Science of the Total Environment 687 (2019) 297–308

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Phthalate esters (PAEs) in atmospheric particles around a large shallow natural lake (Lake Chaohu, China)

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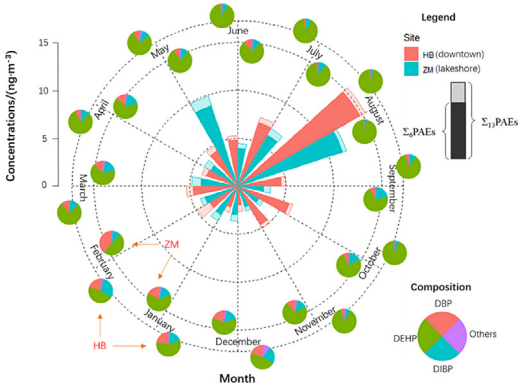
HIGHLIGHTS

- First investigation of atmospheric PAEs in natural lake.
- DEHP, DIBP and DBP were the main PAEs in atmospheric particles around Lake Chaohu.
- Condensation of DIBP and DBP at low temperature may lead to their temporal variations.
- The transport pathway for different PAE congeners was disparate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 April 2019
Received in revised form 31 May 2019
Accepted 3 June 2019
Available online 06 June 2019

Editor: Shuzhen Zhang

Keywords:
Phthalate esters (PAEs)
Spatiotemporal variations
Composition
Atmospheric particles
Lake Chaohu

ABSTRACT

The pollution of phthalate esters (PAEs) remains an important issue in the world. Current studies mainly focused on atmospheric PAEs in urban area with strong anthropogenic activities, but there were no studies on PAEs in the ambient air around large natural lake. This paper focused on two sites around Lake Chaohu to investigate the monthly occurrence, composition and source of PAEs in the atmospheric particles around large shallow natural lake. New insights into atmospheric PAEs in large shallow natural lake and the overall fate of PAEs in lake ecosystem were given. The concentrations of the Σ_{13}PAEs in atmospheric particles were at a significantly low level ranging from 2740 to 11,890 pg·m^{-3} and 2622 to 15,331 pg·m^{-3} in ZM (the lakeshore site) and HB (the downtown site), respectively. There were no statistically significant differences of PAEs between ZM and HB. The highest atmospheric PAE concentrations in August were likely related to the long-range transport from Guangdong Province. Di(2-ethylhexyl) phthalate (DEHP), diisobutyl phthalate (DIBP) and dibutyl phthalate (DBP) were the main PAE congeners. Temporally, DIBP and DBP had the highest fractions in winter and the lowest fractions in summer. It might be justified by the condensation of DIBP and DBP from gas phase to particulate phase at low temperature. Multimedia comparison of PAE profiles in Lake Choahu revealed that low molecular weight (LMW) congeners were transported mainly through water while high molecular weight (HMW) congeners were transported mainly through atmosphere.

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https://doi.org/10.1016/j.scitotenv.2019.06.034
0048-9697/

1. Introduction

Phthalate esters (PAEs) are ester congeners of phthalic acids, which are synthesized by phthalic anhydrite and different alcohols (Kashyap and Agarwal, 2018). Due to their excellent performance, they have been used in various manufacturing industries for several decades (Zhu et al., 2018). PAEs were widely used as additives in personal care products, medical devices, toys, building materials, electronics, food packages, inks and adhesives, and plasticizers in polyvinyl chlorides (PVCs) and other polymers (Gomez-Hens and Aguilar-Caballos, 2003; Jonsson et al., 2003; Franco et al., 2007; Katsikantami et al., 2016). While the extensive use of PAEs has greatly improved our life quality, it also led to their frequent detection in air (Kong et al., 2013; Chi et al., 2017), water (Paluselli et al., 2018), soil (Wang et al., 2017), sediment (Mi et al., 2019) and organisms (Zhu et al., 2006; Wang et al., 2015). The adverse effects of PAEs and their metabolites, such as DNA damage (Al-Saleh et al., 2017), pregnancy loss (Toft et al., 2012), sperm quality decline (Tian et al., 2019), respiratory diseases (Shi et al., 2018) and obesity (Buckley et al., 2016; Dong et al., 2017), have also been widely concerned since 1980s (Kluwe et al., 1982; Kamrin, 2009). Due to their toxicity and widespread occurrence (Hauser and Calafat, 2005; Heudorf et al., 2007; Net et al., 2015), PAEs have been restricted or limited in many regions such as the United States (Keith and Telliard, 1979; CPSC, 2017), European Union (EU, 2005), and China (Zhou et al., 1991; SAC, 2014). Prior to 1980s, dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP) had been included in the list of "priority pollutants" (Keith and Telliard, 1979). Although PAEs were gradually replaced by other non-phthalate substitutes, PAEs still accounted for 65% of global plasticizer consumption in 2017, and the global plasticizer consumption will still grow in the future (IHS Markit, 2018). PAEs were revealed as the most abundant endocrine disrupting chemicals (EDCs) in ambient air (Salapasidou et al., 2011; Salgueiro-González et al., 2013; Teil et al., 2016). Therefore, the pollution of PAEs remains an important issue, especially in China (Sun et al., 2013; Wang et al., 2014a; IHS Markit, 2018).

PAEs are semi-volatile organic compounds (SVOCs) with vapor pressures ranging from 0.263 Pa for DMP to 3.63×10^{-8} Pa for ditridecyl phthalate (DTDP) (Net et al., 2015). They can easily enter into atmosphere from indoor materials because of their non-chemical bonding properties with polymer matrix (Xu et al., 2012; Sampath et al., 2017), and were easily absorbed into solid particles due to their high octanol-air partition coefficient (K_{OA}) values (Net et al., 2015). Atmosphere plays an important role in the environmental behavior process of PAEs. PAEs were distributed globally via atmospheric transport over long distances (Xie et al., 2007; Lenoir et al., 2016). Therefore, atmospheric PAEs in outdoor environments were also been extensively concerned in many countries, such as China (Wang et al., 2008; Zeng et al., 2010; Zhu et al., 2016; Li et al., 2018), India (Sampath et al., 2017), Mexico (Quintana-Belmares et al., 2018), Greece (Salapasidou et al., 2011), Czech (Růžičková et al., 2016), France (Teil et al., 2006, 2016), Spain (Aragón et al., 2012; Salgueiro-González et al., 2013) and Sweden (Thurén and Larsson, 1990). DEHP, DBP and diisobutyl phthalate (DIBP) were the predominant PAEs in particulate phase (Ma et al., 2014; Růžičková et al., 2016; Quintana-Belmares et al., 2018), while DMP and DEP were the prevailing PAEs in gas phase (Li et al., 2019). In addition to the physicochemical properties of PAEs (Teil et al., 2016), their fate in outdoor atmosphere was also influenced by more complicated factors such as the weather condition (Li et al., 2018), temperature (Teil et al., 2006), photochemical reactions (Bao et al., 2011; Lei et al., 2018a, 2018b, 2018c), particulate organic carbon (POC) (Zeng et al., 2010) and anthropogenic activities (Thurén and Larsson, 1990; Teil et al., 2016).

To date, the occurrence, composition and spatiotemporal variation of atmospheric PAEs in indoor and outdoor environments were well studied, and the human exposure to PAEs was also estimated. However, current studies mainly focused on atmospheric PAEs in urban area with strong anthropogenic activities such as downtown (Quintana-Belmares et al., 2018), suburb (Ma et al., 2014) and industrial zone (Růžičková et al., 2016); few studies concerned about PAEs in ambient air around natural environments (Teil et al., 2016; Li et al., 2019). As an important component of the Earth's Critical Zone, lake plays a vital role in the sustainable development of socioeconomy due to its highly interaction of resource, environment, ecology and irreplaceable ecosystem service function (Costanza et al., 1997; Richter and Mobley, 2009; Tolonen et al., 2014; Kankaala et al., 2018). As a part of lake ecosystem, ambient air participates in the water-gas exchange of various contaminants (Poissant et al., 2000; Wilkinson et al., 2005; Meng et al., 2008), and atmospheric deposition is an important source of contaminants (Franz et al., 1998; Qin et al., 2013). However, as far as we know, there were no studies on PAEs in the ambient air around large natural lake. Whether there are differences in the composition characteristics of PAEs in the atmosphere and other environmental media in the lake ecosystem is still unknown.

