



Seasonal distribution of phthalate esters in surface water of the urban lakes in the subtropical city, Guangzhou, China

Feng Zeng^{a,*}, Jiaxin Wen^a, Kunyan Cui^b, Lina Wu^c, Min Liu^c, Yangjie Li^a, Yujun Lin^a, Fang Zhu^a, Zhiling Ma^a, Zunxiang Zeng^a

^a School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangdong, Guangzhou 510275, China

^b Instrumental Analysis and Research Center, Sun Yat-sen University, Guangdong, Guangzhou 510275, China

^c Department of Applied Chemistry, East China Institute of technology, Jiangxi, Fuzhou 344000, China

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ABSTRACT

Urban lakes are vulnerable to the accumulation of toxic and/or potentially toxic contaminants, such as phthalate esters (PAEs) from urban stormwater runoff, atmospheric deposition, as well as untreated discharge of industrial wastewater and municipal sewage. The concentrations of 16 PAEs in surface water from 15 urban lakes in the subtropical city, Guangzhou, were measured, respectively in spring, summer and winter 2006, to elucidate the effect of the seasonal variation in climate conditions on the distribution of PAEs. Seasonal variations of the Σ_{16} PAEs concentrations, ranging, respectively from 0.47 to 6.19 $\mu\text{g L}^{-1}$ and from 24.9 to 221 $\mu\text{g g}^{-1}$, were measured in the dissolved and suspended particulate matter (SPM) phases. The highest concentrations of PAEs were present in summer. The spatial distribution of PAEs was site-specific. Of the 16 PAEs, dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), di(4-methyl-2-pentyl) phthalate (DMPP), di(2-ethylhexyl) phthalate (DEHP) were present in all the samples analyzed, and dominated by DnBP, DiBP and DEHP. Composition profile of PAEs indicated that the application of DnBP/DiBP is relatively high in the Pearl River Delta (PRD). Longer/branching alkyl PAEs likely adsorb to SPM in aquatic environments. Normalized partition coefficient (K_{OC}) between the dissolved water and SPM was correlated with *n*-octanol/water partition coefficient (K_{OW}) to understand the environmental behavior of PAEs.

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1. Introduction

The urban environment is affected by local, anthropogenic activities, including municipal, industrial, commercial, and agricultural operations, especially in many cities of the developing world in Asia [1]. Emissions of toxic and/or potentially toxic contaminants are often vastly accelerated, inevitably rendering the urban environment, particularly susceptible to environmental degradation and contamination [2].

Phthalate esters (PAEs) are a class of chemical compounds that are widely used in both industrial processes and consumer products. Global production of plastics has reached a level of ~ 150 million tons year⁻¹ [3]. Widespread use of PAE-containing products has led that elevated levels of PAEs are ubiquitous in urban environmental matrices [4–10]. Some PAEs (e.g. di-*n*-butyl phthalate (DnBP), di(2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP)) and their metabolites are estrogenic and exhibit adverse reproductive effects [11]. Currently, the occurrence, fate, and poten-

tial for ecological effects of PAEs in the urban environment are causing increasing environmental concern.

Guangzhou, the capital of Guangdong Province and the most important industrial city in the Pearl River Delta (PRD), is the largest urban center in southern China, with a total area of 7434 km² and a population over 10 million. The PRD is a tropical/subtropical region. It has a mean annual precipitation of 1800 mm and mean air temperature of 21.8 °C, with occasional typhoon and thunderstorm activity. Both natural and man-made urban lakes are managed for water supply, flood control, recreation, or some other direct human use. Urban lakes can be important habitats for a variety of aquatic life, as well as an aesthetic resource to communities. Although significant advances have been made in controlling point-sources, urban lakes have received frequent inputs of contaminants (e.g. PAEs) from various sources including urban stormwater runoff, atmospheric deposition, municipal/industrial effluents, etc. [1,7,12,13]. Growing urban population and levels of industrialization inevitably increase the fluxes of PAEs from terrestrial and atmospheric sources to urban lakes, threatening human and ecosystem health. The aim of our study was to find out the effect of the seasonal variation in climate conditions on the distribution of PAEs in surface water of the urban lakes Guangzhou.

* Corresponding author. Tel.: +86 20 8411 4133; fax: +86 20 8411 2245.

E-mail address: ceszf@mail.sysu.edu.cn (F. Zeng).

