Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake

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HIGHLIGHTS

- Monthly variation in PAEs was first investigated in a large Chinese shallow lake.
- Ecological and health risks with uncertainty were determined.
- PAEs with low and high level of carbon would be from different sources.
- DnBP predominated within PAE congeners and posed a much greater ecological risks.
- The studied PAE congeners posed little health risks to the nearby citizens.

ABSTRACT

The spatio-temporal distributions and the ecological and health risks of PAEs in surface water of Lake Chaohu, the fifth largest lake in China, were studied based on the monthly monitoring of six PAE congeners from May 2010 to April 2011. The annual total concentration of the six PAE congeners (Σ_6PAE) in the surface water ranged from 0.467 to 17.953 μg L^{-1}, with the average value of 4.042 ± 3.929 μg L^{-1}. The di-n-butyl phthalate (DnBP) that dominated the Σ_6PAE at 65.8% was found at its highest and lowest levels in the western lake (TX) and eastern drinking water source area (JC), respectively. The temporal distributions of Σ_6PAE showed that the highest and lowest levels were observed in September 2010 and June 2010, respectively. The different relationships between the runoff and the PAEs with low and high levels of carbon might suggest their different sources. The DnBP had much greater ecological risks than the other studied PAE congeners as indicated by its potential affected fractions (PAFs) and the margin of safety (MOS10). The PAE congeners studied posed little health risk to the nearby male and female citizens.

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1. Introduction

Phthalate esters (PAEs) account for approximately 92% of the produced plasticizers and dominate the production and consumption of plasticizers worldwide (Rahman and Brazel, 2004). In 2004, nearly 6 million tons of PAEs were produced and consumed worldwide (Xie et al., 2007). In China, 1.3 million tons of PAEs, mainly di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP), are produced and consumed. Thirty-one percent of PAEs, primarily DEHP, are imported (CPCIA, 2009). Previous studies have shown that PAEs are endocrine-disrupting chemicals (EDCs) as indicated by developmental and behavioral abnormalities after extensive exposure

to PAEs; also, the alkyl chain length and the hydroxylation of PAEs significantly affected the binding to estrogen receptors and peroxisome proliferator-activated receptors (Harris et al., 1997; Jobling et al., 1995; Moore, 2000; Okamoto et al., 2011). PAEs such as diethyl phthalate (DEP) and DnBP can alter the human serum albumin's conformational structure (Zhou et al., 2012). Extensive exposure to PAEs will increase the risks to human reproductive development.

In aquatic ecosystems, PAEs hydrolyze at slow rates with half-lives ranging from approximately 3 years for dimethyl phthalate (DMP) to 2000 years for DEHP (Wolfe et al., 1980). The PAE photo-oxidation process is also relatively slow with half-lives ranging from 2.4 to 12 years for DEP and DnBP and 0.12 to 1.5 years for DEHP (Howard, 1991). Nevertheless, biodegradation plays a critical role in the fate of PAEs, and mixed microbial populations can completely mineralize PAEs (Kurane, 1986). Studies have indicated that aerobic degradation rates are up to 10 times faster than anaerobic degradation rates. The PAE degradation rates ranged from days to weeks (Yuan et al.,

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2002). Low- and mid-molecular-weight PAEs (DMP, DnBP and butylbenzyl phthalate (BBP)) did not seem to demonstrate significant biomagnification or biodilution, while high-molecular-weight PAEs (DEHP and di-n-octyl phthalate (DnOP)) showed significant biodilution (Mackintosh et al., 2004) due to their desorption and degradation in the ecosystem (Mackintosh et al., 2006). The main source of PAEs is water from streams or other surface runoff followed by atmospheric deposition and the discharge from wastewater treatment plants (Fauser et al., 2009).

Due to the physicochemical properties and biogeochemical cycling of PAEs, they are detected in various media. The water phase is very important in aquatic ecosystems, and PAEs have been detected in this phase in Europe, the United States, and Japan (Clark et al., 2003; Dargnat et al., 2009; Peijnenburg and Struijs, 2006; Vitali et al., 1997). The PAEs in the surface water of large rivers, including the Yellow River and Yangtze Rivers, and large and urban lakes in China have been monitored over the past five years (He et al., 2011; Sha et al., 2007; Wang et al., 2008; Yang et al., 2009; Zeng et al., 2008, 2009). DnBP and DEHP have been detected at very high levels worldwide, and concentrations of DEP, BBP and DnOP in the domestic water are lower than in Western countries.

The ubiquity and the slow hydrolysis and photolysis rate of PAEs determine their potential accumulation in aquatic organism communities and has drawn scientific interest, particularly with regard to the toxicity and ecotoxicity of PAEs for aquatic microorganisms, algae, invertebrates, and fish in freshwater or saltwater (Staples et al., 1997). The acute toxicities of DMP, DEP, DnBP, and BBP for aquatic organisms were 29–337 mg L^{-1}, 10.3–131 mg L^{-1}, 0.35–6.29 mg L^{-1}, and 0.21–5.3 mg L^{-1}, respectively, and the toxicity of PAEs increases with increasing alkyl chain length. Although PAEs present a potential health risk to human beings, water treatment processes have been shown to purify 90% of phthalates. Additional PAEs can be removed by boiling the water (Shi et al., 2012). Urban populations have clean water because of advanced water treatment facilities, but rural populations that drink lake and well water with little treatment have a high hazardous risk from PAEs as do aquatic organisms in natural ecosystems (Yang et al., 2012). Therefore, it is necessary to assess the ecological and health risks of PAEs regularly. A number of ecotoxicity tests have been performed to provide suitable amounts of data for risk evaluations (Adams et al., 1995; Staples et al., 1997, 2011). The predicted no-effect concentrations (PNECs) calculated by methods adopted by the US EPA (United States Environmental Protection Agency) and the Netherlands showed that PAEs did not pose a ubiquitous threat to aquatic organisms in North American and Western European surface waters (Staples et al., 2000). A hazard quotient (HQ) method was applied to assess the PAEs' aquatic ecological risk, which did not exceed the criterion in Thailand and posted little ecological risk to aquatic organisms in the river basin in Chongqing, China (Luo et al., 2009; Sirivithayapakorn and Thuyviang, 2010).

Lake Chaohu (117.18°–117.50° E, 31.25°–31.42° N), a shallow freshwater lake that is located in East China, has a subtropical monsoon climate and is one of the five largest freshwater lakes in China, had a yearly average water level of 8.37 m and a reservoir capacity of 1.72–3.23 billion cubic meters. The lake has suffered from serious eutrophication (major pollution from the total nitrogen and total phosphorus) in the last decades. Moreover, various persistent toxic substances have been detected in recent years (Li et al., 2010; Xu et al., 1999, 2001; Zhang et al., 2007). Although the surface water PAE concentrations in Lake Chaohu have been reported in recent years (Yang et al., 2009), their temporal variation and potential ecological and health risks are still unknown. The objectives of the present study are (1) to perform a monthly investigation into the PAE occurrence and composition in the Lake Chaohu surface waters, (2) to ascertain the temporal and spatial variation of PAEs in the surface water and (3) to evaluate the ecological and health risks of PAEs in the surface water.