Lake Chaohu (117°17′–117°51′ E, 31°25′–31°43′ N) is located in the central of Anhui Province (Fig. 1), which is the fifth largest natural shallow freshwater lake in China (He et al., 2019). It is crucial for the development of its catchment due to its ecosystem service functions such as water resource supply, climate regulation and biodiversity maintenance (Zhang et al., 2016; Wu et al., 2018; Yin et al., 2018). However, the rapid socioeconomic development in Lake Chaohu catchment in recent decades has led to serious PAE contaminations (Kang et al., 2016), and the ecosystem health of Lake Chaohu had been threatened (He et al., 2016a). Therefore, the issue of PAE contaminations in Lake Chaohu was recently concerned, and the occurrences of PAEs in the surface water (He et al., 2013), suspended particulate matter (SPM) (He et al., 2019), sediment (Kang et al., 2016) and pore water (He et al., 2016b) of Lake Chaohu were investigated. However, atmospheric PAEs in Lake Chaohu are still unknown. Hence, the objectives of this study are: (1) to investigate the monthly occurrence, composition and source of PAEs in atmospheric particles around Lake Chaohu, (2) to compare the differences of atmospheric PAEs in the lakeshore and downtown area, (3) to analyze the influencing factors of atmospheric PAEs around Lake Chaohu, and (4) to reveal the composition characteristics of PAEs in different environmental media of Lake Chaohu. This study is expected to give new insights into atmospheric PAEs in large shallow natural lake and the overall fate of PAEs in lake ecosystem.

2. Materials and methods

2.1. Reagents and materials

High-performance liquid chromatography (HPLC) grade dichloromethane (DCM), n-hexane (HEX) and pesticide grade acetone (ACE) were all purchased from Thermo Fisher Scientific, Waltham, Massachusetts, USA for the extraction, separation and dilution of PAEs. Anhydrous sodium sulfate, silica and alumina (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used for the clean-up of PAEs. The pretreatment of solid reagents and glassware were all the same with our previous study (He et al., 2019).

Standard mixture of PAEs, including DMP, DEP, DIBP, DBP, bis(4-methyl-2-pentyl) phthalate (BMPP), diamyl phthalate (DAP), BBP, hexyl-2-ethylhexyl phthalate (HEHP), di(2-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), DEHP, DnOP, dinonyl phthalate (DNP), were concerned in this study. 3,4,5,6-deuterated DBP was selected as surrogate standard (SS), while 3,4,5,6-deuterated DEP and 3,4,5,6-deuterated DnOP were selected as internal standards (IS). PAE standard mixture, SS and IS were all purchased from AccuStandard Inc., New Haven, Connecticut, USA, and diluted to a working standard solution by HEX and ACE.

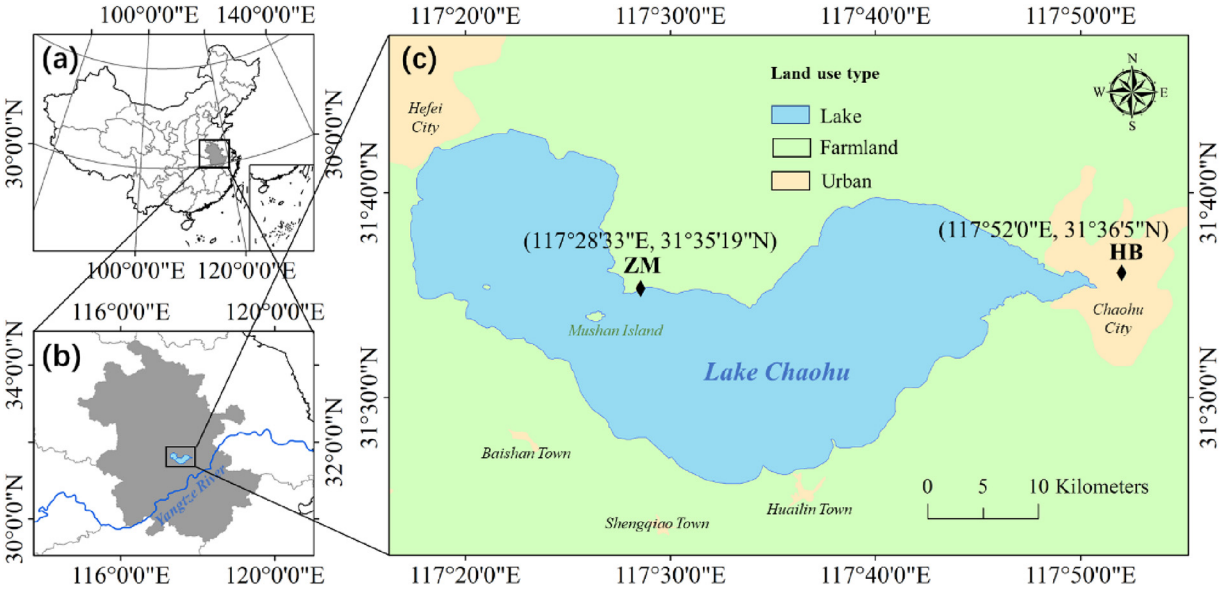


Fig. 1. Locations of (a) Anhui Province, (b) Lake Chaohu and (c) the air sampling sites in Lake Chaohu. ZM: lakeshore site. HB: downtown site.

2.2. Sampling collection

Atmospheric particles (PM_{10}) around Lake Chaohu were collected by using an active sampler (PM10-PUF-300, Guangzhou, China) from June 2011 to May 2012 once a month for 48 h (See Table S1 for more details). The sampling sites were shown in Fig. 1. Two sampling sites, ZM and HB, were set to compare the difference of atmospheric particulate PAEs on the lakeshore and in the downtown of a lakeside city, respectively. Site ZM (117°28′33″ E, 31°35′19″ N) was located in the roof of a fisherman's house, and site HB (117°52′0″ E, 31°36′5″ N) was located in the Chaohu Environmental Protection Agency in the downtown of Chaohu City. Sites ZM and HB were approximately 40 km apart.

Atmospheric particulate PAEs were collected by filtering gas through a glass fiber filter (GFF, 200 mm × 150 mm). The GFF was baked at 450 °C for 6 h and packed by aluminum foil before use. The sampling time and volume were provided in Table S1. After collection, the GFF was folded, packed in aluminum foil, taken back to the laboratory, stored in a desiccator and analyzed within seven days.

2.3. Sample analysis

In the laboratory, 200 ng of SS was added to the GFF before Soxhlet extraction. DCM was employed to extract PAEs and an anhydrous sodium sulfate-silica-alumina (1 cm, 12 cm and 6 cm from top to bottom respectively) chromatography column was used for clean-up. The procedures of extraction and clean-up of atmospheric particulate PAEs were the same with our previous method for particulate PAEs in water (He et al., 2019). Before analysis, 200 ng of IS were added.

PAEs were analyzed using an Agilent 6890 gas chromatography (GC) coupled with a 5973 mass spectrometer detector (MSD) (Agilent Technologies Inc., California, USA). A DB-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm, J&W Scientific, USA) was employed. The analysis and quantitation methods were all the same with our previous study (He et al., 2019).

2.4. Quality control and quality assurance (QC/QA)

During each sampling procedure, field blank samples were set to deduct the background contamination during sampling, transport, storage of air samples and analysis procedure. Field blank GFFs were treated all the same as the real samples except for collecting air samples. Only DIBP, DBP and DEHP were detected in field blank samples, their concentrations were at least one magnitude lower than real samples. For GC/MSD analysis, the internal calibration method was used for quantitation (see Table S2 for more details). The R-square values of the linear calibration curves of each compound were all larger than 0.99. The SS was added to each GFF sample for monitoring the pretreatment and analysis processes. The recovery of SS ranged from 85% to 90%. The method recoveries and the instrument detection limits (IDLs) of each PAE congener were listed in Table S2.

2.5. Air mass source analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was employed to trace the source and the transport pathway of the air mass during sampling duration (Stein et al., 2015). Archived NCEP/NCAR (National Centers for Environmental Prediction/National Centers for Atmospheric Research) Global Reanalysis Data (1948-present, 2.5° × 2.5°, freely available at ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis) was used as meteorological data in the HYSPLIT model. The model was run by TrajStat 1.4.7 plugin in MeteoInfo 1.7.5 (freely available at http://meteothink.org/downloads/index.html) (Wang et al., 2009; Wang, 2014). In this study, 72-h backward trajectories of air mass in sampling locations were started to calculate once per hour during sampling duration, and 48 trajectories for each atmospheric sample were therefore obtained. The start height was set as 10 m above ground level (AGL) and the top of model was set as 1000 m AGL. The 48 trajectories for each atmospheric sample were clustered by using Euclidean distance method.