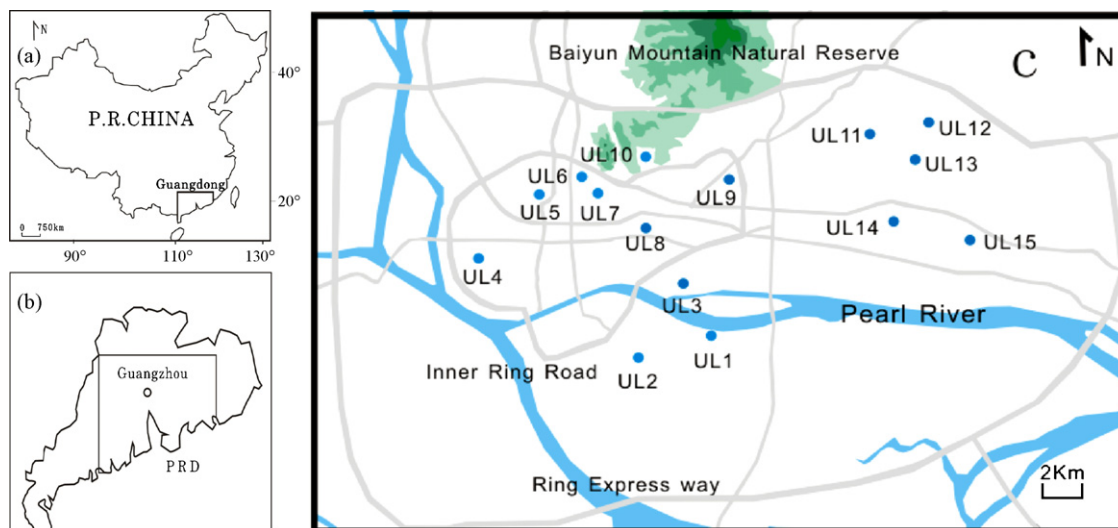


Fig. 1. Schematic showing the geographical locality of (a) the Guangdong Province in China; (b) Guangzhou city in the Guangdong Province and Pearl River Delta (PRD) region; and (c) the sampling sites within Guangzhou city.

2. Materials and methods

2.1. Chemicals and materials

Sixteen PAEs standard mixture containing dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), DnBP, dimethylglycol phthalate (DMGP), di(4-methyl-2-pentyl) phthalate (DMPP), di(2-ethoxyethyl) phthalate (DEEP), di-*n*-amyl phthalate (DnAP), di-*n*-hexyl phthalate (DnHP), BBP, di(hexyl-2-ethylhexyl) phthalate (HEHP), di(2-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), DEHP, di-*n*-nonyl phthalate (DnNP), di-*n*-octyl phthalate (DnOP) at 1000 $\mu\text{g mL}^{-1}$ each, and surrogate standards, consisting of diisophenyl phthalate, di-*n*-phenyl phthalate, di-*n*-benzyl phthalate, in a mixture solution of 500 $\mu\text{g mL}^{-1}$ each, were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Internal standard, benzyl benzoate, was acquired initially as a solid of 99% purity (Aldrich Chemicals, Gillingham, Dorset, USA).

Neutral silica gel (80–100 mesh), and alumina (100–200 mesh) were cleaned with methanol (MeOH), dichloromethane (DCM), and *n*-hexane using Soxhlet extractor for 72 h, activated at $180 \pm 1^\circ\text{C}$, $250 \pm 1^\circ\text{C}$ for 12 h, and then deactivated with 3% (w:w) of deionized water (extracted with DCM/*n*-hexane), respectively. Anhydrous sodium sulfate was baked at 420°C for 12 h and stored in sealed glass jars. Filter paper was extracted with methanol, DCM, and *n*-hexane with Soxhlet extractor for 72 h prior to use. Glass fiber filters (GF/F, 47 mm diameter, 0.7 μm pore size, Whatman International Ltd., Maidstone, England) were wrapped in pre-cleaned aluminum foil and baked for 12 h at 420°C and stored in an air and moisture tight container.

Water was filtered by Milli-Q and double distilled. All organic solvents used were of analytical grade, and redistilled using glass system. Laboratory glassware was soaked overnight in $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ solution, washed with tap water and redistilled water, baked at 300°C for 12 h, and then rinsed with acetone, DCM, and *n*-hexane.

2.2. Sampling and sample preparation

A detailed description of the sampling area and sample collection methods was given elsewhere [7]. Surface water samples were collected from 15 urban lakes (namely UL1–UL15 in Fig. 1), located in old residential (commercial/industrial), new residential, industrial districts and suburban areas in Guangzhou, respectively in

spring (on 10–15 April 2006), summer (on 13–18 August 2006) and winter (on 10–15 December 2006), and separated into “dissolved phase” and suspended particulate matter (SPM) by a vermicular system with glass fiber filters (GF/F). Prior to extraction, each sample was spiked with surrogate standards, diisophenyl phthalate, di-*n*-phenyl phthalate, di-*n*-benzyl phthalate. 2.0 L of the filtrate samples were placed in separating funnels and extracted triplicately with 100 mL of DCM. The filters loaded with SPM were freeze-dried, weighed, and Soxhlet-extracted for 48 h with DCM. All extracts were concentrated, flowed through anhydrous sodium sulfate, solvent-exchanged to *n*-hexane, and further reduced to approximately 1.0 mL under gentle nitrogen flow.

Concentrated extracts were cleaned and fractionated on a 10-mm i.d. 1:2 alumina/silica gel glass column packed, from the bottom to top, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). The column was washed with 20 mL of hexane and 70 mL the mixed solvent of DCM/*n*-hexane (3:7, v:v), respectively. Then PAEs were eluted with 40 mL the mixed solvent of acetone/*n*-hexane (2:8, v:v). The extracts were concentrated using a rotary evaporator and reduced to 0.1 mL under a stream of purified N_2 . Known quantities of internal standard were added to the sample prior to instrumental analysis.