2. Materials and methods

2.1. Reagents and materials

Methanol (pesticide grade) and n-hexane (high-performance liquid chromatography grade (HEX, HPLCG)), which were used for the activation of the SPE column, and dichloromethane (DCM, HPLCG), which was used for elution, were purchased from Tedia Co. Inc., Fairfield, Ohio, USA. A PAE stock standard mixture was prepared by diluting n-hexane with a commercial 6 PAE standard mixture (Accustandard Inc., New Haven, Connecticut, USA), which included 1000 μg mL^{-1} each of DMP, DEP, DnBP, BBP, DEHP, and DnOP. The working standard solution was prepared by diluting the stock standard with n-hexane. 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, Connecticut, USA. A solid phase extraction (SPE) device and C18 SPE cartridges (ENVI-18, 6 mL, 500 mg) were purchased from Supelco Co., Bellefonte, Pennsylvania, USA. Granular anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and glass fiber membranes wrapped with aluminum foil were heated at 650 °C and 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.

2.2. Sampling and preprocessing

A total of 44 samples were collected from 3 to 4 sampling sites monthly from May 2010 to April 2011 (Fig. 1). The sample site TX, located in the northwestern region of Lake Chaohu, was once the drinking water source for the citizens of Hefei City, which is the capital of the Anhui Province, but was replaced because of eutrophication. The sample site JC, located in the northeastern region of Lake Chaohu, currently provides the water for the Chaohu City waterworks. The sample site ZM is located at a scenic location. The sample site MS is located near Lake Chaohu's center island, which divides the lake.

Ten liters of water were collected at a 0.5 m depth (representative of the mixed water columns) of the lake from each sampling site. After shaking and mixing, a 1-L aliquot of each sample was filtered through a 0.45-μm glass fiber filter using a filtration device consisting of a peristaltic pump (BT-001, Baoding Longer Precision Pump Co., Ltd., China) and a filter plate with a diameter of 142 mm. Several drops of concentrated sulfuric acid were added into the dissolved phase of the water samples to adjust the pH to 2. The samples were then passed through an SPE cartridge containing an octadecyl silane-bonded silica (ODS) C18 filler, which had been cleaned twice with 5 mL of a DCM:HEX (1:1) mixture, activated by 6 mL of methanol, and finally washed using 10 mL of ultrapure water. During the activation and washing with the ultrapure water, the liquid level remained tangent to the filler to keep the C18 wet. After extracting the target compounds from the water, the SPE cartridges were blown dry using the SPE device, wrapped with aluminum foil, and stored in desiccators.

2.3. Elution and GC/MS analyzing

Ten milliliters of a DCM:HEX (1:1) mixture (2 repetitions of 5 mL) were used to elute the C18 SPE cartridge, which was jointed to an anhydrous sodium sulfate (5 g) cartridge. The extracts were concentrated to approximately 1 mL in an eggplant-shaped flask using a vacuum rotary evaporator (N1100 V-WD, Tokyo Rikakikai Co., Ltd., Japan) at a temperature below 38 °C. The IS was added to the flask. The samples were sealed in vials and stored at −20 °C before analysis.
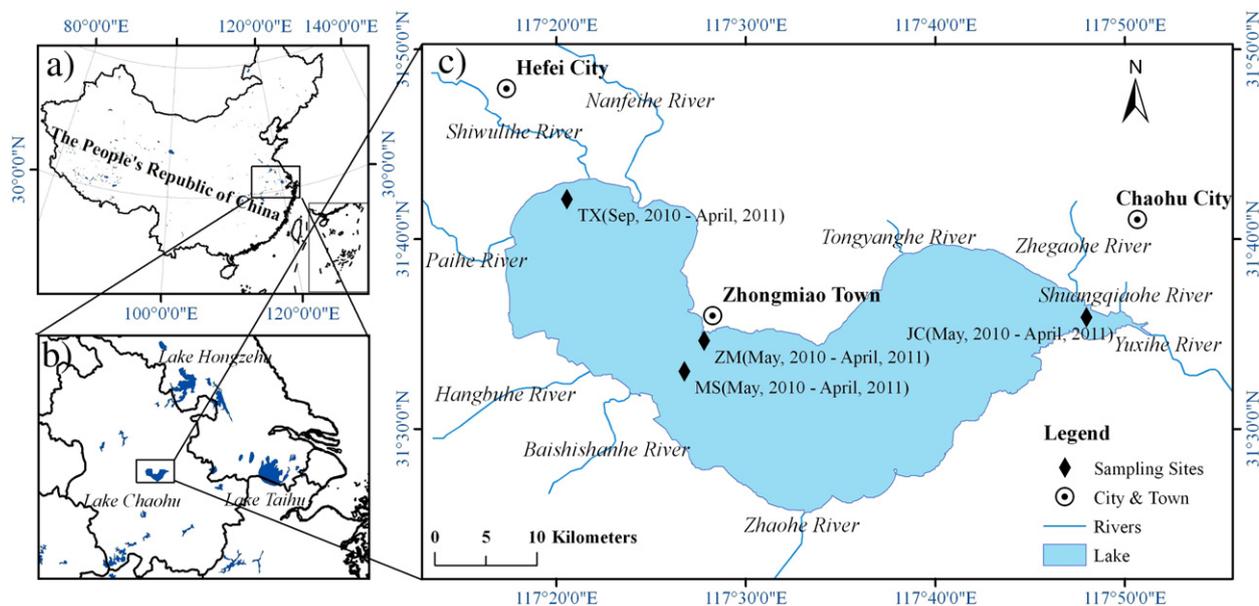
Fig. 1. Geographical localities of (a) Lake Chaohu in China, (b) Lake Chaohu in East China and (c) the sampling sites in Lake Chaohu with their sampling times.

The samples 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 samples were injected by auto-sampling 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^{-1} from 60 °C to 300 °C, where the temperature was maintained for 15 min. Helium was used as both the carrier (1 mL min^{-1}) and makeup gas (50 mL min^{-1}). The temperatures of the inlet, quadrupole, and ion source were 280 °C, 150 °C and 246 °C, respectively. Quantitation was performed using the internal calibration method based on a six-point calibration curve for individual PAEs. The quantitative ion was 153 for 3,4,5,6,d4-DEP, 3,4,5,6,d4-DnBP and 3,4,5,6,d4-DnOP, 149 for DEP, DnBP, BBP, DEHP and DnOP, and 163 for DMP.

2.4. Quality control and quality assurance

Three to four parallel samples with three procedural blanks were processed for each monthly sampling site. The instruments were recalibrated using calibration standards for each of the monthly samples. In addition, SS were added to 40% of the samples to investigate matrix effects. The surrogate recoveries were from 99% to 145% for 3,4,5,6,d4-DnBP. The recoveries of the 6 PAEs were 92.9%–96.1% for DMP, 93.7%–98.8% for DEP, 84.3%–107.8% for DnBP, 66%–83.9% for BBP, 60.5%–88.5% for DEHP, and 70.0%–92.8% for DnOP. DnBP and DEHP were both found in small amounts in the procedural blanks. The quantitation limits of the individual PAEs were 1 ng L^{-1} for BBP and 0.5 ng L^{-1} for the remaining PAEs.

2.5. Statistical and evaluation methods

Statistical analysis and cluster analysis (CA) were conducted using the SPSS software. Forty four samples were used to calculate the minimum, median, maximum, and mean for the whole lake over the entire year. The risk evaluation methods were described in Text S1 and Text S2 in detail in the supplementary material. The ecological risk assessment was based on the species sensitivity distribution and a Bayesian inference with uncertainty evaluation and was conducted using the WinBUGS and Matlab software.

Human risk assessments considering real conditions, such as body weight, height and sex, were evaluated using the Matlab software. Two methods were described as follows.