2.6. Statistical analysis

All statistical analyses were performed using R 3.5.1 (R Core Team, 2018). Data distribution was described by the skewness and kurtosis using R package "moments" (Komsta and Novomestky, 2015). The data distribution was tested by Shapiro-Wilk test at the significant level of $p = 0.05$ with a null hypothesis of normal distribution. The results of the skewness, kurtosis and p-value were shown in Tables S3 and S4. According to Tables S3 and S4, log-normal distribution was better to describe most of the PAE congeners. Therefore, the occurrences of atmospheric PAEs around Lake Chaohu were described by geometric mean, median and range. Two nonparametric methods, Wilcoxon test and Kruskal-Wallis test, were employed to compare the differences of

atmospheric PAEs and PAE profiles in multiple environmental media, respectively. The significant levels of these nonparametric tests were also set at $p = 0.05$ with null hypotheses of no true location shift.

3. Results and discussion

3.1. Occurrence of atmospheric PAEs

The concentrations of PAEs in atmospheric particles around Lake Chaohu were shown in Table 1. DMP, DEP, DIBP, DBP, BBP, DEHP, DnOP and DNP were detected in ZM and HB in all months. The concentrations of the Σ_{13}PAEs ranged from 2740 to 11,890 pg·m^{-3} and 2622 to 15,331 pg·m^{-3} with median values of 4125 pg·m^{-3} and 5059 pg·m^{-3} in ZM and HB, respectively. DEHP was the predominant congener in both ZM and HB ranging from 1957 to 11,339 pg·m^{-3} and 1229 to 14,418 pg·m^{-3} with median values of 2683 pg·m^{-3} and 4196 pg·m^{-3}, which was followed by DIBP and DBP. The occurrence of atmospheric DEHP was approximately an order of magnitude higher than DIBP and DBP, two orders of magnitude higher than DMP and BBP, and over three orders of magnitude higher than other PAEs. The six priority pollutants (Σ_6PAEs) proposed by United States Environmental Protection Agency (USEPA), DMP, DEP, DBP, BBP, DEHP and DnOP (Keith and Telliard, 1979), accounted for 86.9% ± 6.4% (mean ± standard deviation, S.D.) of the Σ_{13}PAEs. The concentrations of the Σ_6PAEs ranged from 2345 to 11,532 pg·m^{-3} and 2005 to 14,752 pg·m^{-3} with median values of 3571 pg·m^{-3} and 4649 pg·m^{-3} in ZM and HB, respectively. Among the other seven nonpriority pollutants, DIBP had a similar residue level with DBP in both ZM and HB, ranging from 356 to 993 pg·m^{-3} and 348 to 1462 pg·m^{-3} with median values of 617 pg·m^{-3} and 508 pg·m^{-3}, respectively.

In addition to this study, some previous studies about PAEs in atmospheric particles were summarized in Table 2. Comparing with other studies, the concentrations of PAEs in atmospheric particles were at a significantly low level. In field area, the average concentrations of atmospheric particle-bound PAE congeners in the lakeshore of Lake Chaohu (ZM site) were 2.8-fold to 258-fold lower than the average concentrations of the corresponding $PM_{2.5}$-bound PAE congeners in Mount Tai (Li et al., 2019). In city area, the concentrations of atmospheric PAEs in the downtown of Chaohu City (HB site) were lower than those in metropolitan cities such as Shanghai (Ma et al., 2014), Nanjing (Wang et al., 2008), Tianjin (Kong et al., 2013; Zhu et al., 2016) and Paris (Teil et al., 2006), as well as some small cities such as Tarragona (Aragón et al., 2012), A Coruña (Salgueiro-González et al., 2013) and Thessaloniki (Salapasidou et al., 2011). However, the concentrations of atmospheric PAEs in Chaohu City were at a similar level with those in Mexico City (Quintana-Belmares et al., 2018).

According to Table 2, the occurrence of particulate-phase PAEs in the atmosphere posed an obvious site-specific pattern. Indoor air, especially the traffic micro-environments (Chi et al., 2017) and new decorated rooms (Pei et al., 2013), had the highest PAE residue level, which was followed by outdoor air in urban area. Ambient air in the field had the lowest PAE residue level. This pattern was in accord with the spatial variations of atmospheric PAEs in France that PAE occurrences decreased from urban area to forest (Teil et al., 2016). In addition, Chen et al. (2018) also found $PM_{2.5}$-bound PAEs in indoor air were higher than outdoor air. It indicated that anthropogenic activities were important sources of PAEs and greatly influenced their atmospheric concentrations. Comparing with indoor air, the occurrence of PAEs in outdoor air decreased by orders of magnitude (Table 2). It is associated with the air dilution and diffusion effects (Li et al., 2018) and the photochemical reactions (Bao et al., 2011; Barreca et al., 2014; Lei et al., 2018a, 2018b, 2018c). Chaohu City is a county-level city with a population of nearly one million people, and farmland was the main land use type around Lake Chaohu (Fig. 1). To this end, the intensity of anthropogenic activities was relatively weak (Kong et al., 2013). Therefore, it was reasonable that the concentrations of PAEs in atmospheric particles around Lake Chaohu were significantly lower than other studies.

3.2. Spatiotemporal variations of atmospheric PAEs

Spatiotemporal variations of atmospheric Σ_6PAEs and Σ_{13}PAEs around Lake Chaohu were shown in Fig. 2. In the downtown area (HB site), the concentrations of Σ_{13}PAEs and Σ_6PAEs fluctuated around 4586 pg·m^{-3} and 4009 pg·m^{-3} respectively, in all months except July and August. Σ_{13}PAEs and Σ_6PAEs were both found to have the highest values in August and the lowest values in December. The temporal variation in the lakeshore area (ZM site) was similar to the downtown area. Σ_{13}PAEs and Σ_6PAEs were both found to have the highest values in August, but the lowest values were found in November. In addition, Σ_{13}PAEs and Σ_6PAEs both appeared another peak value in May. Except for May, July and August, the concentrations of the Σ_{13}PAEs and

Table 1
Summary of concentrations (pg·m^{-3}) of PAEs in atmospheric particles at the lakeshore and downtown sites in Lake Chaohu.

PAEs	ZM (lakeshore site)					HB (downtown site)					p-Value[d]
	Minimum	Maximum	Median[a]	Geometric mean[b]	N[c]	Minimum	Maximum	Median	Geometric mean	N	
DMP	6.85	88	30.6	23.2	12	2.42	70.4	20.6	18.9	12	0.569
DEP	1.22	16.5	3.46	3.44	12	1.08	7.41	3.18	3.12	12	0.519
DIBP	356	993	617	592	12	348	1462	508	518	12	0.129
DBP	178	1607	499	462	12	127	966	304	323	12	0.012
BMPP	N.D.[e]	7.84	3.15	2.94	7	N.D.	2.77	1.76	1.29	5	0.076
DAP	N.D.	4.77	2.11	2.00	5	N.D.	1.98	1.43	1.18	7	0.554
BBP	0.511	79.8	22.1	12.6	12	1.10	151	20.8	13.5	12	0.850
HEHP	N.D.	5.51	1.17	1.32	8	0.444	2.20	0.724	0.837	12	0.850
DBEP	N.D.	5.94	4.43	4.16	2	N.D.	2.95	2.29	2.25	5	1.000
DCHP	N.D.	3.66	1.55	1.40	7	N.D.	1.17	0.771	0.688	8	0.097
DEHP	1957	11,339	2683	3353	12	1229	14,418	4196	3851	12	0.233
DnOP	3.66	29.4	7.03	8.56	12	3.41	33.4	8.58	9.34	12	0.569
DNP	0.56	18.3	4.36	3.72	12	0.93	17.4	4.18	3.98	12	0.970
Σ_6PAEs[f]	2345	11,532	3571	4071	12	2005	14,752	4649	4505	12	0.380
Σ_{13}PAEs[g]	2740	11,890	4125	4740	12	2622	15,331	5059	5150	12	0.339

[a] Reported medians were calculated by removing N.D.
[b] Reported geometric means were calculated by removing N.D.
[c] N: the number of samples.
[d] p-Value of paired Wilcoxon signed rank test with a null hypothesis of no true location shift.
[e] N.D.: not detected.
[f] Σ_6PAEs: the sum of 6 priority pollutants, including DMP, DEP, DBP, BBP, DEHP and DnOP.
[g] Σ_{13}PAEs: the sum of 13 PAE congeners we concerned.