2.3. Instrumental analysis

The extracted compounds were determined with an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC–MS) (Agilent Technologies, Avondale, PA, USA), operating in electron impact and selective ion monitoring modes (SIM), and a DB-5MS capillary column (30 m \times 250 μm i.d.; 0.25 μm film thickness, J&W Scientific). The transfer line and the ion source temperature were maintained at 280 and 230°C , respectively. The column temperature program was initiated at 80°C for 1.0 min, increased to 180°C at a rate of $10^\circ\text{C min}^{-1}$, held for 1.0 min, and finally ramped at 2°C min^{-1} – 300°C , held for 10 min. The flow rate of the carrier gas helium was kept constant at 0.8 mL min^{-1} . The extracts (1.0 μL) were injected onto GC–MS in splitless mode with an inlet temperature of 300°C .

Quantitation was performed using the internal calibration method based on five-point calibration curve for individual PAEs. Benzyl benzoate was used as internal standards for the quantification of PAEs.

Table 1 Summary of concentrations of PAEs in the dissolved water and SPM of the urban lakes in Guangzhou City, respectively in summer, spring and winter.

PAEs	Spring						Summer						Winter					
	Dissolved phase			SPM			Dissolved phase			SPM			Dissolved phase			SPM		
	Range	Median	D.F.	Range	Median	D.F.	Range	Median	D.F.	Range	Median	D.F.	Range	Median	D.F.	Range	Median	D.F.
DMP	0.007–0.019	0.011	100	0.012–0.031	0.021	100	0.012–0.032	0.017	100	0.021–0.422	0.0297	100	0.005–0.023	0.008	100	0.006–0.028	0.009	100
DEP	0.032–0.092	0.064	100	0.131–0.317	0.238	100	0.059–0.117	0.077	100	0.208–0.383	0.294	100	0.013–0.062	0.028	100	0.079–0.187	0.107	100
DtBP	0.281–1.75	0.495	100	11.4–53.3	21.8	100	0.884–2.86	1.28	100	35.2–89.5	51.4	100	0.161–0.971	0.321	100	6.09–31.9	12.5	100
DnBP	0.274–1.30	0.397	100	8.72–46.2	16.3	100	0.729–2.43	1.18	100	21.2–77.6	37.5	100	0.128–0.738	0.237	100	5.08–24.7	8.56	100
DMGP	N.D.–0.11	0.078	40	N.D.–0.162	0.083	80	N.D.–0.125	0.091	26	N.D.–0.246	0.101	80	N.D.–0.076	0.024	73	N.D.–0.102	0.053	80
DMPP	0.009–0.037	0.016	100	0.171–1.03	0.431	100	0.011–0.041	0.017	100	0.321–1.07	0.267	100	0.006–0.017	0.012	100	0.019–0.628	0.312	100
DEEP	N.D.–0.140	0.037	83	N.D.–0.108	0.078	33	N.D.–0.094	0.047	93	N.D.–0.249	0.108	40	N.D.–0.019	0.014	13	N.D.–0.007	0.047	27
DnAP	N.D.	N.D.	0	N.D.–0.179	0.074	93	N.D.	N.D.	0	N.D.–0.208	0.096	93	N.D.	N.D.	0	N.D.–0.164	0.029	93
DnHP	N.D.	N.D.	0	N.D.–0.238	0.102	60	N.D.	N.D.	0	N.D.–0.295	0.101	67	N.D.–0.035	0.035	7	N.D.–0.274	0.183	47
BBP	N.D.	N.D.	0	N.D.–0.662	0.142	73	N.D.	N.D.	0	N.D.–0.729	0.135	87	N.D.	N.D.	0	N.D.–0.451	0.096	67
HEHP	N.D.–0.022	0.022	7	N.D.–0.195	0.109	60	N.D.	N.D.	0	N.D.–0.148	0.055	67	N.D.	N.D.	0	N.D.–0.571	0.099	47
DBEP	N.D.–0.168	0.168	7	N.D.–0.182	0.107	47	N.D.–0.058	0.058	7	N.D.–0.207	0.046	47	N.D.	N.D.	0	N.D.–0.169	0.109	33
DCHP	N.D.–0.076	0.076	7	N.D.–0.673	0.109	87	N.D.	N.D.	0	N.D.–0.142	0.047	87	N.D.–0.041	0.022	13	N.D.–0.515	0.074	67
DEHP	0.123–0.432	0.218	100	11.0–40.4	22.8	100	0.286–0.687	0.427	100	25.0–58.9	42.1	100	0.105–0.339	0.183	100	11.7–36.8	20.9	100
DnPP	N.D.	N.D.	0	N.D.–0.091	0.071	47	N.D.	N.D.	0	N.D.–0.117	0.079	47	N.D.	N.D.	0	N.D.–0.069	0.056	33
DnOP	N.D.	N.D.	0	N.D.–0.133	0.101	73	N.D.–0.006	0.003	20	N.D.–0.142	0.106	80	N.D.–0.005	0.005	7	N.D.–0.107	0.08	80

Reported concentrations were corrected by subtracting the mean blank values. D.F.: Detection frequency (%) ($n = 15$). ND: concentration was lower than the MDL.