To obtain the temporal ecological risks of PAEs with their uncertainties, we employed two indicators that were calculated by our self-built SSD platform, the Bayesian Matbugs Calculator (BMC): the potential affected fraction (PAF) and the margin of safety (MOS10) (Aldenberg and Jaworska, 2000; Knoben et al., 1998; Solomon et al., 1996). An introduction and detailed data processing information for this platform are included in Text S1 in Supporting Information (SI). Some parameters and results are summarized in Tables S1–S6. Table S7 lists the best SSD models, which were selected based on the toxicity or exposure, and their parameters with a certain posterior distribution. The parameters' posterior distribution for 6 PAEs and their monthly exposure data in Lake Chaohu are shown in Fig. S2. SSD curves with a 95% credible interval (CI) for the toxicity and monthly exposure data of 6 chemicals in Lake Chaohu are shown in Fig. S3.

To investigate the human health risks posed by the PAE congeners in the surface water from the source area, the carcinogenic risk of DEHP and the non-carcinogenic risks of 6 PAE congeners were calculated using the method proposed by the United States Environment Protection Agency (USEPA) (USEPA, 1989). The method was slightly modified in our study. Body weight (BW) and body surface area (A$_{sb}$) were no longer constant. The body surface area was calculated using an empirical formula that included variable BW and body height (H). Random BW and H data from the normal distribution of male and female BW and H were produced using MATLAB. Thus, a Monte Carlo analysis (MCA) with 100,000 samplings was performed to assess the carcinogenic and non-carcinogenic risks with the uncertainty of the PAEs. The human risk assessment methods are described in Text S2 in SI. The risk distributions for each PAE congener are shown in Fig. S5 and Fig. S6.

3. Results and discussions

3.1. PAE occurrence and composition

The individual concentrations of the 6 PAEs in the Lake Chaohu surface water were determined for each month from May 2010 to April 2011 by statistical analysis and are summarized in Table 1. The annual Σ$_6$PAE concentration ranged from 0.467 to 17.953 μg L^{-1}

Table 1
Statistical summary of the annual PAE concentrations in the surface water from each sampling site, µg L^{-1}.

		DMP	DEP	DnBP	BBP	DEHP	DnOP	Σ_6PAEs
JC (2010.5–2011.4)	D.F.[a]	100	100	100	75	83	17	100
	Distributions[b]	LN	N	LN	N	N	N	LN
	Mean ± S.D.[c]	1.106 ± 1.147	0.133 ± 0.063	0.924 ± 1.080	0.066 ± 0.039	0.231 ± 0.167	0.035 ± 0.014	2.411 ± 1.765
	Median	0.644	0.139	0.662	0.090	0.178	0.035	1.840
	Range[d]	0.016–3.670	0.006–0.212	0.123–4.221	N.D.–0.091	N.D.–0.576	N.D.–0.035	0.796–6.797
MS (2010.5–2011.4)	D.F.	100	100	100	75	100	17	100
	Distributions	LN	N	N	N	N	N	N
	Mean ± S.D.	0.238 ± 0.377	0.145 ± 0.071	4.201 ± 3.532	0.070 ± 0.040	0.162 ± 0.065	0.040 ± 0.016	4.805 ± 3.430
	Median	0.132	0.142	4.142	0.090	0.182	0.040	4.696
	Range	0.062–0.196	0.024–0.283	0.070–10.886	N.D.–0.092	N.D.–0.252	N.D.–0.045	0.765–11.266
ZM (2010.5–2011.4)	D.F.	100	100	100	75	100	17	100
	Distributions	N	N	LN	N	N	N	LN
	Mean ± S.D.	0.123 ± 0.069	0.136 ± 0.064	3.084 ± 4.394	0.073 ± 0.042	0.215 ± 0.118	0.033 ± 0.013	3.618 ± 4.355
	Median	0.123	0.145	1.744	0.090	0.199	0.033	2.278
	Range	0.015–0.270	0.012–0.207	0.324–16.135	N.D.–0.107	N.D.–0.324	N.D.–0.037	0.467–16.485
TX (2010.9–2011.4)	D.F.	100	100	100	88	100	25	100
	Distributions	N	LN	LN	LN	N	N	LN
	Mean ± S.D.	0.139 ± 0.073	0.157 ± 0.086	5.430 ± 5.257	0.076 ± 0.045	0.182 ± 0.101	0.032 ± 0.013	5.983 ± 5.356
	Median	0.139	0.140	2.881	0.091	0.169	0.032	3.408
	Range	0.073–0.186	0.119–0.237	0.564–17.529	N.D.–0.105	N.D.–0.283	N.D.–0.036	1.212–17.953
Lake Chaohu (2010.5–2011.4)	D.F.	100	100	100	77	95	18	100
	Distributions	None	N	LN	None	N	None	LN
	Mean ± S.D.	0.425 ± 0.744	0.142 ± 0.061	3.226 ± 4.040	0.071 ± 0.028	0.197 ± 0.107	0.035 ± 0.005	4.042 ± 3.929
	Median	0.148	0.143	1.727	0.090	0.190	0.036	2.624
	Range	0.015–3.670	0.006–0.283	0.070–17.529	N.D.–0.107	N.D.–0.576	N.D.–0.045	0.467–17.953

[a] D.F.: detection frequency (%).
[b] LN: logarithm-normal distribution; N: normal distribution; None: the dataset obey neither LN nor N.
[c] S.D.: standard deviation.
[d] N.D.: concentration is below limits of quantitation.

(4.042 ± 3.929 µg L^{-1}) in Lake Chaohu. The Σ_6PAE concentrations in the surface water from the eastern drinking water source area (JC), the middle of the lake (MS) and the western area of the lake (TX) ranged from 0.796 to 6.797 µg L^{-1} (2.411 ± 1.765 µg L^{-1}), 0.765 to 11.266 µg L^{-1} (4.805 ± 3.430 µg L^{-1}) and 1.212 to 17.953 µg L^{-1} (5.983 ± 5.356 µg L^{-1}), respectively. The median value of the Σ_6PAE concentrations showed that the MS area seemed to have the highest PAE pollution, followed by the TX, ZM and JC areas. MS was located near Mushan Island, which is a scenic location. We found that much plastic trash was scattered on the beach of the island because waste treatment was not seriously executed. The ZM area was located far away from the island but near Zhongmiao Town, where there was plastic litter on the beach. So, although the locations of MS and ZM were close to one another, their PAE pollution for most months was quite different. Except for DnOP, which was detected at a frequency of 18%, individual PAEs were widely disbursed, were detected monthly and had a detection frequency (DF) ranging from

77% to 100%. According to the median values of the individual PAEs, the preponderant PAE species was DnBP, with 47.3% of the Σ_6PAE in April 2011; this percentage is lower than the value observed in April 2007 (Yang et al., 2009). However, the DnBP content, which ranged from 0.564 to 1.285 µg L^{-1} in April 2011, is much higher in the present study. By the annual median value, the DnBP concentrations dominated the Σ_6PAE with a ratio value of 65.8% and were followed by the values for DEHP, DMP, DEP, BBP and DnOP.