Table 2
Global comparison for particulate-phase PAEs in atmosphere (unit: $ng \cdot m^{-3}$).

Media	Size	Zone	Location	N	PAEs [mean (minimum - maximum)]								References
					DMP	DEP	DIBP	DBP	BBP	DEHP	DnOP	Others	
Field	PM_{10}	Lakeshore	Lake Chaohu, China	12	0.032 (0.007–0.088)	0.004 (0.001–0.016)	0.621 (0.356–0.992)	0.558 (0.178–1.607)	0.027 (0.0005–0.080)	4.003 (1.957–11.339)	0.011 (0.004–0.029)	0.012 (0.002–0.039)	This study
	$PM_{2.5}$	Mountain	Mount Tai, China	49	0.19	1.03	2.03	1.57	0.09	12.5	0.45	1.62	Li et al., 2019
City	$PM_{2.5}$	Suburb	Shanghai, China	39	0.32(ND-2.68)	0.19(ND-0.81)	12.6(0.55–42.7)	6.72(0.52–24.9)	0.47(ND-14.1)	39.5(5.63–154)	NS	NS	Ma et al., 2014
	PM_{10}	Suburb	Shanghai, China	38	0.26(ND-2.42)	0.14(ND-0.85)	15.9 (0.74–53.22)	7.91(1.16–27.7)	0.51(ND-14.2)	107(5.00–441)	NS	NS	Ma et al., 2014
	TSP	Suburb	Nanjing, China	10	0.3(0.01–0.5)	0.2(0.03–0.4)	NA	3.1(0.7–7.8)	0.2(0.02–0.7)	1.2(0.1–2.9)	0.2(0.01–0.7)	NA	Wang et al., 2008
	PM_{10}	Suburb	Tarragona, Spain	10	0.42(ND-1.17)	2.53(ND-7.85)	114.90 (28.09–529.54)	NA	0.032(ND-0.21)	5.36 (<MQL-21.78)	1.00(0.05–0.20)	NS	Aragón et al., 2012
	$PM_{2.5}$	Suburban, urban and industrial area	A Coruña, Spain	10	0.169 (<MQL-0.404)	1.024(ND-3.336)	NS	13.75 (0.258–54.68)	NS	0.727 (0.375–1.259)	NS	NS	Salgueiro-González et al., 2013
	PM_{10}	Downtown	Chaohu, China	12	0.028 (0.002–0.070)	0.004 (0.001–0.007)	0.563 (0.348–1.462)	0.388 (0.127–0.966)	0.036 (0.001–0.151)	4.689 (1.229–14.418)	0.012 (0.003–0.033)	0.010 (0.002–0.025)	This study
	$PM_{2.5}$	Downtown	Tianjin, China	15	0.54(ND-4.96)	0.30(ND-3.19)	NS	8.72(ND-46.97)	0.08(ND-0.51)	75.68 (ND-349.89)	0.33(ND-1.50)	NS	Kong et al., 2013
	PM_{10}	Downtown	Tianjin, China	35	0.88(ND-7.90)	0.73(ND-12.79)	NS	12.90(ND-110.31)	0.15(ND-0.96)	98.29 (ND-730.12)	0.83(ND-12.20)	NS	Kong et al., 2013
	TSP	Downtown	Nanjing, China	10	1.1(0.7–3.3)	0.4(0.1–0.9)	NA	10.0(4.1–17.9)	0.6(0.15–1.7)	4.6(1.1–11.4)	0.3(0.05–0.5)	NA	Wang et al., 2008
	$PM_{2.5}$	Downtown	Tianjin, China	16	0.14(0.03–0.90)	0.07(0.02–0.20)	NS	1.93(0.51–7.64)	0.02 (0.001–0.37)	6.26 (0.26–52.50)	0.05 (0.001–0.60)	NS	Zhu et al., 2016
	PM_{10}	Downtown	Tianjin, China	16	0.18(0.04–1.32)	0.08(0.02–0.27)	NS	2.24(0.57–6.38)	0.02 (0.001–0.66)	10.79 (0.79–21.62)	0.10 (0.003–1.17)	NS	Zhu et al., 2016
	PM_{10}	Downtown	Thessaloniki, Greece	20	ND	ND	NS	1.55(0.43–3.36)	0.50(0.04–0.98)	12.08(ND-45)	ND(ND-0.11)	NS	Salapasidou et al., 2011
	Particle	Downtown	Paris, France	18	0.1(0.0–0.3)	0.4(0.1–0.9)	NS	1.9(0.6–4.6)	0.3(0.1–0.5)	5.4(2.4–10.4)	0.1(0–0.6)	NS	Teil et al., 2006
	PM_{10}	Downtown	Mexico City, Mexico	7	NS	ND	0.028(ND-0.196)	0.094(ND-0.288)	ND	2.321 (0.861–4.934)	NS	0.055 (0.018–0.121)	Quintana-Belmares et al., 2018
	$PM_{2.5}$	Downtown	Mexico City, Mexico	7	NS	ND	ND	0.129(ND-0.401)	0.009(ND-0.062)	1.067 (0.229–2.904)	NS	0.026 (ND-0.067)	Quintana-Belmares et al., 2018
Indoor	Particle	Bus		105	2286.4 (53.265–5155.7)	1009.2 (136.73–1599.1)	6319.8 (637.4–18,546)	1942.1 (630.98–4426.3)	1645.4 (784.52–3434.8)	2056.8 (1054.0–17,173)	1209.5 (769.51–1957.1)	8810.8	Chi et al., 2017
	Particle	Subway		40	1362.7 (69.609–2872.7)	775.29 (80.441–1190.0)	3109.6 (1070.6–6302.2)	1528.4 (582.32–3455.8)	1313.8 (718.80–2209.5)	3118.3 (1382.8–9317.7)	1008.8 (769.51–1207.1)	7818.11	Chi et al., 2017
	Particle	Taxi		30	1714.6 (373.56–2850.4)	1461.8 (101.11–2871.7)	3201.3 (1135.7–5435.8)	1127.9 (499.29–1964.3)	2237.2 (970.73–3708.7)	3223.3 (1373.0–18,101)	1071.0 (764.14–1252.7)	8040.9	Chi et al., 2017
	Particle	Private car		60	3648.8 (61.433–12,756)	1631.0 (101.69–10,602)	10,771 (606.36–21,983)	2274.8 (160.32–8202.5)	1906.8 (670.85–2856.9)	3709.7 (1026.8–28,025)	1236.2 (764.16–2650.9)	9776.7	Chi et al., 2017
	Particle	Residential and office buildings	Xi'an, China	28	0.10(ND-1.75)	NA	1.62(ND-7.97)	1.06(ND-4.92)	NA	1.04(0.09–4.16)	NA	NA	Wang et al., 2014b
	Particle	New decorated bedroom	Hangzhou, China	10	226.3(ND-695.2)	547.8 (140.3–857)	NS	1075(484–1737.8)	1674 (678–2248.3)	717(559–8954)	ND	NS	Pei et al., 2013
	Particle	New decorated living room	Hangzhou, China	10	800 (278.2–1321.8)	619(211–846.4)	NS	1174(541–2007.2)	2039(ND-3497)	1682 (275–3469.6)	ND	NS	Pei et al., 2013
	Particle	New decorated study room	Hangzhou, China	10	146(ND-564.4)	216.7(ND-423)	NS	950(ND-1250)	2008(468–2359)	1565 (599–3926.9)	ND	NS	Pei et al., 2013
	PM_{10}	Residential dwellings	Tianjin, China	13	9.022 (0.254–47.464)	1.549 (0.083–7.400)	NS	318.366 (7.325–1466.197)	0.633 (0.010–8.033)	92.299 (2.623–304.902)	0.206(ND-2.597)	NS	Zhang et al., 2014
	$PM_{2.5}$	Residential dwellings	Tianjin, China	13	2.993 (0.188–25.304)	0.750 (0.065–4.512)	NS	130.675 (5.774–1132.126)	0.318 (0.010–4.786)	44.363 (0.867–179.756)	0.099(ND-0.784)	NS	Zhang et al., 2014
	Particle	Indoor places	Vietnam	97	1.02(ND-20.4)	9.95(ND-181)	52.2(ND-340)	41.4(1.22–280)	1.74(ND-7.73)	129(ND-576)	7.11(ND-78.4)	21.89	Tran et al., 2017
	Particle	Indoor places	Albany, New York, USA	60	0.35(ND-2.40)	67.8(0.34–466)	53.6(1.29–579)	42.8(0.85–451)	3.31(0.11–59.8)	27.0(2.04–90.3)	<MQL(ND-0.67)	NA	Tran and Kannan, 2015
	Particle	Dwelling	Paris, France	30	<0.1	1.0(<1.0–3.7)	30.2(<5–115)	17.0(2.9–57.8)	2.4(1.1–14.6)	41.5(21.7–158)	NS	NA	Blanchard et al., 2014

Abbreviations: PM: particulate matter, TSP: total suspended particle, <MQL: lower than method quantitation limit, ND: not detected, NA: not available, NS: not studied, N: sample size.