2.4. Quality control and quality assurance

For each batch of 10 field samples, a procedural blank, a spiked blank, a spiked matrix sample, a spiked matrix duplicate, and a sample duplicate were processed. The instruments were calibrated daily with calibration standards. In addition, surrogate standards were added to all the samples to monitor matrix effects. The surrogate recoveries were $81.3 \pm 11.8\%$ for diisophenyl phthalate, $64.2 \pm 9.16\%$ for di-*n*-phenyl phthalate and $112 \pm 10.6\%$ for di-*n*-benyl phthalate in water and SPM samples. Recoveries of the 16 PAEs ranged from 70.2% to 110% (relative standard deviations <11.5%) in the spiked dissolved water and SPM blank samples, from 71.8% to 102.1% (relative standard deviations <10.2%) in the spiked water and SPM matrix samples. Only small concentrations of DnBP, DiBP and DEHP were found in procedural blanks and they were appropriately subtracted from those in the sample extracts. The concentrations of PAEs were corrected according to the recovery ratios for the surrogates. Instrumental detection limits using the present methods were calculated by signal-to-noise ratio of 10 which were ranging from 1 to 9 pg. The method detection limits (MDLs) were derived from the blanks and quantified as mean field blanks plus three times of the standard deviation (3σ) of field blanks.

2.5. SPM, POC, and DOC measurement

Contents of SPM, particulate organic carbon (POC) and dissolved organic carbon (DOC) were determined by triplicatedly with 1000 mL of unfiltered water which were passed through pre-combusted and pre-weighed filters (47 mm diameter, 0.7 μm pore size). The filters were then dried, re-weighed for SPM, and analyzed for POC with an elemental analyzer (Elementar, Vario, EL III, Germany). The filtrates were analyzed for DOC with a total organic carbon analyzer (Shimadzu TOC-VCPH, Kyoto, Japan).

2.6. Statistical analysis

Statistical analyses were performed with SPSS 12.0 for Windows (SPSS Inc., Chicago, IL).

3. Results and discussion

3.1. Seasonal variation of the Σ_{16} PAEs concentrations in surface water from the urban lakes

The individual concentrations of 16 PAEs in surface water from the urban lakes, respectively in spring, summer and winter 2006, are shown in Table 1. PAEs were detected in all the samples analyzed, which indicate that PAEs are ubiquitous environmental contaminants.

The Σ_{16} PAEs concentrations in the dissolved and SPM phases ranged from 0.835 to 3.73 $\mu\text{g L}^{-1}$ ($1.59 \pm 0.846 \mu\text{g L}^{-1}$), 2.23 to 6.19 $\mu\text{g L}^{-1}$ ($3.46 \pm 1.17 \mu\text{g L}^{-1}$), 0.470 to 2.17 $\mu\text{g L}^{-1}$ ($0.937 \pm 0.485 \mu\text{g L}^{-1}$), and from 33.6 to 142 $\mu\text{g g}^{-1}$ (dry weight, – dw) ($71.3 \pm 32.6 \mu\text{g g}^{-1}$ dw), 82.9–221 $\mu\text{g g}^{-1}$ ($140.9 \pm 43.4 \mu\text{g g}^{-1}$ dw), 24.9–93.2 $\mu\text{g g}^{-1}$ ($47.5 \pm 22.2 \mu\text{g g}^{-1}$ dw), respectively in spring, summer and winter. Dissolved and SPM-bound PAEs exhibit similar seasonal trend. The highest levels of Σ_{16} PAEs were observed in summer and the lowest were in winter. These results agree with other reports for polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), mainly caused by urban stormwater runoff and atmospheric deposition [13,14]. In most cities in China sanitary waste and stormwater are combined in the same sewer system. If the combined flow exceeds the interceptor capacity, overflows are directly discharged to receiving waters (e.g. urban creeks and

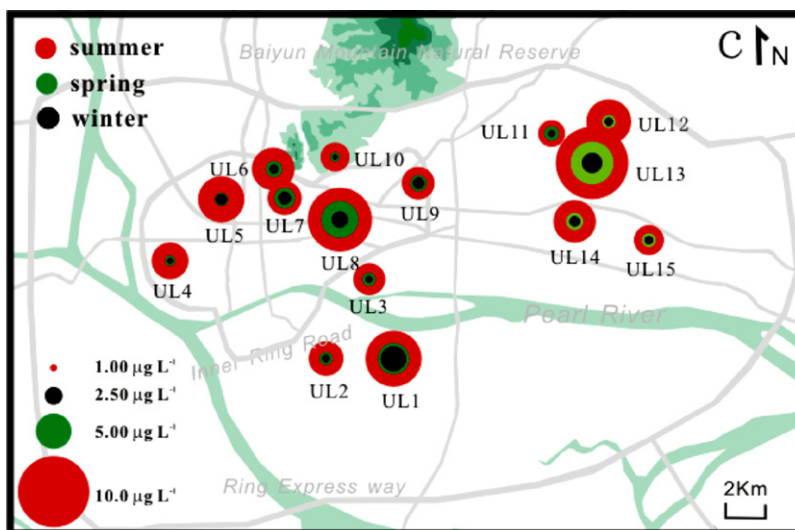


Fig. 2. Spatial distribution of Σ_{16} PAEs in the surface water from the urban lakes of the subtropical city, Guangzhou, respectively in summer, spring and winter 2006 (dissolved and SPM-associated PAEs, $\mu\text{g L}^{-1}$).