A summary of the individual PAE concentrations is shown for water bodies around the world in Table S1. Although the DMP content was lower than that in the surface water in Canada (Clark et al., 2003), it was much higher than that in recent years in domestic water bodies, such as the Yangtze River, the Yellow River and the urban lakes in Guangzhou (Sha et al., 2007; Wang et al., 2008; Zeng et al., 2008, 2009). DMP was the major component of anti-mosquito oil, and the difference in DMP concentration might result from the usage of anti-mosquito oil. Lower concentrations of DEP, BBP and DnOP were
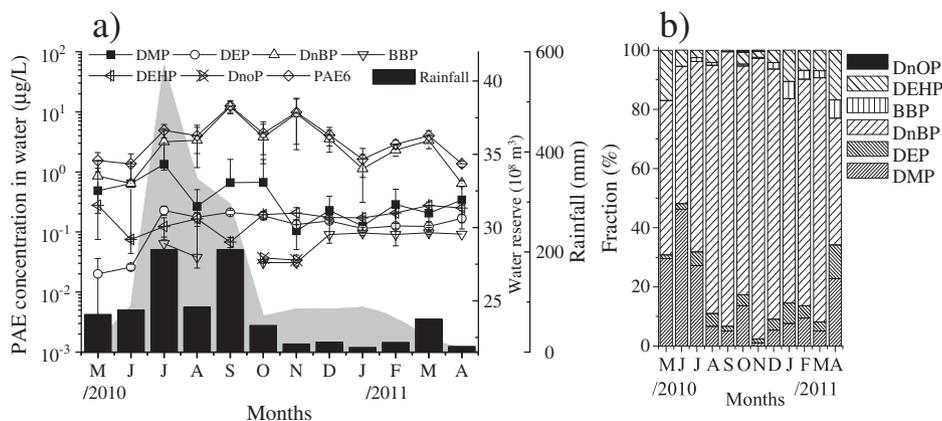
Fig. 2. Temporal variations of individual PAE concentrations (a) and their compositions (b) in the Lake Chaohu surface water from May 2010 to April 2011 (The water reserve variation in Lake Chaohu is shown in the grey background area of Chart a.).
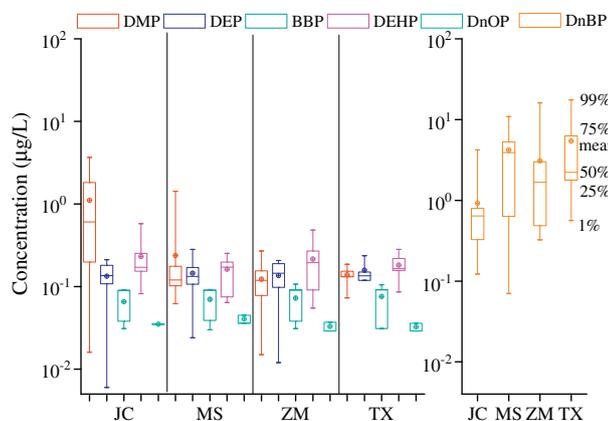
Fig. 3. Spatial variations of the annual individual PAE concentrations in the Lake Chaohu surface water.

detected in domestic water bodies, including those in our present study, while water bodies in Western countries faced a more serious pollution risk from the 3 PAEs (Clark et al., 2003; Vitali et al., 1997). As the main PAE components, DnBP and DEHP were detected at very high levels worldwide. However, the concentrations of DnBP and DEHP found in the present study were much lower than those found in the Yangtze River, the Yellow River and the surface water in Western countries (Clark et al., 2003; Sha et al., 2007; Vethaak et al., 2005; Wang et al., 2008). Additionally, the DnBP pollution level in Lake Chaohu was much higher than in the urban lakes of Guangzhou, while the concentrations of DEHP were similar at each location (Zeng et al., 2008, 2009). Microorganisms in the aquatic ecosystem played a critical

Fig. 4. Cluster analysis of individual PAEs with DnBP (a) and without DnBP (b), sampling time without data normalization (c) and with data normalization to 0–1 (d) and sampling sites without data normalization (e) and with data normalization to 0–1 (f).

role in the PAE concentrations' differences between rivers and lakes. Large rivers such as the Yellow River and Yangtze River were at lower eutrophic levels. Their microorganisms were not as active as that in eutrophic lakes. Both aerobic and anaerobic biodegradation would appear in eutrophic lakes due to algae. Thus, the PAE concentrations were lower in eutrophic lakes. Urban lakes in Guangzhou seemed to encounter more stress than Lake Chaohu, but reasonable controls were executed to protect urban lakes from plastic garbage pollution. On the contrary, Lake Chaohu confronted the PAE pollution from both agricultural plastic waste, such as plastic film wrecks, and daily life plastic waste, such as plastic bags. However, these control measures were not seriously implemented.

3.2. Temporal variation of individual PAEs

Individual PAE concentrations in the Lake Chaohu surface water are shown in Fig. 2a for each month from May 2010 to April 2011. The concentrations of PAEs with low levels of carbon, such as DMP and DEP, reached their peak values in July. Their residual levels began to fluctuate in stable concentration ranges beginning in November. The DnBP and BBP had moderate carbon levels. The DnBP concentrations gradually increased monthly but then began to slowly decrease after the peak month of September. The BBP concentration was not consistently detected, and a subtle increasing trend was found month-by-month with levels stabilizing starting in December. The concentrations of DEHP, which contains high levels of carbon, have diminished over time. DnOP was only detected in October and November. The highest concentration of $\Sigma_6 PAE$ was observed in September 2010, and the lowest was in June 2010. In contrast, the lowest concentration of $\Sigma_6 PAE$ in the urban lakes of Guangzhou was measured in December (Zeng et al., 2009). The compositional variation of individual PAEs is shown in Fig. 2b. The ratios of PAEs with low and high carbon levels initially decreased but eventually increased over the entire year. The lowest ratio (2.4%) of PAEs with low carbon levels was observed in November, and the lowest ratio (0.5%) of PAEs with high carbon levels was observed in September. The DnBP ratio initially increased but then decreased, and its peak ratio value was 92.8%.