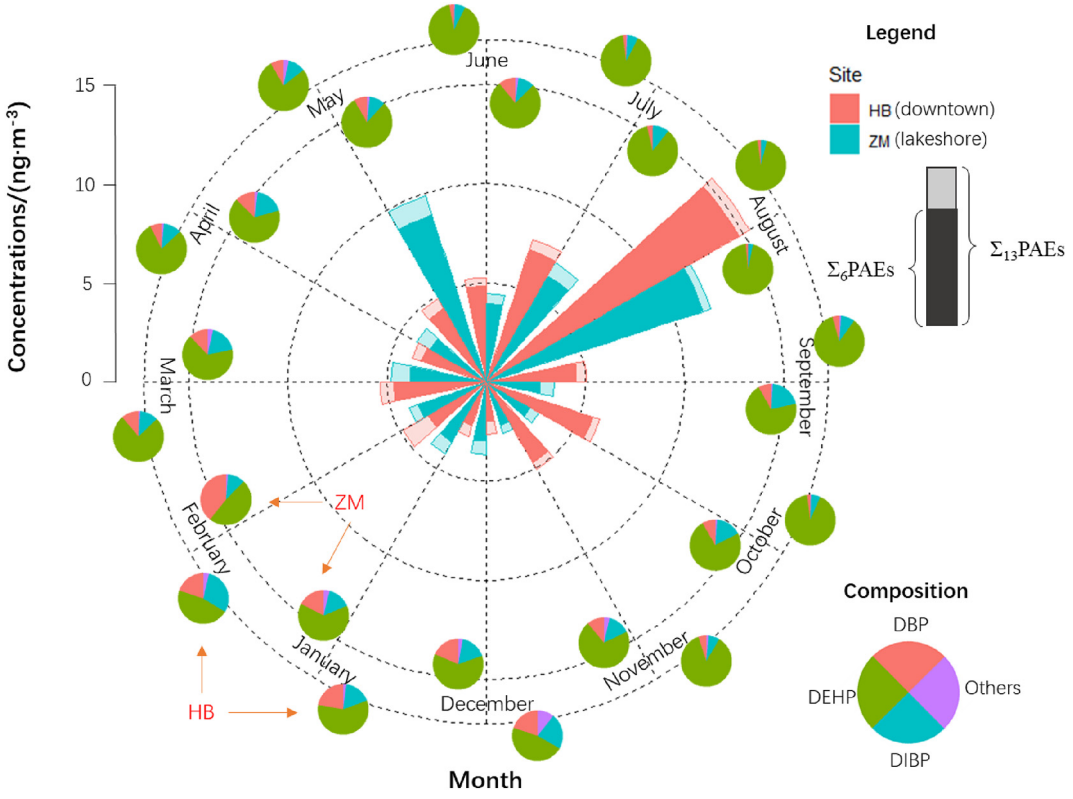


Fig. 2. Spatiotemporal variations and compositions of atmospheric particulate-phase PAEs in the lakeshore and downtown areas around Lake Chaohu.

Σ_6PAEs fluctuated around 3834 pg·m^{-3} and 3222 pg·m^{-3} in the other months, respectively.

The concentrations of Σ_{13}PAEs and Σ_6PAEs in the downtown area were both over 30% higher than those in the lakeshore area during August to November, and over 30% lower in January, May and December (Fig. 2). To determine whether there were annually significant differences of atmospheric PAEs between ZM and HB, the paired Wilcoxon signed rank test was employed. The results were listed in Table 1. According to Table 1, only DBP was found to have significantly spatial difference between ZM and HB ($p < 0.05$), and other PAE congeners showed no spatial differences between ZM and HB. Our results differed from the results in France (Teil et al., 2016), southern India (Sampath et al., 2017) and Nanjing, China (Wang et al., 2008) that the concentrations of atmospheric PAEs decreased from strong anthropogenic area to weak anthropogenic area. It was probably due to the weak anthropogenic activities in Lake Chaohu catchment and relatively less emission intensity of PAEs by considering farmland-dominated land use type and the small scale of Chaohu City. The observed monthly differences might reflect the random fluctuations in the process of sample analysis and indecipherable effects of local micro-environment during sampling durations.

Long-range transport was considered as the main source of PAEs in natural environment with less anthropogenic activities since their production, consumption and emission were highly related to anthropogenic activities (Xie et al., 2007; Net et al., 2015; Li et al., 2019). Therefore, HYSPLIT model was employed to trace the source and transport path of the air mass reaching Lake Chaohu. The calculated backward trajectories were shown in Fig. 3. According to Fig. 3, the source of air mass varied greatly in different months. Atmospheric PAEs around Lake Chaohu mainly came from the provinces in northern China (e.g., in January, February and September), Guangdong Province in southern China (in August), the ocean areas (e.g., in June and July) and the local areas (e.g., in December). Notably, Guangdong Province was the intensive area of manufacturing industries and e-waste dismantling industries in China (Chen et al., 2009). The large amount of PAE consumption and emission during producing and disposing processes led to Guangdong Province been revealed to have the highest PAE residue level in soils and wastewater treatment plants (Niu et al., 2014; Zhu et al., 2019). Therefore, Guangdong Province was a potential source of atmospheric PAEs, and the highest atmospheric PAE concentrations around Lake Chaohu in August was likely related to the long-range transport from this area (Figs. 2 and 3). However, no obvious correlation was found between PAE occurrences and the source (Niu et al., 2014; Zhu et al., 2019) and transport path of the air mass in the other months (Fig. 3). A national investigation revealed that PAE occurrences were at a low residue level in agricultural soils in northern and eastern China (Niu et al., 2014), which reflected a lower regional PAE emissions in these area to some extent. Therefore, it was not surprising to observe the relatively low and stable atmospheric PAE concentrations around Lake Chaohu in all months except August.

3.3. Composition of atmospheric PAEs

3.3.1. Overall characteristics

The monthly compositions of atmospheric PAEs in ZM and HB were presented in Fig. 2. It was obvious that DEHP was the most predominated species in atmospheric particles around Lake Chaohu, which was followed by DIBP and DBP. The fraction of DEHP ranged from 48.5% to 95.4% (71.7% ± 11.6%, mean ± S.D.) and 46.3% to 94.0% (76.8% ± 16.3%) in ZM and HB, respectively. DIBP and DBP had similar fractions ranging from 3.0% to 20.5% (13.7% ± 4.7%) and 3.7% to 30.2% (11.9% ± 7.5%), and from 1.5% to 39.3% (12.7% ± 9.3%) and 2.0% to 22.3% (9.0% ± 7.3%), respectively in ZM and HB. DEHP, DIBP and DBP contributed a total fraction of atmospheric PAEs ranging from 96.2% to 99.9% (98.1% ± 1.2%) and 89.3% to 99.9% (97.8% ± 2.7%) in ZM and HB, respectively.