lakes). Because the combined sewer overflows (CSOs) are composed of a mixture of urban stormwater runoff, sewer deposits, and untreated sanitary sewer flow and can contain various anthropogenic contaminants (e.g. PAEs), especially high concentrations at the early phase of a rainfall event [1]. Rainfalls provide the basic force for urban stormwater runoff and atmospheric deposition. As evidenced by high SPM contents in the wet weather seasons. The contents of SPM in surface water of the urban lakes ranged from 11.2 to 15.5 mg L^{-1} , 15.5 to 21.9 mg L^{-1} , 9.51 to 14.5 mg L^{-1} , with the mean contents of $13.8 \pm 1.51 \text{ mg L}^{-1}$, $16.7 \pm 1.62 \text{ mg L}^{-1}$, $11.5 \pm 1.54 \text{ mg L}^{-1}$, respectively in spring, summer and winter. Meanwhile, the contribution ratios of the Σ_{16} PAEs concentration in SPM to the total Σ_{16} PAEs concentrations were higher during the wet weather season in summer ($40.5 \pm 2.46\%$), and winter ($40.1 \pm 2.73\%$) than those found during the dry weather season in winter ($36.9 \pm 2.02\%$). These contaminated SPM settle finally into the bottom of the urban lakes. It is reasonable to expect that a large amount of PAEs is present in the sediment of the urban lakes as well. In fact high concentrations of PAEs were detected in the sediment of the urban lakes [7].

There was significant variation in the total Σ_{16} PAEs concentrations in surface water from the urban lakes (Fig. 2). Higher Σ_{16} PAEs concentrations were measured in site UL13 (2.88 – $10.2 \mu\text{g L}^{-1}$), which is located in the biggest electronic/electrical commercial town in South China, site UL8 (2.19 – $9.06 \mu\text{g L}^{-1}$), surrounded by dense hospitals, restaurants, and commercial streets, and site UL1 (3.46 – $7.88 \mu\text{g L}^{-1}$), a semi-enclosed lake, connected to the Guangzhou Channel of the Pearl River, receiving a great amount of industrial and domestic PAEs from Guangzhou city. Other higher concentrations of Σ_{16} PAEs were also found at site UL5 (1.51 – $6.46 \mu\text{g L}^{-1}$), UL6 (1.24 – $5.97 \mu\text{g L}^{-1}$), and UL12 (1.12 – $6.29 \mu\text{g L}^{-1}$). Relatively low Σ_{16} PAEs levels were found at site UL15 (1.10 – $4.22 \mu\text{g L}^{-1}$), and UL10 (0.765 – $4.16 \mu\text{g L}^{-1}$), which may be due to their location in new residential and suburban regions. Given the concentration range for PAEs and their spatial variation, it is evident that the impervious urban environment plays a significant role in the dispersion mechanisms of PAEs. PAEs in the atmosphere are generally well-distributed in a relatively small region such as Guangzhou city due to atmospheric advective convection. In addition, it is probably because of the complex environmental conditions of the urban lakes including soil erosion, microbial and photodecomposition activities, sedimentation rate, characteristics of the sediment and local discharge [7,15,16].

Water DOC and SPM POC in surface water of the urban lakes in this study were also investigated, with the mean concentrations of $1.50 \pm 0.70 \text{ mg L}^{-1}$, $2.99 \pm 0.58 \text{ mg L}^{-1}$ and $0.84 \pm 0.29 \text{ mg L}^{-1}$, and $3.8 \pm 0.6\%$, $3.3 \pm 0.5\%$ and $4.6 \pm 0.5\%$, respectively in spring, summer and winter. DOC and POC were not significantly correlated, however, water DOC was correlated to SPM contents. The positive correlation between water DOC and SPM content suggested common pollutant source for these urban lakes. Low Pearson correlation coefficients ($p < 0.05$) between water DOC and dissolved PAEs concentrations in the dissolved water, as well as SPM POC and SPM-bound Σ_{16} PAEs in SPM, was observed, suggesting that PAEs contamination in this study area may be dominated more by local inputs. However, the exact sources of input in each area need further and more detailed study. Further work is also needed to get a detailed understanding of the actual quantities of PAEs that are being directly discharged to the urban lakes.

3.2. PAE congener profiles in the dissolved water and SPM in the urban lakes

Of the 16 PAEs, DMP, DEP, DnBP, DiBP, DMPP and DEHP were present in all the dissolved water samples analyzed (Table 1). DEHP was detected in more than 90% of the dissolved water in spring ($< \text{MDL} = 0.107 \mu\text{g L}^{-1}$) and summer ($< \text{MDL} = 0.140 \mu\text{g L}^{-1}$), but detected only at sites UL1 ($0.019 \mu\text{g L}^{-1}$) and UL2 ($0.008 \mu\text{g L}^{-1}$) in winter. DnAP, HEHP, BBP, DBEP, and DnNP were below their MDLs in all the dissolved water samples analyzed. In the SPM, more PAE congeners were detected. Similar to the dissolved water, DMP, DEP, DnBP, DiBP, DMPP and DEHP were the dominant species. Other major congeners detected in the SPM during the survey were DMGP, DCHP, DnAP and DnHP. BBP and DnOP were detected in the dissolved waters at sites UL1, UL8 and UL13 in summer, whereas they are detectable in more than 70% of the SPM samples.