3.3. Spatial variation of individual PAEs

Spatial variations in the annual concentrations of individual PAEs in the Lake Chaohu surface water are shown in Fig. 3. To compare the variations of PAEs at a specific site, the dataset in the same month was used in the statistical analysis. As indicated by the average content of DnBP, which is the major component of PAEs, we found that the water source area (JC) sustained limited pollution and that the western lake area (TX) sustained serious pollution. However, an independent sample test (IST) showed that the difference was not significant ($p = 0.072 > 0.05$) when equal variances were not assumed. Concentrations of DMP, which is a minor component of PAEs, were found to be high in the JC area, reaching 1.106 μg L^{-1} (0.016–3.670 μg L^{-1}), and low in the TX area. An IST showed that the difference was significant ($p = 0.048 < 0.05$). Runoff and pollution source distributions were the main reasons for spatial variance, and the analysis details are in Section 3.7. The remaining PAE congeners showed little variance across the above sampling sites. The monthly data for individual PAEs at specific sampling sites were tested for their distribution, and the results are presented in Table 1. Normal and logarithmic-normal distributions were observed in these datasets. To investigate the compositions of each PAE at the sampling sites, the mean, geomean and median were used, as is shown in Fig. S1. According to the mean and geomean, we determined that DnBP dominated the total PAEs in Lake Chaohu except at site JC. In the eastern water source area, the PAEs with high and low carbon levels could not be neglected either.
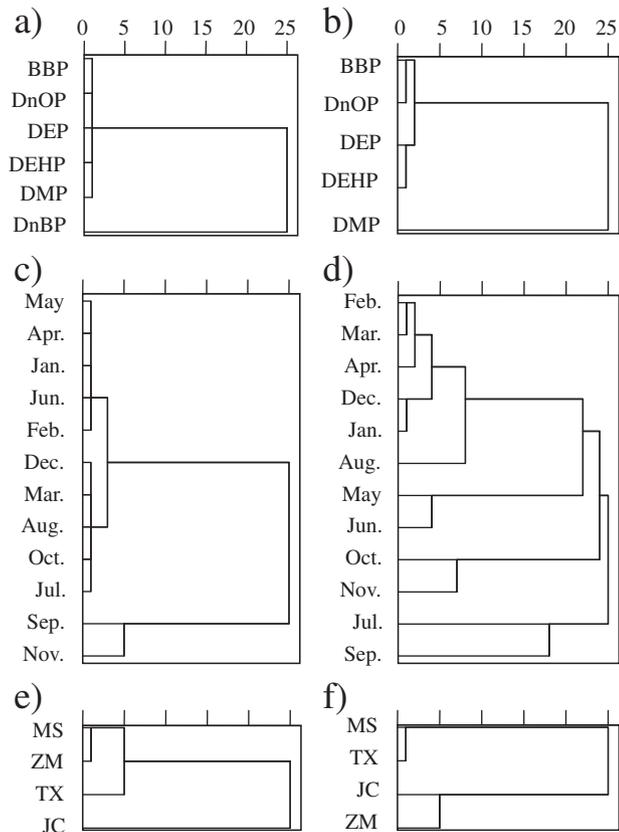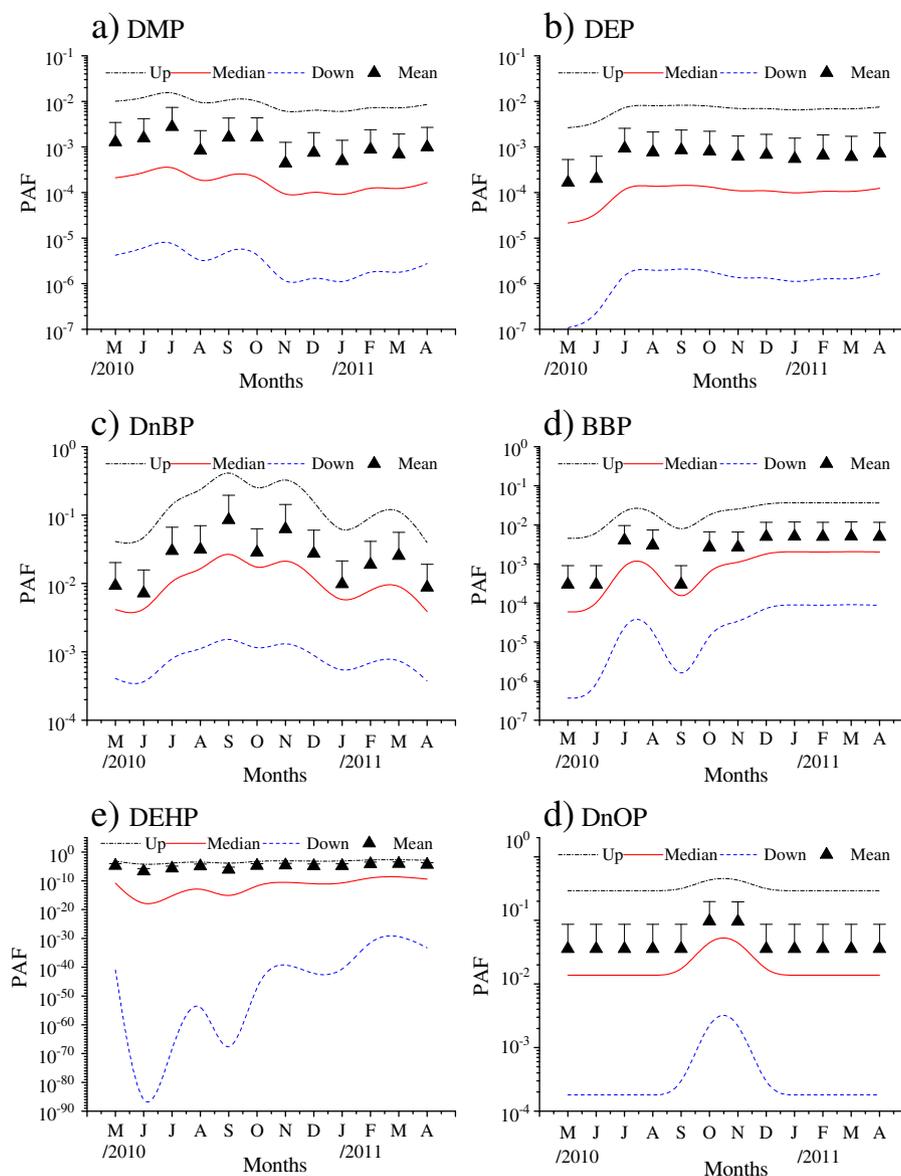
Fig. 5. Temporal ecological risks of PAE congeners with uncertainty boundaries. The "up" line (dash–dot), the "median" line (solid) and the "down" line (dash) denote ecological risks at the high, middle and low levels, respectively. The triangle scatters with error-bars denote the risk calculated using the mean values of the parameters in Table S7.

3.4. Cluster analysis (CA) of the PAEs, sampling times and sites

Similarities according to CA among PAE congeners, sampling months and sampling sites are shown in Fig. 4. The PAE congeners were divided into two obvious clusters as shown in Fig. 4a. The classification depended significantly on the concentration quantity. Therefore, DnBP, which had a higher residual level, belonged to one cluster, and the remaining PAEs belonged to the other cluster. After excluding DnBP, another CA was performed, as shown in Fig. 4b. Three additional clusters were extracted. Combined with the temporal variations shown in Figs. 2a and 3, the CA indicated that the temporal and spatial variations of DMP was different from the other two clusters. Although DEP, BBP, DEHP and DnOP exhibited little variance over the entire year, they were still divided into two types according to their different residual levels. A CA was performed to identify the similarities between sampling months, as shown in Fig. 4c and d. A CA with absolute PAE concentration values indicated that the clusters were strongly dependent on the DnOP concentration,

as shown in Figs. 4c and 2a. A CA with relative PAE concentration values led to a much finer categorization depending on the ratio values of each PAE congener. Two main clusters were extracted, indicating that the characteristics of the PAEs were similar in September and July. The rainfall and water levels for both months were much higher than in the other months. The sampling sites were classified according to the CA. A CA using absolute PAE concentration values showed that the characteristics of PAEs in the surface water from the western, center, and eastern areas of the lake were dissimilar. A CA using relative PAE concentration values illustrated the similarity between the MS and TX regions.

3.5. Temporal ecological risks of PAEs based on the SSD model

After entering the concentrations of PAEs into the BMC and choosing the best model, the temporal ecological risks of the PAE congeners with uncertainty boundaries were automatically calculated and are shown in Fig. 5. The low-level risk of DnBP was above 10^{-4},

Table 2
Median values of the non-carcinogenic risk with a 95% CI calculated for male and female Chaohu City residents when the sampled water was used for drinking and bathing.

Chemicals	DMP	DEP	DnBP
Max month (MaM)	Jul.	Jul.	Sep.
Min month (MiM)	May	May	Jun.
Drinking, male, 10^{-8}			
Median (95%CI)	1.7 (1.2–2.4)	4.6 (3.2–6.5)	174 (120–249)
Median (95%CI) at MaM	9.7 (6.7–13.8)	32.3 (22.3–46.1)	1110 (767–1586)
Median (95%CI) at MiM	0.04 (0.03–0.06)	7.0 (4.8–10.0)	0.20 (0.14–0.28)
Drinking, female, 10^{-8}			
Median (95%CI)	1.9 (1.3–2.8)	5.2 (3.5–7.6)	198 (135–291)
Median (95%CI) at MaM	11.0 (7.5–16.2)	8.0 (5.4–11.7)	1265 (862–1857)
Median (95%CI) at MiM	0.05 (0.03–0.07)	0.23 (0.15–0.33)	36.8 (25.1–54.0)
Bathing, male, 10^{-11}			
Median (95% CI)	18.6 (16.4–22.2)	50.1 (44.2–59.5)	1915 (1689–2276)
Median (95% CI) at MaM	106 (93.7–126)	76.8 (67.7–91.2)	12,211 (10,773–14,512)
Median (95% CI) at MiM	0.48 (0.42–0.56)	2.2 (1.9–2.6)	355 (313–422)
Bathing, female, 10^{-11}			
Median (95% CI)	19.2 (16.7–23.5)	51.6 (44.8–63.1)	1974 (1713–2412)
Median (95% CI) at MaM	109 (95–134)	79.1 (68.7–96.7)	12,587 (10,925–15,378)
Median (95% CI) at MiM	0.49 (0.43–0.60)	2.2 (2.0–2.7)	366 (317–447)