To reveal the possible driving mechanism of the PAE profile pattern in this study, the PAE profiles from different references were collected and compared in Fig. 4. Mean values of each PAE congener listed in Table 2 were taken for calculating the percentage. Although the

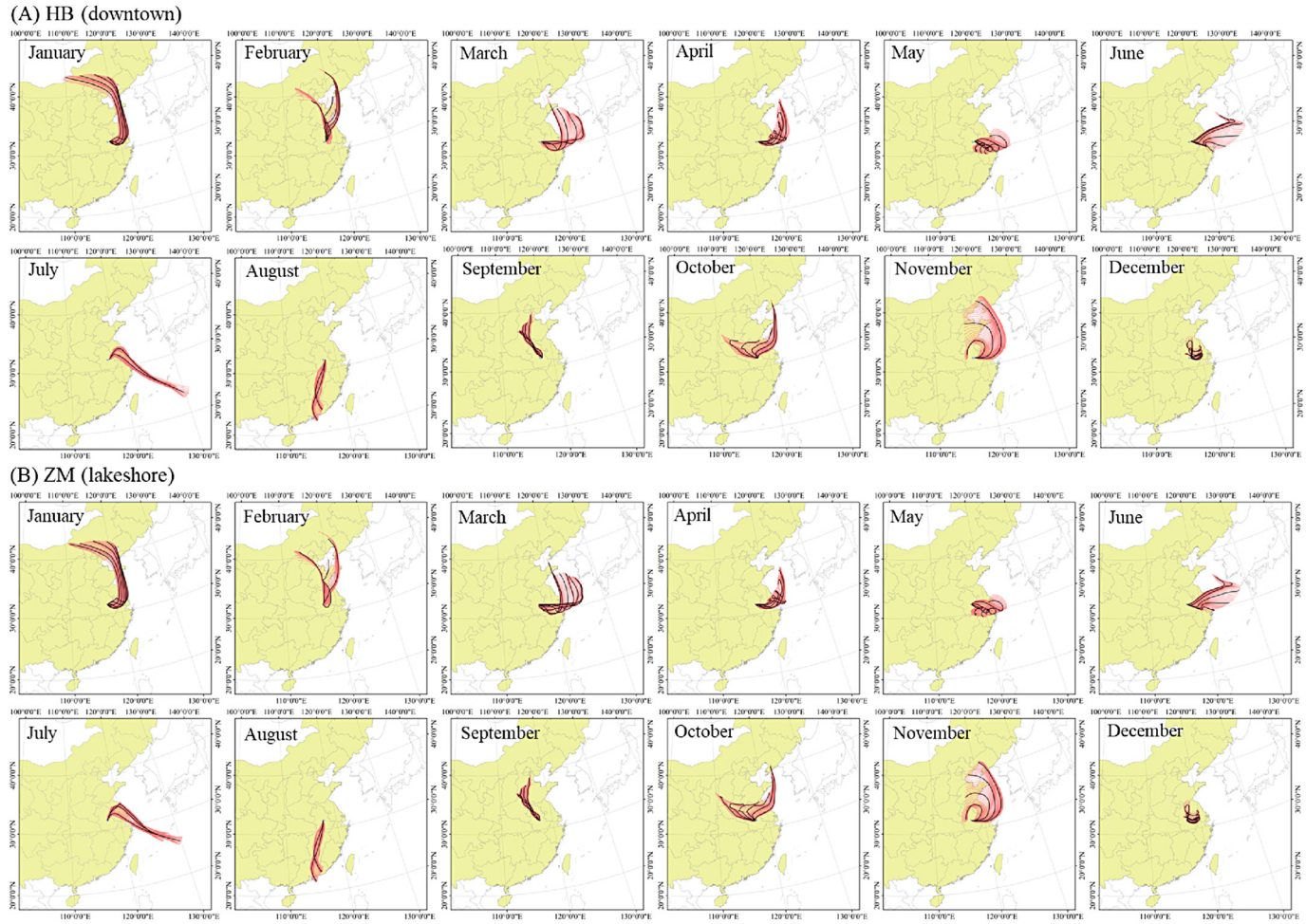


Fig. 3. Calculated air mass backward trajectories arriving at Lake Chaohu during June 2011 to May 2012. Red trajectories: 72-hour backward trajectories during sampling time (output per hour, 48 trajectories in total). Black trajectories: clustered backward trajectories by Euclidean distance. Meteorological data: NECP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) Global Reanalysis (1948-present). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conditions, sampling sites, sampling durations, particle size were different (Table 2), they provided a site-specific profile pattern. PAE profiles in atmospheric particles between indoor and outdoor environments existed significant differences. The fractions of low molecular weight (LMW) PAEs such as DMP, DEP, DIBP and DBP were higher in indoor air than outdoor air.

For outdoor environments, it was apparent that DEHP had the highest fraction in most studies, which was followed by DIBP and DBP (Fig. 4). However, the fractions of DMP, DEP, BBP, DnOP and other PAEs were extremely low, ranging from 0.7% to 17.4% with a median value of 2.8%. Unlike indoor environment, outdoor environment was more open, so the profiles of PAEs in atmospheric particles will be affected by various factors such as photochemical reactions (Wang et al., 2016) and gas-solid partitioning (Staples et al., 1997; Pei et al., 2013). For LMW PAEs such as DMP and DEP, they tended to distribute in gas phase because of their high volatility (Staples et al., 1997; Pei et al., 2013). For high molecular weight (HMW) PAEs containing longer alkyl chains, it was reported that their atmospheric photooxidation half-lives were shorter than LMW PAEs (Staples et al., 1997). In addition to the short photooxidation half-lives, the low volatility of HMW PAEs was also an unignorable factor for their profile pattern in atmospheric particles (Net et al., 2015). However, their consumption amounts might exert a significant influence on PAE profiles in outdoor environment (Kong et al., 2013). Opposite to other HMW PAEs, DEHP was found to have high fractions in outdoor atmospheric particles worldwide. It was due to its high amounts of production, consumption and emission (CPCIA, 2009; Wang et al., 2014a; Sampath et al., 2017; Kashyap and Agarwal, 2018), although it was hard to volatilize (Net et al., 2015) and its experimental atmospheric half-life was just about 1 day (Behnke et al., 1987).

Comparing with indoor and city environments, PAEs had the most similar profiles in the field (Fig. 4). It might be justified by the intensity of anthropogenic activities and the deviation degree from steady state. Indoor environment was strongly influenced by anthropogenic activities and was probably on a non-equilibrium state so that PAE profiles varied a lot and LMW PAEs had relatively higher fractions. Outdoor environment was more open than indoor environment, so the influence of anthropogenic activities was weaker. Besides, outdoor environment was close to the steady state of photochemical reactions and partitioning equilibriums. Therefore, PAE profiles in outdoor environment were more similar, especially in the field.

3.3.2. Spatiotemporal characteristics

Due to DEHP, DBP and DIBP were found to be the main components of PAEs in atmospheric particles around Lake Chaohu, the spatiotemporal fractions of the remaining PAE congeners were not discussed in this study.

Spatially, the profiles of PAEs in ZM and HB were similar, and the monthly variations of PAE profiles were also accordant. It might be justified by the short distance (40 km apart) of the two sites and the similar contamination conditions due to the weak anthropogenic effects in Lake Chaohu catchment. Temporally, DIBP and DBP had the highest fractions