The relative contributions of the 16 PAE congeners to the Σ_{16} PAEs concentration in the dissolved and SPM phases, respectively in spring, summer and winter, are presented in Fig. 3. It is clear that DiBP was the most abundant in the dissolved waters, contributions ranging from 29.7% to 46.8% ($38.8 \pm 5.0\%$), 38.4% to 46.4% ($42.7 \pm 2.4\%$) and 28.8% to 44.9% ($37.7 \pm 4.5\%$). The next dominant PAEs was DnBP, ranging from 23.4% to 39.8% ($32.7 \pm 4.7\%$), 32.8% to 42.0% ($37.9 \pm 2.3\%$) and 27.0% to 36.9% ($31.6 \pm 3.0\%$), followed by DEHP, ranging from 10.5% to 20.0% ($15.4 \pm 3.0\%$), 9.2% to 17.9% ($13.3 \pm 2.6\%$) and 14.6% to 28.2% ($20.6 \pm 4.0\%$) of the Σ_{16} PAE con-

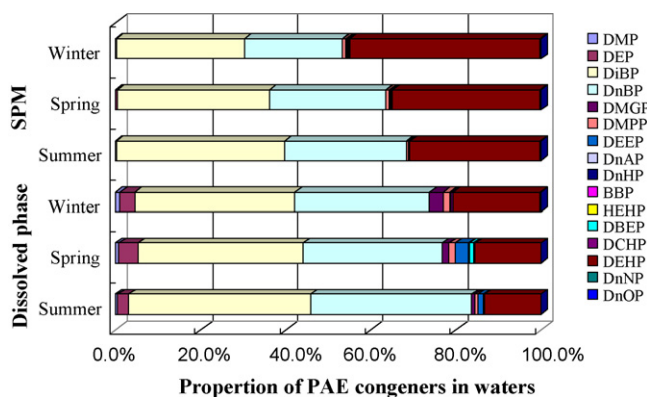


Fig. 3. Proportion of PAE congeners to the Σ_{16} PAEs concentration in the dissolved water and SPM, respectively in summer, spring and winter.

centrations, respectively in spring, summer and winter. In SPM the contribution of DEHP increased significantly, ranging from 28.0% to 40.9% ($34.6 \pm 4.6\%$), 23.0% to 39.8% ($30.7 \pm 4.9\%$), and 35.4% to 56.2% ($44.2 \pm 6.0\%$), and DiBP/DnBP decreased, ranging from 30.1% to 40.4% ($35.8 \pm 3.2\%$), 35.2% to 42.5% ($39.5 \pm 2.2\%$) and 23.6% to 36.7% ($30.1 \pm 4.0\%$), and 24.7% to 32.5% ($27.4 \pm 2.3\%$), 21.6% to 35.1% ($28.7 \pm 3.6\%$) and 17.5% to 27.0% ($23.0 \pm 3.0\%$), respectively in spring, summer and winter. Increased rates for DEHP in winter have been measured in both the dissolved waters and SPM as a consequence of re-suspended sediment due to lower water depth and softer surface of sediment by the northeastern monsoon from inland China and dry deposition [8,17,18]. In fact, the longer the alkyl-chain, the lower the solubility and the higher the octanol/water partition coefficient (K_{OW}) [19], which frequently rate-limiting for biodegradation, volatilization, and subsurface transport.

Obviously, DnBP, DiBP, and DEHP dominated PAEs in surface water from the urban lakes, accounting for >85% and >95% of the total PAEs in dissolved and SPM phases, respectively. This result is consistent with the commonly reported findings that DnBP, DiBP and DEHP are the dominant components of the PAEs distribution pattern in air [8,17,18], water [5,6,20], sediment [21–24], and biota [9,25], supported by Vitali et al. [4] observation that DEHP and DnBP/DiBP are the most commonly produced PAEs. This does not reflect the usual pattern of plastic industry production dominated by DEHP reported in other studies [21,23,26].

3.3. Distribution of PAEs in the dissolved water and SPM of the urban lakes

Distribution of hydrophobic organic contaminants (e.g. PAEs) between the dissolved and SPM phases is likely involved highly dynamic sorption and desorption processes governed by the interaction of the contaminants with POC and DOC, and is also affected by other transport and mass transfer processes [27,28]. The relative contribution of the dissolved and SPM-bound PAEs in surface water of the urban lakes of Guangzhou in summer, spring and winter is shown in Fig. 4. Averagely, the dissolved phase contributed, respectively for 97.8%, 94.8%, 72.9%, 67.3%, and 64.3% of total DMP, DEP, DMPP, DnBP, DiBP and DEHP contamination in surface water of the urban lakes.