Chemicals	BBP	DEHP	DnOP
Max month (MaM)	Mar.	Feb	Nov.
Min month (MiM)	May, Jun., Sep.	May–Jul.	May–Sep., Dec.–Apr.
Drinking, male, 10^{-8}			
Median (95% CI)	5.1 (3.5–7.2)	219 (151–313)	0.33 (0.23–0.47)
Median (95% CI) at MaM	12.0 (8.3–17.1)	758 (524–1083)	46.7 (32.3–66.7)
Median (95% CI) at MiM	0.07 (0.05–0.09)	0.33 (0.23–0.47)	0.33 (0.23–0.47)
Drinking, female, 10^{-8}			
Median (95% CI)	5.8 (4.0–8.5)	249 (170–367)	0.37 (0.26–0.55)
Median (95% CI) at MaM	13.7 (9.3–20.0)	864 (589–1268)	53.2 (36.3–78.1)
Median (95% CI) at MiM	0.07 (0.05–0.11)	0.37 (0.26–0.55)	0.37 (0.26–0.55)
Bathing, male, 10^{-11}			
Median (95% CI)	55.6 (49.1–66.1)	2410 (2126–2864)	3.6 (3.2–4.3)
Median (95% CI) at MaM	131 (116–157)	8334 (7352–9904)	513 (453–610)
Median (95% CI) at MiM	0.72 (0.64–0.86)	3.6 (3.2–4.3)	3.6 (3.2–4.3)
Bathing, female, 10^{-11}			
Median (95%CI)	57.3 (49.7–70.0)	2484 (2156–3035)	3.7 (3.2–4.6)
Median (95%CI) at MaM	135 (117. −166)	8590 (7456–10,495)	529 (459–646)
Median (95%CI) at MiM	0.75 (0.65–0.91)	3.7 (3.2–4.6)	3.7 (3.2–4.6)

and its high-level risk approached 0.7 in September. According to the mid-level risk, which ranged from 0.003 to 0.028, DnBP posed the greatest threat to the ecosystem during the summer. Although the maximum detection limit of DnOP was assigned for the sampling sites, in sites where DnOP was not detected, the low-level risk was still above 10^{-4}. DMP, DEP and BBP posed less ecological risks to aquatic organisms. The risks for those congeners were generally above 10^{-6} at the lowest level. DMP threatened the ecosystem during the rainy seasons because of its high risk at the middle level ($>10^{-4}$). The risk of DEP and BBP gradually increased with time. The risks at the middle level began to fluctuate on a plateau beginning in August for DEP and January for BBP. Their "plateau" risks at the middle level were 10^{-4} and 10^{-3} for DEP and BBP, respectively. The ecological risk of DEHP was very low; its risk at the high level was $<10^{-3}$, and the range of its risk at the middle level was from 5.5×10^{-22} to 3.8×10^{-9}. According to their temporal ecological risks, the PAE congeners were ranked as follows: DnOP > DnBP > BBP > DMP > DEP > DEHP.

Considering that MOS10 was calculated by combining ecological toxicity and exposure data, the SSD curves, which are the best fits to the original data, were used. Therefore, the mean-relative-deviance (MRD) values between the original data and the predicted data were calculated, as shown in Table S8; the results indicated that the SSD curves using the median parameters values provided a better fit. The MOS10, calculated by dividing the 10th percentile of the ecological toxicity data SSD by the 90th percentile for the cumulative distribution of the exposure data, is shown in Fig. S4. The MOS10 of DnBP ranged from 1.7 to 12.6, which is much lower than that of the other PAE congeners, indicating that the Lake Chaohu aquatic ecosystem was significantly threatened by DnBP. The DnBP risk was

severe at the TX site. The MOS10 values for the remaining PAE congeners at the JC, MS and ZM sites were all greater than 100, indicating that their ecological risks were relatively low. A further study combining ecological risks can be conducted when the congeners' toxicity mechanisms are clear.

Predicted no-effect concentrations (PNECs) calculated by the methods adopted by the US EPA and the Netherlands showed that PAEs did not pose a ubiquitous threat to aquatic organisms in North American and Western European surface waters (Staples et al., 2000). A hazard quotient (HQ) method was applied to assess the PAEs' aquatic ecological risk, which did not exceed the criterion in Thailand and posted little ecological risk to aquatic organism in river basin in Chongqing, China (Luo et al., 2009; Sirivithayapakorn and Thuyviang, 2010). However, to our knowledge, no researcher used MOS10 as indicator for assessing aquatic ecological risk of PAEs. MOS10 combining ecological toxicity and exposure data, it has been used to assess ecological risk of 1,2,4-trichlorobenzene successfully (Zolezzi et al., 2005).

3.6. Human health risks of PAEs in the drinking water source area

The distributions of risks for females were generally to the right of the distributions of risks for males, indicating that the PAEs posed a greater threat to females. PAEs have been shown to influence sperm activity in males (Okamoto et al., 2011); in contrast, a number of the PAE congeners showed extremely weak estrogenic activity, and others were found to be inactive (Harris et al., 1997; Moore, 2000). Increased use of the polluted water for drinking or bathing increased the risks to the citizens.

Table 3
Pearson correlation between the monthly concentration of PAEs and monthly meteorological hydrological parameters in different scenarios.

	WR[a]	CWR	Rf	Ev	WI$_{rain}$	WI$_{runoff}$	WI$_{yxh}$	WI$_{flh}$	WI$_{zh}$	WI$_{other}$
Scenario No. 1[b]										
DMP	0.694*	0.631*	0.793**	0.377	0.690*	0.605*	0.170	0.788**	0.788**	0.869**
DEP	0.616*	0.170	0.404	−0.082	0.566	0.135	0.296	0.582*	0.366	0.386
DnBP	0.284	−0.065	0.413	−0.018	0.527	−0.106	0.494	0.429	0.140	0.381
BBP	−0.155	0.163	−0.466	−0.621*	−0.095	0.177	−0.585*	−0.384	−0.020	−0.441
DEHP	−0.589*	−0.318	−0.587*	−0.455	−0.375	−0.303	−0.217	−0.624*	−0.452	−0.527
DnOP	−0.185	−0.269	−0.242	−0.375	−0.006	−0.279	0.155	−0.163	−0.197	−0.142
Σ$_6$PAEs	0.359	0.016	0.475	0.005	0.587*	−0.027	0.475	0.495	0.229	0.449
Scenario No. 2										
DMP	0.052	0.04	0.227	0.333	0.027	0.038	0.141	0.11	0.126	0.234
DEP	0.326	0.205	−0.187	.624*	−0.559	0.266	−0.29	0.189	0.071	−0.107
DnBP	0.848**	0.581*	0.576*	0.475	0.292	0.571	0.088	0.878**	0.691*	0.656*
BBP	−0.534	−0.319	−0.900**	−0.363	−0.684*	−0.262	−0.427	−0.686*	−0.582*	−0.775**
DEHP	−0.359	−0.464	−0.51	−0.243	−0.365	−0.443	−0.04	−0.425	−0.594*	−0.572
DnOP	0.468	−0.345	0.323	0.666*	−0.073	−0.349	0.583*	0.521	−0.145	0.134
Σ$_6$PAEs	0.820**	0.57	0.574	0.498	0.276	0.561	0.098	0.866**	0.676*	0.663*

[a] WL, CWR, Rf, Ev, WI$_{rain}$, WI$_{runoff}$, WI$_{yxh}$, WI$_{flh}$, WI$_{zh}$, and WI$_{other}$ are the abbreviations of water level, water reserve, monthly change of water reserve, monthly rainfall, monthly evaporation, monthly water inflow from rainfall above the lake, monthly water inflow from surface runoff, monthly water inflow from River Yuxihe, monthly water inflow from River Fenglehe, monthly water inflow from River zhaohe, and monthly water inflow from other rivers.

