7, respectively. The contents of Σ_6PAEs, ΣPAEs, as well as individual PAEs, including DMP, DEP, DIBP, DnBP, DEEP, DBEP, and DnOP in the L4 and L8 sediment cores, were significantly positively correlated with the percentage of sand particles but significantly negatively correlated with the percentage of fine sand particles (Table 6). A significantly positive relationship was found between TOC and the contents of Σ_6PAEs, ΣPAEs, as well as low-molecular-weight PAEs (DMP, DEP, DIBP, DnBP,

Table 5 Content, range, and detection rate of PAEs in the L4 and L8 sediment cores from Lake Chaohu

	Detection rate (%)		Range (ng/g)		Average content (ng/g)	
	L4	L8	L4	L8	L4	L8
DMP	100	100	3.83–269.64	3.87–48.02	51.1±53.60	19.49±10.3
DEP	100	100	1.71–21.92	1.83–7.71	6.29±5.30	3.93±1.55
DIBP	100	100	308.84–2392.24	129.60–1180.04	1014.67±555.80	543.11±279.33
DnBP	100	100	1009.89–33894.69	932.41–21095.29	9023.51±8791.23	4435.37±4455.67
DMEP	0	0	ND	ND	ND	ND
BMPP	0	0	ND	ND	ND	ND
DEEP	100	97	2.06–79.81	ND–38.94	21.54±22.92	10.96±10.23
DAP	50	10	ND–26.94	ND–19.30	1.81±4.97	1.25±4.63
DHXP	97	100	ND–3.65	0.09–2.29	1.3±0.90	0.52±0.43
BBP	100	97	0.41–10.41	ND–1.26	2.16±2.27	0.28±0.31
HEHP	0	10	ND	ND–0.49	ND	0.03±0.10
DBEP	37	21	ND–1.19	ND–0.47	0.23±0.36	0.07±0.14
DCHP	17	0	ND–0.83	ND	0.06±0.17	ND
DEHP	97	100	ND–3391.08	33.04–304.35	489.74±734.11	93.22±72.94
DPP	0	0	ND	ND	ND	ND
DPIP	0	0	ND	ND	ND	ND
DnOP	100	100	0.30–9.59	0.24–1.19	2.14±2.49	0.44±0.23
DBZP	13	0	ND–5.19	ND	0.22±0.97	ND
DNP	50	0	ND–0.76	ND	0.14±0.19	ND
Σ_6PAEs			1030.03–34163.57	1022.03–21413.98	9574.95±9199.19	4552.74±4495.68
ΣPAEs			1342.64–36266.03	1154.06–22619.79	10614.91±9732.6	5108.68±4741.14

ND not determined

Fig. 7 Comparisons of average contents of PAEs and their distribution pattern in the L4 and L8 sediment cores from Lake Chaohu



DEEP) in the L4 and L8 sediment cores. However, for the surface sediments, there were no significant relationships found between TOC and PAEs contents. This might be because the surface sediment samples were from ten lake sites (L01–L10) and ten river sites (R01–R10), and the surface sediment collected using a grab sampler was mixed samples of 10–15-cm depth sediment at each site.

Historical variations of PAE composition in the sediment cores

The historical percentage variations of DnBP, DIBP, DEHP, and other PAE components are presented in Fig. 8. From the bottom to surface sediments at both the L4 and L8 sites, there was an increasing trend of percentages for DnBP and a decreasing trend of percentages for DIBP and DEHP (Fig. 9). The opposite trends of percentages between DnBP and DIBP as well as DEHP might be attributed to their usages and different degradation rates. In China, 1.3 million tons of PAEs, mainly DnBP and DEHP, are produced and consumed (He et al. 2013b). DnBP and DEHP were primarily used in agricultural plastic film. DIBP is most widely used plasticizers and softeners in the plastics industry, and one of the most extensive worldwide presences of chemical contaminants. The PAE degradation rates ranged from days to weeks (Yuan et al. 2002). Low-molecular-weight PAEs, such as DnBP, did not seem to demonstrate significant biomagnification or biodilution, while high-molecular-weight PAEs, such as DEHP, showed significant biodilution (Mackintosh et al. 2004) due to their desorption and degradation in the ecosystem (Mackintosh et al. 2006).