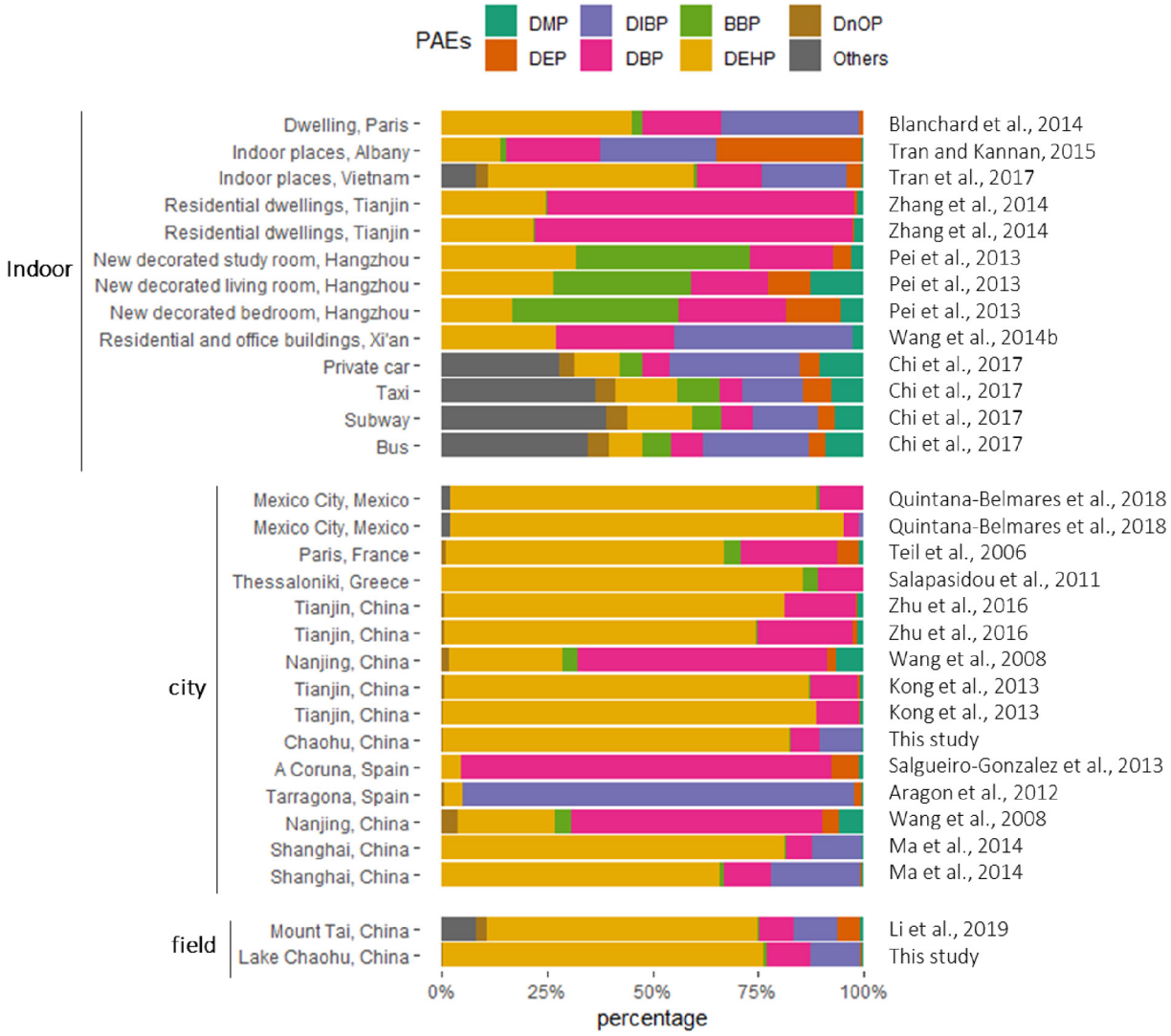


Fig. 4. Global comparison of PAE profiles in atmospheric particles. Mean values of each PAE congeners listed in Table 2 were taken for calculating the percentage.

in winter (December 2011 to February 2012) and the lowest fractions in summer (June to August 2012) (Fig. 2). Previous studies revealed that the presence of PAEs in the atmosphere was associated with air temperature (Teil et al., 2006; Wang et al., 2008). Therefore, air temperature was involved in the temporal variations of PAE profiles in this study. Pearson's correlation analysis illustrated that the fractions of DIBP and DBP had significantly negative correlations with ambient air temperature ($p < 0.0001$), and the results of linear regression showed that the DBP and DIBP fractions significantly decreased with the rise of air temperature (Fig. 5A). This temperature-associated phenomenon might be justified by the condensation of DIBP and DBP from gas phase to particulate phase at low temperature. Regrettably, gas-phase PAEs in the atmosphere around Lake Chaohu were not studied. However, it was reported that LMW PAEs like DMP and DBP tended to distribute in gas phase while HMW PAEs such as DEHP tended to exist in particulate phase (Pei et al., 2013). Moreover, Teil et al. (2006) found that the concentrations of PAEs in gas phase decreased with the reduction of air temperature. We noted that the octanol-air partition coefficients ($LogK_{OA}$) of DIBP, DBP and DEHP were 8.54, 8.54 and 10.53, respectively (Net et al., 2015). It revealed that DIBP and DBP were more volatile than DEHP. Hence, the fraction ratios of DIBP to DEHP and DBP to DEHP in atmospheric particles should decrease with the elevation of air temperature. According to Fig. 5B, these two fraction ratios both presented significantly negative correlation with the air temperature ($p < 0001$), which partly demonstrated our hypothesis of the PAE condensation phenomenon at low temperature.

3.4. The profiles of PAEs in different environmental media of Lake Chaohu

The fractions of DMP, DEP, DIBP, DBP, BBP, DEHP, DnOP and other PAE congeners (see Table S5 for details) in each atmospheric particle, pore water (He et al., 2016b), sediment (Kang et al., 2016), water and SPM (He et al., 2019) samples collect in Lake Chaohu were employed to give a holistic pattern of PAE profiles in natural lake. The sample sizes were 24, 17, 19, 79 and 79 for atmosphere, pore water, sediment, water and SPM, respectively. The fractions of each PAE congeners were presented in Fig. 6A and the profiles of PAEs in different environmental media were shown in Fig. 6B.

According to Fig. 6A, the fractions of different PAE congeners showed different patterns. Kruskal-Wallis test illustrated that the fractions of each PAE congener were significant different among atmospheric particles, water, SPM, pore water and sediment ($p < 10^{-14}$). It revealed the transport pathway for different PAE congeners was disparate. DMP had higher fractions in SPM and sediment, while DEP and DIBP were mainly distributed in water and SPM. Pore water was found to have the highest DBP fractions (87.4% ± 8.2% on average). Therefore, these LMW congeners were transported mainly through water such as surface runoff and river input. For HMW PAEs, DEHP and DnOP, they were both

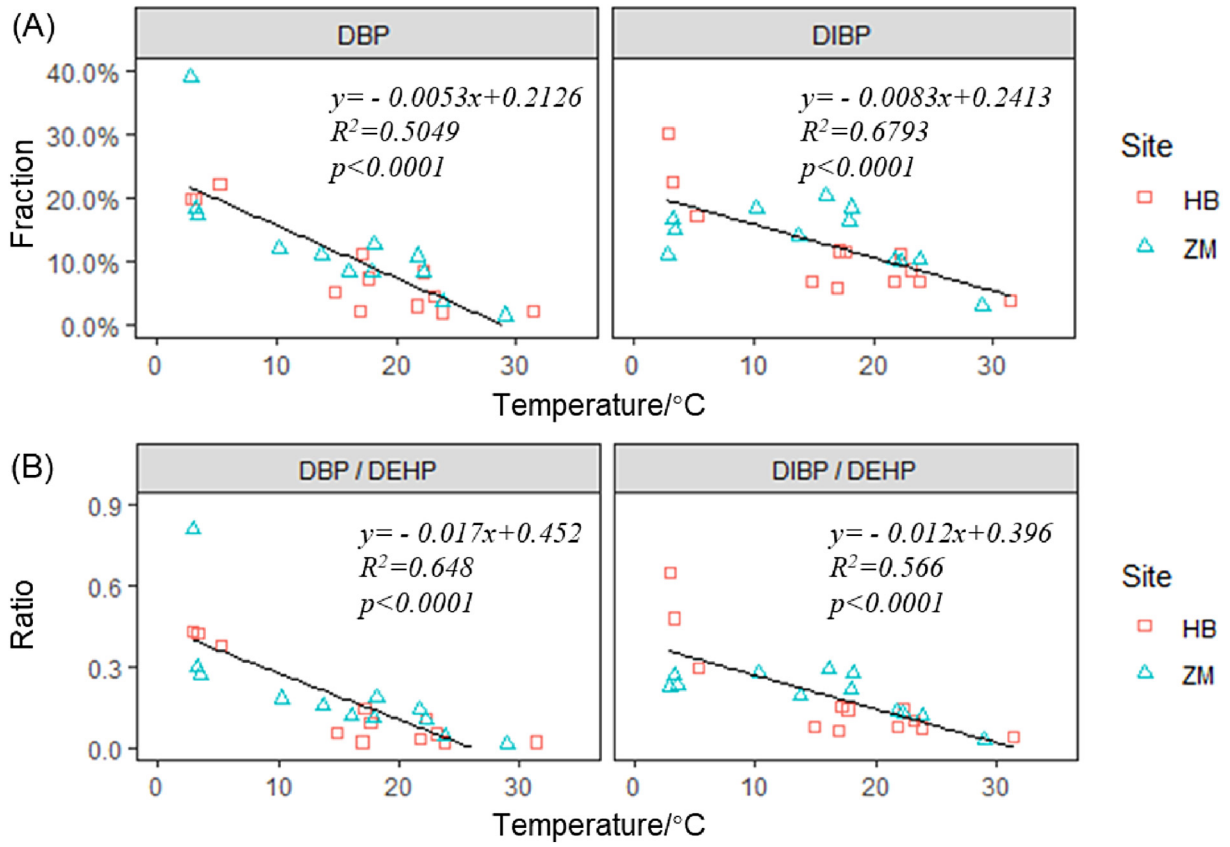


Fig. 5. Relationships for ambient air temperature with (A) the fractions of DBP and DIBP in atmospheric particles, and (B) their fraction ratios to DEHP.

found to have the highest fractions in atmospheric particles. It illustrated that DEHP and DnOP were transported mainly through atmosphere. The distinct phenomena were associated with the physical properties of different PAE congeners. DMP, DEP, DIBP and DBP were relatively hydrophilic with $\log K_{OW}$ (octanol-water partition coefficient) < 4.5 while DEHP and DnOP were relatively hydrophobic with $\log K_{OW}$ > 7.5 (Net et al., 2015). Comparing with LMW PAEs, DEHP and DnOP were easily distributed in particles but were hard to desorption, aqueous migration distance of particles was limited due to the deposition of particles.