The organic carbon normalized distribution coefficients K_{OC} ($=100 \times C_{SPM}/(C_{water} \times POC\%)$) were calculated for selected PAEs components (e.g. DMP, DEP, DnBP, DiBP and DEHP). As shown in Fig. 5, a sufficiently good correlation exists between $\log K_{OC}$ and $\log K_{OW}$ for the PAEs [19]. This is consistent with the distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), PAHs, PCBs distribution between the dissolved water and SPM/soil [23,28,29]. It was also noted that the slopes of the correlation

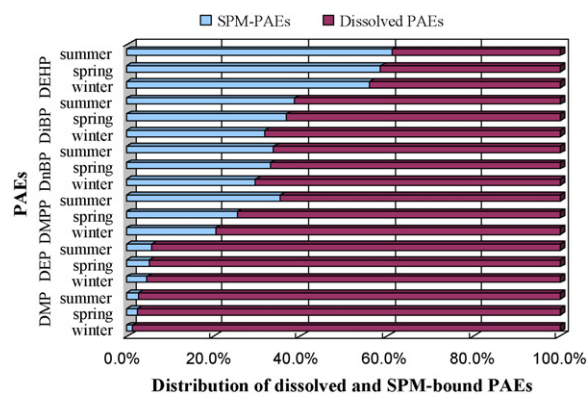


Fig. 4. The contribution patterns of the dissolved and SPM-bound PAEs (e.g. DMP, DEP, DMPP, DnBP, DiBP and DEHP) in surface water of the urban lakes in the subtropical city, Guangzhou, respectively in summer, spring and winter.

between $\log K_{OC}$ and $\log K_{OW}$ obtained in the present study were substantially less than 1 (Fig. 5), which is similar to that found in the seawater of the False Creek Harbor [23]. This indicates the measured partition coefficients do not increase to the degree expected with increasing hydrophobicity. Possibly because the dissolved-PAEs concentrations were overestimated due to the presence of colloids, dissolved organic matter (DOM), and very fine particulates that passed through GF/F. The presence of these additional sorbent phases would increase the solubility of more hydrophobic PAEs (e.g. DEHP) to a larger degree than that of less hydrophobic PAEs.

3.4. Comparison of PAEs in surface waters with other results

Although the data on all 16 PAEs are limited, the concentrations for DMP, DEP, DnBP, DiBP, BBP and DEHP in both the dissolved and SPM phases have been routinely reported from other studies (Table 2).

The total concentrations of DEHP in surface water of the urban lakes in Guangzhou city, including both the dissolved and SPM-DEHP were comparable to those present in the Netherlands [30], the Rieti District, Italy [4], the False Creek Harbor, Canada [23], San Diego Country, California, USA [31], the Tama River, Tokyo Bay, Japan [32], the Yangze River and the Yellow River, China [8,33], and lower than those determined in the Taihu lake and the Taiwan rivers, China [22,34], the Klang River Basin, Malaysia [21], the Brandenburg and Berlin, Germany [35], and the Eastern Cape, South Africa

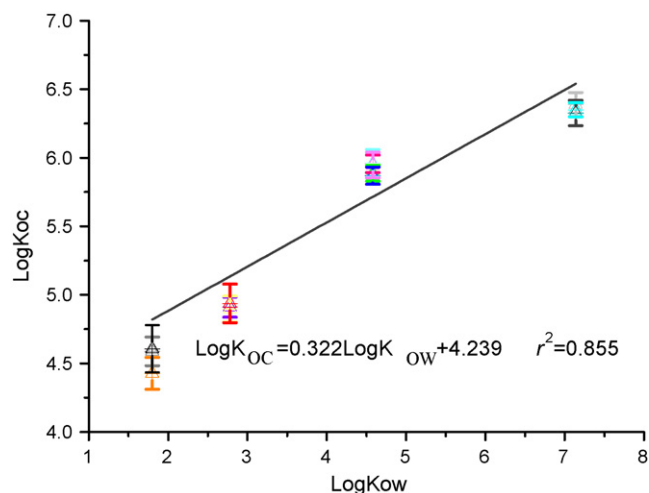


Fig. 5. Relationship between $\log K_{OW}$ and $\log K_{OC}$ for PAEs in the waters collected at the urban lakes of the subtropical city, Guangzhou.

Table 2
Summary of DMP, DEP, DiBP, DnBP, BBP, DnOP and DEHP concentrations in the surface waters around the world.