Fig. 8 Historical variations of the residual levels of ΣPAEs, DnBP, DIBP, and DEHP in the L4 and L8 sediment cores from Lake Chaohu

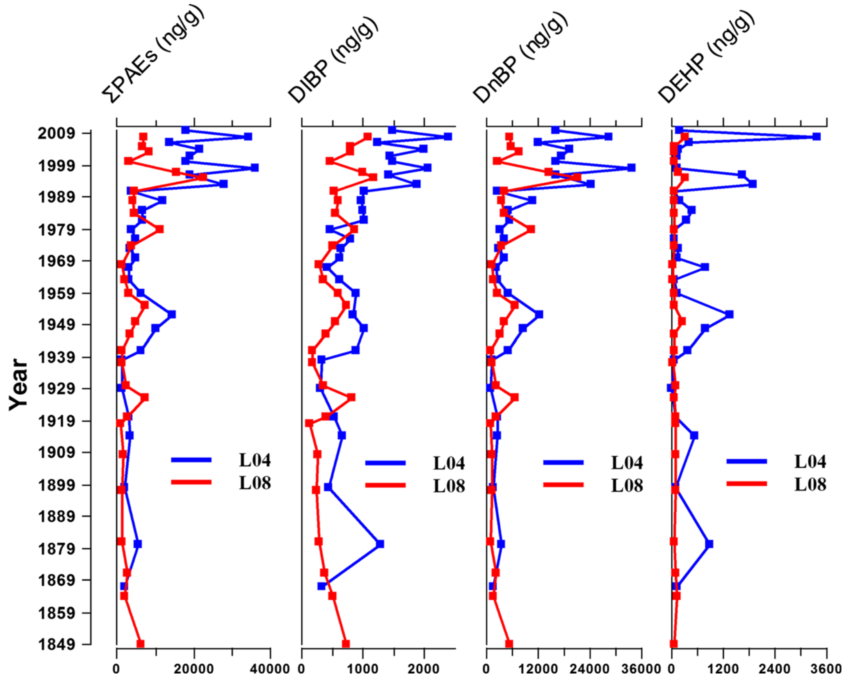


Table 6 Pearson correlation between PAE contents and particle sizes of sediment cores from Lake Chaohu

Parameters	L4			L8		
	Clay	Silt	Sand	Clay	Silt	Sand
DMP	0.008	−0.609**	0.542**	−0.210	−0.244	0.238
DEP	−0.136	−0.619**	0.555**	−0.417*	−0.571**	0.519**
DIBP	−0.313	−0.770**	0.751**	−0.546**	−0.556**	0.561**
DnBP	−0.266	−0.777**	0.749**	−0.443*	−0.493**	0.501**
DEEP	−0.185	−0.913**	0.857**	−0.693**	−0.821**	0.823**
DAP	−0.208	−0.370	0.374	0.219	−0.289	0.152
DHXP	0.238	0.091	−0.072	−0.020	0.143	−0.115
BBP	0.025	−0.164	0.148	−0.314	−0.121	0.134
HEHP	–	–	–	0.599	0.981	−0.971
DBEP	−0.723*	−0.632*	0.608*	−0.786	−0.866*	0.874*
DCHP	−0.268	−0.111	0.134	–	–	–
DEHP	−0.198	−0.165	0.215	−0.296	−0.241	0.205
DnOP	−0.008	−0.381*	0.384*	−0.120	−0.154	0.169
DBZP	0.678	0.547	−0.52	–	–	–
DNP	−0.259	−0.443	0.491	–	–	–
Σ_6PAEs	−0.266	−0.769**	0.743**	−0.444*	−0.493**	0.500**
ΣPAEs	−0.272	−0.777**	0.752**	−0.458*	−0.504**	0.511**

*The correlation is significant at the 0.05 level (two-tailed); **the correlation is significant at the 0.01 level (two-tailed)

Table 7 Pearson correlation between PAE contents and TOC in the surface sediments and sediment cores