The fractions of BBP were extremely low and only several high fraction values were observed in sediment, so its transport pathway was no longer discussed. The highest fractions of other congeners were found in sediment. It was due to the numbers of detected congeners and their relatively high residue level.

According to Fig. 6B, the profiles of PAEs in atmospheric particles were significantly different from other environmental media. Comparing with other media, DEHP was the most abundant congener in atmosphere. Therefore, controlling atmospheric DEHP was an effective and essential strategy to reduce its worldwide spread. Although the patterns of PAE profiles in different media were different, DIBP was found to have similar fractions with DBP in atmosphere, sediment, SPM and water, and its fraction in pore water was just followed after DBP. A toxicological study reported that DIBP had comparable toxic effect to DBP (Borch et al., 2007). Therefore, DIBP should attract more attention not only in aquatic environments (He et al., 2019) but also in atmosphere.

4. Conclusion

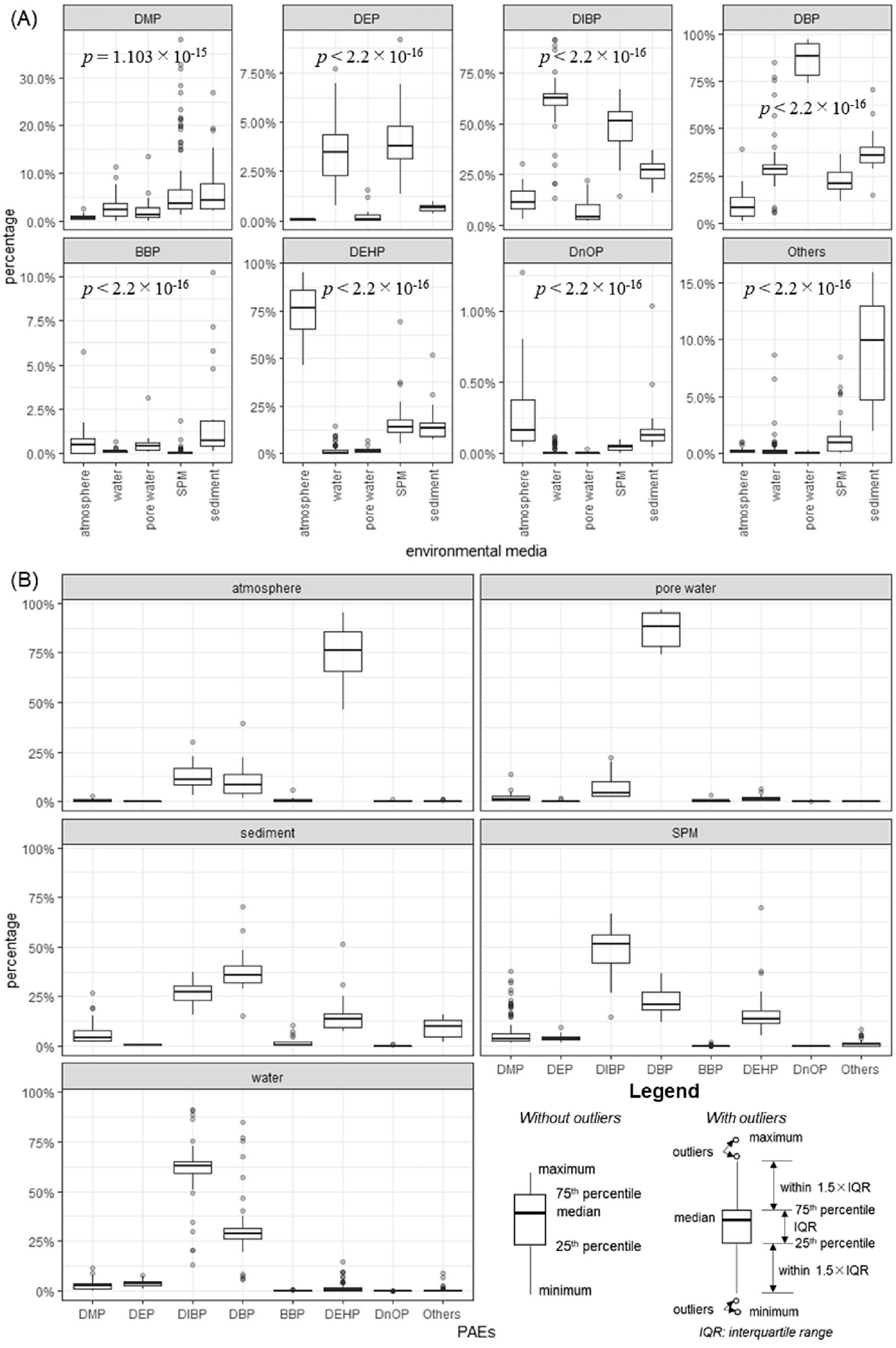
This paper studied the atmospheric PAEs in two sites around a large shallow natural lake (Lake Chaohu, China). The concentrations of the Σ_{13}PAEs ranged from 2740 to 11,890 pg·m^{-3} and 2622 to 15,331 pg·m^{-3} with median values of 4125 pg·m^{-3} and 5059 pg·m^{-3} in ZM (the lakeshore site) and HB (the downtown site), respectively. Comparing with other studies, the concentrations of PAEs in atmospheric particles were at a significantly low level. There were no statistically significant differences of PAEs between ZM and HB. It was probably due to the weak anthropogenic activities in Lake Chaohu catchment and relatively less emission intensity of PAEs. The highest atmospheric PAE concentrations around Lake Chaohu in August were likely related to the long-range transport from Guangdong Province. DEHP, DIBP and DBP were the main PAE congeners with a total fraction of atmospheric PAEs ranging from 96.2% to 99.9% (98.1% ± 1.2%) and 89.3% to 99.9% (97.8% ± 2.7%) in ZM and HB, respectively. Temporally, DIBP and DBP had the highest fractions in winter and the lowest fractions in summer. It might be justified by the condensation of DIBP and DBP from gas phase to particulate phase at low temperature. Multimedia comparison of PAE profiles in Lake Choahu revealed that LMW congeners were transported mainly through water while HMW congeners were transported mainly through atmosphere. Controlling atmospheric DEHP was an effective and essential strategy to reduce its worldwide spread, and DIBP should attract more attention in atmosphere.

Acknowledgements

This study was financially supported by the National Project for Water Pollution Control (2012ZX07103-002) and the National Natural Science Foundation of China (NSFC) (41271462, 41030529). This work is also supported by a grant from the 111 Project (B14001) and by the Undergraduate Student Research Training Program of the Ministry of Education.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.034.


(A)
DMP
DEP
DIBP
DBP
BBP
DEHP
DnOP
Others
$p = 1.103 \times 10^{-15}$
$p < 2.2 \times 10^{-16}$
percentage
atmosphere
water
pore water
SPM
sediment
environmental media
(B)
atmosphere
pore water
sediment
SPM
water
DMP
DEP
DIBP
DBP
BBP
DEHP
DnOP
Others
PAEs
Legend
Without outliers
maximum
75th percentile
median
25th percentile
minimum
With outliers
outliers
maximum
within 1.5×IQR
75th percentile
median
IQR
25th percentile
within 1.5×IQR
outliers
minimum
IQR: interquartile range

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