[b] Scenario No. 1 denotes that meteorological hydrological parameters from May, 2010 to April, 2011 were used to do Pearson correlation analysis (PCA) and Scenario No. 2 denotes that meteorological hydrological parameters from Mar, 2010 to Feb., 2011 were used to do PCA.

* Denotes that correlation is significant at the 0.05 level (2-tailed).

** Denotes that correlation is significant at the 0.01 level (2-tailed).

The median values, with 95% confidence intervals (CI), of the human health risks are summarized in Table 2 and Table S8. According to the cancer statistics, risk management and remediation goals, the acceptable carcinogenic risk of chemical pollutants was less than one in one million (10^{-6}), and the acceptable non-carcinogenic hazard index (HI) was 1.0 (USEPA, 1989). The present study showed that PAEs posed little carcinogenic or non-carcinogenic risk to the citizens of Chaohu City. The greatest carcinogenic risks to males and females from DEHP from drinking the water were recorded in February at 9.096×10^{-10} (6.284×10^{-10}–12.993×10^{-10}) and 10.363×10^{-10} (7.063×10^{-10}–15.211×10^{-10}). The carcinogenic risk of DEHP was greater than that of DDTs and HCHs in Lake Chaohu (He et al., 2012). Although the non-carcinogenic risks to citizens were negligible, DnBP posed a potential threat to humans. The non-carcinogenic HI of DnBP for females when the water was used for drinking or bathing reached 1.265×10^{-5} (0.862×10^{-5}–1.857×10^{-5}) and 1.259×10^{-5} (1.093×10^{-5}–1.538×10^{-5}) in September. The carcinogenic risk of DnBP was greater than that of DDTs and HCHs in Lake Chaohu (He et al., 2012).

3.7. The effects of meteorological and hydrological factors on the PAE temporal–spatial distributions

The determinations of meteorological–hydrological factors (Table S10) were described in Text S3 in SI, and their correlations with the monthly PAE concentrations are presented in Table 3.

The runoff caused by rainfall was an important driving factor influencing the temporal distribution of PAEs. There was a positive correlation between the concentrations of PAEs with low levels of carbon, such as DMP and DEP, and the agricultural runoff from the River Fenglehe, while a negative correlation between the concentrations of PAEs with high levels of carbon, such as BBP and DEHP, and the runoff was found. Although the solubility of DMP and DEP were 5.2 g L^{-1} and 0.6 g L^{-1}, respectively, which indicates their potential abundance in the dissolved phase of water, their daily production and consumption were extremely low. Therefore, the residual DMP and DEP levels were very low. However, a larger agricultural runoff inflow might increase the DMP and DEP concentrations, as was shown in our study. The different relationships between PAEs with low and high levels of carbon and the runoff might suggest different sources.

An interesting phenomenon was observed whereby the highest Σ$_6$PAE and DnBP levels were found 2 months after the highest water levels. Therefore, another Pearson correlation between the meteorological & hydrological parameters from Mar. 2010 to Feb. 2011 and monthly PAE concentrations was performed in Scenario No. 2 in Table 3. The water reserve, rainfall, and river runoff were all influencing factors in the DnBP distribution. The production and consumption of PAEs, the water solubility and the octanol/water partition coefficient (Kow) were used to explain the seasonal variation of individual PAEs (Cousins and Mackay, 2000; Cousins et al., 2003; Ellington, 1999). DnBP and DEHP dominated the domestic plasticizers (CPCIA, 2009). The widespread use of DnBP with a high solubility (9.9 mg L^{-1}) and moderate Kow (1.86×10^4) determined its abundance in both the dissolved and particle phases of water. The runoff from cities and towns carried sewage and solid waste that contained plastic materials into the lake during the rainy season (July, August and September 2010), and most of the DnBP in the particle phase was retained by the lake. The release of DnBP from particles increased its concentration in the dissolved phase significantly, especially when the water levels decreased. However, DEHP was hardly dissolved in water and was easily absorbed by organic matter in the particle phase suggesting that it would seldom be detected in the dissolved phase.

The reason for the spatial distribution variation also depended on the runoff and the urbanization. Sixty percent of the water from the Lake Chaohu basin flows into the western lake suggesting that more PAEs might be carried into the lake. Moreover, the Nanfeihe River in the northwest region of the lake flowed through the urban area of Hefei City, the Anhui Province capital, which is home to 5.7 million citizens. The river continuously carried large amounts of sewage and solid waste. During the rainy season, the quantity increased significantly. In contrast, Chaohu City is a small city of only 0.8 million citizens. No large river flows through the city. Additionally, only one river, which is located in the eastern region of the lake, flows out of the lake. Generally, water flows from the western area of the lake to the eastern area resulting in moderate pollution in the center area of Lake Chaohu.

3.8. Suggestions for the PAE pollution controlling in Lake Chaohu

Based on the analysis above, we considered that meteorological and hydrological factors were only driving factors, and the real

reasons were that untreated plastic waste was discarded on the beach and plastic products were widely used. Very large cities such as Hefei City produce more pollution than small cities such as Chaohu City. To reduce the PAE pollution, manufacturing new plasticizers with low toxicity, quantity reduction and improving the usage efficiency of plastic and recycling plastic waste are all good and basic strategies to control PAE spatially and temporally.

4. Conclusion

The annual total concentration of the six PAE congeners in the surface water ranged from 0.467 to 17.953 $\mu g L^{-1}$, with the average value of 4.042 ± 3.929 $\mu g L^{-1}$. DnBP, which dominated the Σ_6PAE at 65.8%, was found at the highest and lowest levels in the western lake (TX) and in the eastern drinking water source area (JC), respectively. The temporal distributions of Σ_6PAE showed that the highest and lowest levels were observed in September 2010 and in June 2010, respectively, which might be mainly attributed to the difference in the rainfall runoff. The different relationships between the runoff and the PAEs with low and high levels of carbon might suggest their different sources. The DnBP had much greater ecological risks than the other studied PAE congeners, as indicated by its PAFs and MOS10. The studied PAE congeners posed little health risk to the nearby male and female citizens.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.05.049.

References

Adams WJ, Biddinger GR, Robillard KA, Gorsuch JW. A summary of the acute toxicity of 14 phthalate-esters to representative aquatic organisms. Environ Toxicol Chem 1995;14:1569–74.

Aldenberg T, Jaworska JS. Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. Ecotoxicol Environ Saf 2000;46:1–18.

Clark K, Cousins TI, Mackay D, Yamada K. Observed concentrations in the environment. In: Hutzinger O, editor. The handbook of environmental chemistry. Berlin/Heidelberg: Springer; 2003. p. 125–77.

Cousins I, Mackay D. Correlating the physical–chemical properties of phthalate esters using the 'three solubility' approach. Chemosphere 2000;41:1389–99.

Cousins TI, Mackay D, Parkerton TF. Physical–chemical properties and evaluative fate modelling of phthalate esters. In: Hutzinger O, editor. The handbook of environmental chemistry. Berlin/Heidelberg: Springer; 2003. p. 57–84.