Location		DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	References
Dissolved PAEs ($\mu\text{g L}^{-1}$)									
The Tama River, Tokyo Bay, Japan		<MDL–0.092	<MDL–0.310	<MDL–0.033	<MDL–0.540	<MDL–0.061	<MDL–3.60	<MDL	[32]
The Netherlands		<MDL–0.190	<MDL–2.30	–	<MDL–3.100	<MDL–1.800	<MDL–5.000	<MDL–0.078	[20]
The North Sea (German Bight)		<MDL–0.00068	0.00003–0.0102	–	0.00045–0.0066	<MDL–0.00026	0.00052–0.0044	–	[17]
The San Diego Country, California	Wet season	0.098–0.78	1.49	–	1.44–8.30	0.05–1.19	2.67–5.94	–	[31]
	Dry season	<MDL	0.9	–	<MDL	<MDL	<MDL	–	
The Arctic		<MDL–0.0003	<MDL–0.0008	<MDL–0.0002	<MDL–0.0004	<MDL–0.00005	<MDL–0.0033	–	[5]
The Yellow River, China		<MDL–0.581	0.0115–1.09	–	<MDL–26.0	–	0.347–31.8	<MDL–0.071	[33]
The urban lakes, Guangzhou		0.003–0.085	0.015–0.32	0.16–0.92	0.94–3.60	<MDL	0.087–0.63	<MDL	[7]
The Yangtze River, China	Wet season	<MDL–0.295	<MDL–0.365	–	0.014–0.134	–	0.011–0.028	<MDL	[6]
	Dry season	<MDL–0.100	<MDL	–	<MDL–35.65	–	0.011–54.7	0.07–3.20	
SPM-bound PAEs ($\mu\text{g g}^{-1}$)									
The Netherlands		<MDL–160.00	<MDL–2.69	–	<MDL–4.100	<MDL–3.000	<MDL–190	<MDL–0.047	[20]
The Yellow River, China		<MDL–3.01	<MDL–0.131	–	17.6–57.8	–	5.40–630	<MDL	[22]
Total PAEs ($\mu\text{g L}^{-1}$)									
The Klang River Basin, Malaysia		<MDL–0.100	<MDL–0.2	<MDL–3.2	0.8–4.8	–	3.1–64.3	<MDL–1.5	[21]
The Rieti District, Italy		<MDL	<MDL–3.2	<MDL–5.7	<MDL–44.3	<MDL–6.6	<MDL–31.2	<MDL–11.3	[4]
The Brandenburg and Berlin, Germany		–	–	–	0.12–8.8	–	0.33–97.8	–	[35]
The Taiwan river, China		–	<MDL–2.5	–	1.0–13.5	<MDL	<MDL–18.5	–	[22]
The Taihu Lake, China		0.286–84.9	0.247–1.15	0.429–17.1	–	–	0.301–15.1	–	[34]
The Eastern Cape, South Africa		0.03–350.8	0.03–398	–	0.04–1028	–	0.06–2306	–	[36]
The False Creek Harbor, Canada		0.00226–0.00546	0.046–0.351	0.003–0.009	0.050–0.244	0.002–0.006	0.170–0.444	0.005–0.035	[23]
The urban lakes, Guangzhou	Spring	0.007–0.019	0.034–0.097	0.455–2.56	0.413–2.01	<MDL–0.010	0.292–1.05	<MDL–0.133	This study
	Summer	0.012–0.033	0.063–0.123	1.47–4.43	1.07–3.79	<MDL–0.012	0.834–1.60	<MDL–0.007	
	Winter	0.005–0.023	0.014–0.063	0.235–1.43	0.180–1.07	<MDL–0.005	0.237–0.804	<MDL–0.005	

[36]. DnBP concentrations in surface waters from the Eastern Cape, South Africa [36], San Diego Country, California, USA [31], and the Taiwan rivers, China [22,34] were several times higher than those found in the present study. The DiBP concentrations were similar to those obtained from the Klang River Basin, Malaysia [21], the Rieti District, Italy [4], the Taihu lake, China [34], but more than one to two orders of magnitude higher than those found in the other studies [4,21]. DnOP, BBP, DEP and DMP showed relatively low concentrations in all studies [4,20–22], except for DEP and DMP in the Eastern Cape, South Africa [35] and the Taihu lake, China [34].

Based on the ecotoxicology and environmental chemistry of DnBP and DEHP, van Wezel et al. [37] derived environmental risk levels (ERL) of DnBP and DEHP, which were 10 and 0.19 $\mu\text{g L}^{-1}$ in water, respectively. In this study, the mean concentrations of DEHP in surface water of the urban lakes in Guangzhou city were several times higher than the ERL of DEHP, whereas DnBP were lower than its ERL. Toxicity studies [38] have shown that DiBP has similar testicular and developmental effects as DnBP and DEHP, the mean concentrations of DiBP measured in this present study were lower than the ERL. However, the levels of DnBP/DiBP in SPM might be potentially hazardous to organisms in the urban lakes.

4. Conclusions

The composition and distribution of PAEs in surface waters of the urban lakes in Guangzhou varied seasonally. Dissolved and SPM-bound PAEs exhibit similar seasonal trends. Seasonal variation of the Σ_{16} PAEs concentrations was at the mid level of the global values in the surface waters. The spatial distribution of PAEs was site-specific. Of the 16 PAEs, DMP, DEP, DnBP, DiBP, DMPP, and DEHP were present in all the samples analyzed, dominated by DnBP, DiBP and DEHP. Longer/branching alkyl PAEs, more easily undergo sorption in SPM in aquatic environments. K_{OC} between the dissolved water and SPM was correlated with K_{OW} , indicating organic matter in SPM played a dominant role in PAEs partition between the dissolved water and SPM. The proportion of DnBP/DiBP usage is higher in the Pearl River Delta (PRD).

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