	TOC		
	Surface sediments	L4 sediment core	L8 sediment core
DMP	−0.073	0.586**	0.492**
DEP	0.084	0.512**	0.645**
DIBP	0.088	0.692**	0.506**
DnBP	0.130	0.714**	0.533**
BMPP	0.599	–	–
DEEP	0.236	0.896**	0.762**
DAP	−0.004	0.414	0.973*
DHXP	0.569	0.013	0.116
BBP	0.154	−0.020	0.161
HEHP	0.566	–	−0.971
DBEP	0.419	0.294	0.653*
DCHP	0.541	0.033	–
DEHP	0.270	0.039	0.135
DnOP	0.254	0.347	0.136
DBZP	0.586	−0.771	–
DNP	0.505	0.231	–
Σ_6PAEs	0.135	0.704**	0.533**
ΣPAEs	0.135	0.710**	0.534**

*The correlation is significant at the 0.05 level (two-tailed); **the correlation is significant at the 0.01 level (two-tailed)

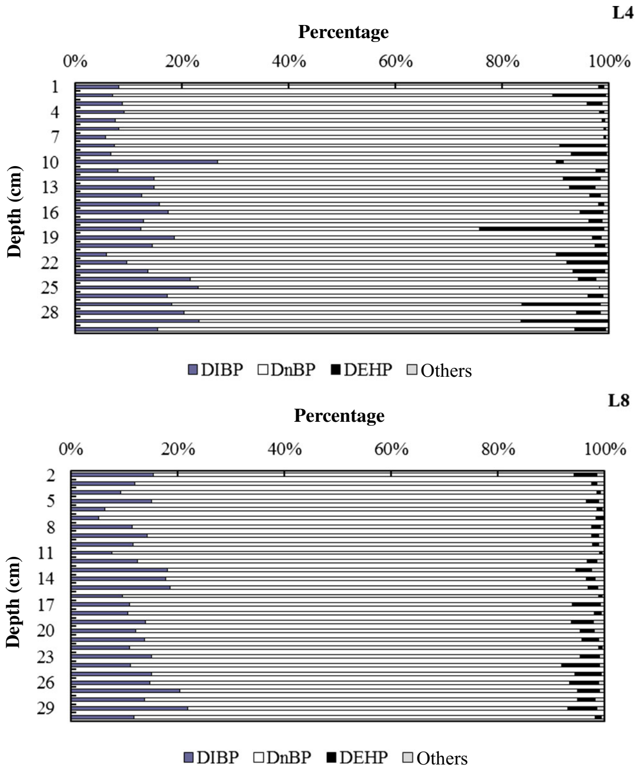


Fig. 9 Historical percentage variations of DnBP, DIBP, DEHP, and PAE components in the L4 and L8 sediment cores from Lake Chaohu

Conclusions

DnBP, DIBP, and DEHP were three dominant PAE components in the surface and core sediments from Lake Chaohu. These findings were in accordance with our previous study on the distributions of PAEs in the lake water. These three dominant PAE components might be considered as priority pollutants in Lake Chaohu, in addition to DMP, DEP, and DnOP currently listed on the Chinese blacklist of priority pollutants. The average contents of $\sum_{16}$PAEs in the surface sediments from the inflow rivers were an order of magnitude higher than those from the lake, and there were similar PAE compositions between the lake and inflow rivers in the western and eastern areas, respectively. This means that there were important effects of PAE input from the inflow rivers on the compositions and distributions of PAEs in the surface sediments. The average contents of DnBP, DIBP, DEHP, and total PAEs (ΣPAEs) in the L4 sediment core were higher than those in the L8 sediment core. The distribution patterns of PAEs in the two sediment cores were highly similar, illustrating the dominance of DnBP, DIBP, and DEHP. An increasing trend was found for the residual levels of ΣPAEs, DnBP, and DIBP from the bottom to surface sediments in both the L4 and L8 sites. Increasing PAE usage with the population growth, urbanization, and industrial and agricultural development in Lake Chaohu watershed would result in the increasing production of PAEs and their resulting presence in the sediments. The surface runoff caused by rainfall and the total organic carbon (TOC) were two important driving factors influencing the residues and distribution of PAEs in the sediments, as indicated by the significant positive relationships between the PAE contents and the percentage of sand particles, as well as TOC contents in the sediment cores.

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