CPCIA. China chemical industry yearbook. Beijing: China National Chemical Information Center; 2009.

Dargnat C, Blanchard M, Chevreuil M, Teil MJ. Occurrence of phthalate esters in the Seine River estuary (France). Hydrol Process 2009;23:1192–201.

Ellington JJ. Octanol/water partition coefficients and water solubilities of phthalate esters. J Chem Eng Data 1999;44:1414–8.

Fauser P, Vikelsoe J, Sorensen PB, Carlsen L. Fate modelling of DEHP in Roskilde Fjord, Denmark. Environ Model Assess 2009;14:209–20.

Harris CA, Henttu P, Parker MG, Sumpter JP. The estrogenic activity of phthalate esters in vitro. Environ Health Perspect 1997;105:802–11.

He H, Hu GJ, Sun C, Chen SL, Yang MN, Li J, et al. Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China. Environ Sci Pollut Res 2011;18:638–48.

He W, Qin N, He Q, Wang Y, Kong XZ, Xu FL. Characterization, ecological and health risks of DDTs and HCHs in water from a large shallow Chinese lake. Ecol Informat 2012;12:77–84.

Howard PH. Handbook of environmental degradation rates. Chelsea, MI: Lewis Publishers Inc.; 1991.

Jobling S, Reynolds T, White R, Parker MG, Sumpter JP. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environ Health Perspect 1995;103:582–7.

Knoben RAE, Beek MA, Durand AM. Application of species sensitivity distributions as ecological risk assessment tool for water management. J Hazard Mater 1998;61:203–7.

Kurane R. Microbial degradation of phthalate esters. Microbiol Sci 1986;3:92–5.

Li RZ, Shu K, Luo YY, Shi Y. Assessment of heavy metal pollution in wstaurine surface sediments of Tangxi River in Chaohu Lake basin. Chin Geogr Sci 2010;20:9–17.

Luo G, Li P, Xu X, Liang Y, Cai W, Du X, et al. Distribution characteristics and ecological security assessment of phthalic acid esters in wet season in the river basins of main districts of Chongqing. Environ Sci Manage 2009;34:166–9. [in Chinese].

Mackintosh CE, Maldonado J, Jing HW, Hoover N, Chong A, Ikonomou MG, et al. Distribution of phthalate esters in a marine aquatic food web: comparison to polychlorinated biphenyls. Environ Sci Technol 2004;38:2011–20.

Mackintosh CE, Maldonado JA, Ikonomou MG, Gobas F. Sorption of phthalate esters and PCBs in a marine ecosystem. Environ Sci Technol 2006;40:3481–8.

Moore NP. The oestrogenic potential of the phthalate esters. Reprod Toxicol 2000;14: 183–92.

Okamoto Y, Ueda K, Kojima N. Potential risks of phthalate esters: acquisition of endocrine-disrupting activity during environmental and metabolic processing. J Health Sci 2011;57:497–503.

Peijnenburg W, Struijs J. Occurrence of phthalate esters in the environment of the Netherlands. Ecotoxicol Environ Saf 2006;63:204–15.

Rahman M, Brazel CS. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. Prog Polym Sci 2004;29:1223–48.

Sha YJ, Xia XH, Yang ZF, Huang GH. Distribution of PAEs in the middle and lower reaches of the Yellow River, China. Environ Monit Assess 2007;124:277–87.

Shi W, Hu XX, Zhang FX, Hu GJ, Hao YQ, Zhang XW, et al. Occurrence of thyroid hormone activities in drinking water from Eastern China: contributions of phthalate esters. Environ Sci Technol 2012;46:1811–8.

Sirivithayapakorn S, Thuyviang K. Dispersion and Ecological Risk Assessment of Di (2-Ethylhexyl) Phthalate (DEHP) in the Surface Waters of Thailand. Bull Environ Contam Toxicol 2010;84:503–6.

Solomon KR, Baker DB, Richards RP, Dixon DR, Klaine SJ, LaPoint TW, et al. Ecological risk assessment of atrazine in North American surface waters. Environ Toxicol Chem 1996;15:31–74.

Staples A, Adams WJ, Parkerton TF, Gorsuch JW, Biddinger GR, Reinert KH. Aquatic toxicity of eighteen phthalate esters. Environ Toxicol Chem 1997;16:875–91.

Staples CA, Parkerton TF, Peterson DR. A risk assessment of selected phthalate esters in North American and Western European surface waters. Chemosphere 2000;40: 885–91.

Staples CA, Guinn R, Kramarz K, Lampi M. Assessing the chronic aquatic toxicity of phthalate ester plasticizers. Hum Ecol Risk Assess 2011;17:1057–76.

USEPA. Risk assessment guidance for superfund. Human health evaluation manual, part A. EPA/540/1-89/002, 2012, vol. 1. Washington, D.C.: Office of Emergency and Remedial Response; 1989

Vethaak AD, Lahr J, Schrap SM, Belfroid AC, Rijs GBJ, Gerritsen A, et al. An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of the Netherlands. Chemosphere 2005;59:511–24.

Vitali M, Guidotti M, Macilenti G, Cremisini C. Phthalate esters in freshwaters as markers of contamination sources — a site study in Italy. Environ Int 1997;23:337–47.

Wang F, Xia XH, Sha YJ. Distribution of phthalic acid esters in wuhan section of the Yangtze River, China. J Hazard Mater 2008;154:317–24.

Wolfe NL, Steen WC, Burns LA. Phthalate ester hydrolysis — linear free energy relationships. Chemosphere 1980;9:403–8.

Xie ZY, Ebinghaus R, Temme C, Lohmann R, Caba A, Ruck W. Occurrence and air–sea exchange of phthalates in the arctic. Environ Sci Technol 2007;41:4555–60.

Xu FL, Jorgensen SE, Tao S, Li BG. Modeling the effects of ecological engineering on ecosystem health of a shallow eutrophic Chinese lake (Lake Chao). Ecol Model 1999;117:239–60.

Xu FL, Tao S, Dawson RW, Li PG, Cao J. Lake ecosystem health assessment: indicators and methods. Water Res 2001;35:3157–67.

Yang LH, Cheng SP, Wu ZB. Anthropogenic organic contaminants in water and surface sediments of large shallow eutrophic Chaohu Lake, China. Fresenius Environ Bull 2009;18:2048–54.

Yang H, Wright JA, Gundry SW. Water accessibility: boost water safety in rural China. Nature 2012;484:318-318.

Yuan SY, Liu C, Liao CS, Chang BV. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. Chemosphere 2002;49:1295–9.

Zeng F, Cui KY, Xie ZY, Liu M, Li YJ, Lin YJ, et al. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. Environ Int 2008;34:372–80.

Zeng F, Wen JX, Cui KY, Wu LN, Liu M, Li YJ, et al. Seasonal distribution of phthalate esters in surface water of the urban lakes in the subtropical city, Guangzhou, China. J Hazard Mater 2009;169:719–25.

Zhang W, Xu J, Xie P. Metals in surface sediments of large shallow eutrophic lake chaohu, china. Bull Environ Contam Toxicol 2007;79:242–5.

Zhou XM, Lu WJ, Su L, Shan ZJ, Chen XG. Binding of phthalate plasticizers to human serum albumin in vitro: a multispectroscopic approach and molecular modeling. J Agric Food Chem 2012;60:1135–45.

Zolezzi M, Cattaneo C, Tarazona JV. Probabilistic ecological risk assessment of 1,2,4-trichlorobenzene at a former industrial contaminated site. Environ Sci Technol 2005;39:2920–6.