Space-time characteristics of 16 PM$_{2.5}$-bound phthalates (PAEs) in ambient air from Shanghai: Profiles, sources, meteorological effects, and exposure risks

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Abstract

Generated by chemical combinations between alcohols and phthalic anhydrides, phthalates are a group of synthetic chemicals broadly utilized as plasticizers. They occur
in both particle and gas phases in the air causing threats to human health. In the study in
hands, LC-MS/MS was employed for the analysis of PM$_{2.5}$-PAEs in 128 ambient PM$_{2.5}$
samples from nine locations (urban, sub-urban and coastal) in Shanghai between February
2015 and September 2021. Six PAE congeners, namely di-n-butylphthalate (DBP),
dimethylphthalate (DMP), diisononylphthalate (DINP), di-2-ethylphthalate (DEP),
diisobutyl phthalate (DIBP) and di (2-propylheptyl) phthalate (DPHP), which are grouped
as (∑6PAEs) were the most profuse species (with detection frequency (DF) ranging from
44.5% to 85.9%), with concentrations ranging between 26.85 (DEP) to 1840 ng/m$^3$ (DIBP).
Two congeners (DBP and DIBP) contributed significantly (79.4%) to the overall
concentration of PAEs in the campaign, and exhibited a strong positive correlation
(Spearman: $r = 0.876$, $p < 0.05$). Densely populated sites and those situated in periphery of
manufacturing areas seemed to exhibit higher mean concentrations of ∑6PAEs. Daily
mean and median concentrations comprising all the species (∑16PAEs) were generally
higher in samples collected during colder periods (38.3 and 37.5 ng/m$^3$, respectively) rather
than within samples gathered in warmer periods (31 and 26.9 ng/m$^3$, respectively), though
there wasn't a statistically significant difference between mean concentrations for both
periods (ANOVA: $p > 0.05$, F stat. < F critical). Statistically significant correlations were
found between temperature and concentrations of both DBP and ∑16PAEs ($p < 0.05$, $r =
0.34$ and $0.35$, respectively). Among population groups, an elevated daily intake (EDI)
ranging from 1.04 to 27.95 ng kgBW$^{-1}$day$^{-1}$ was found for toddlers, with the highest
estimated hazard index of $1.5 \times 10^{-2}$.

**Key words:** Seasonal profiles, health risk assessment, PM$_{2.5}$-associated PAEs, temporal
variations, Source identification
1. Introduction

Fine particulate matter (PM$_{2.5}$) is a core outdoor air quality threat. Once inhaled, it can penetrate in human's lungs and settle within alveoli (Gunasekar and Stanek, 2011). Studies have linked the exposure to PM$_{2.5}$ with health issues like cardiovascular and respiratory diseases, birth problems, lung cancer, DNA damage, oxidative stress and diabetes (Bowe et al., 2018; Lamichhane et al., 2015; Pun et al., 2017; Song et al., 2017; Ying et al., 2014), which are thought to depend on PM$_{2.5}$-associated components. The diverse composition of PM$_{2.5}$ reflects a complexity of PM$_{2.5}$ exposure-health outcomes. Thus, PM$_{2.5}$ is globally considered as a concern to public health, and it has instigated the World Health Organization (WHO) to develop reference benchmarks for evaluating health risks stemming from the exposure to particles.

As a part of substances adsorbed on the surface of PM$_{2.5}$, phthalate esters (PAEs) are carried to human's airways alongside the particles (Liu et al., 2017; Zou et al., 2016). They are widely used as plasticizers in polymers, more importantly, in polyvinyl chloride (PVC) (Bajracharya et al., 2021). They are also enormously incorporated in a range of consumer products such as electronics (Zhang et al., 2019a), personal care products (Stuchlík-Fišerová et al., 2022), food packages (Cheshmazar et al., 2021), adhesive and inks (Hou et al., 2021), toys (Souza et al., 2022) as well as building materials (Lin et al., 2021). The global consumption and production of PAEs is estimated to reach 11 billion tons per year (CDC, 2015; LCSP, 2011), while the production of diethylhexylphthalate (DEHP) and di-n-butylphthalate (DBP) is estimated to reach 394 and 134 tons, respectively (Xu et al.,
In 2011, China alone consumed approximately 2.2 billion tons (CPPIU, 2011). Being chemically detached from a polymeric matrix, PAEs can leach out of hosting materials into the environment (Liang and Xu, 2014; Xie et al., 2005), and they have been identified as the most abundant endocrine disrupting compounds (EDCs) in ambient air (He et al., 2019). Due to their relatively high octanol-air partition coefficient, they are readily adsorbed onto solid materials, particularly fine particles (PM$_{2.5}$) (Net et al., 2015). Their principal gateways to human body are through dermal contact (Olkowska and Gržinić, 2022), oral ingestion (Provencher et al., 2020) and inhalation (Wang et al., 2022). Numerous studies have associated PAEs exposure with a number of health impairments, for instance, cardiovascular disorders (Mariana et al., 2016), breast cancer (López-Carrillo et al., 2010), hypertension (Trasande and Attina, 2015) and developmental toxicity (Liu et al., 2012). Thus, strict regulations banning or limiting the production of PAEs have been in place in China, the United States and European Union (EU) (EU, 2005; Keith and Telliard, 1979; Zhou and Fu, 1991).

Lately, PAEs have been characterized for different environmental media including surface water, dust, soil and groundwater (Kotowska et al., 2020; Wei et al., 2020; Xu et al., 2022; Zhang et al., 2022). Evaluating PM$_{2.5}$-PAEs has also been conducted in different countries such as Spain (Sánchez-Piñero et al., 2022), Czech republic (Růžičková et al., 2016), India (Shankar et al., 2023), Puerto Rico (Toro-Heredia et al., 2021) and Mexico (Quintana-Belmares et al., 2018). Keeping an eyesight on China, a range of studies have characterized PM$_{2.5}$-PAEs from various regions. At Mount Tai, the long-range atmospheric transport was confirmed as the source of two PAEs (DEHP and dimethylphthalate (DMP)) (Zhen et al., 2019). In Beijing, the key sources of outdoor PM$_{2.5}$-PAEs were reported to be
personal care products and cosmetics (PCPCs), disposed industrial wastewater, plasticizers and sewage (Chen et al., 2018), when anthropogenic activities were suggested as a major source of PAEs in PM$_{2.5}$ collected during winter in Beijing. Moreover, a positive relation was observed between PAE concentrations and elemental carbon (EC), PM$_{2.5}$ and organic carbon (OC). It was also noted that concentrations and compositions did not significantly fluctuate during night and day times (Li et al., 2022). In four Chinese megacities, the concentrations of PM$_{2.5}$-PAEs were higher in samples gathered in warmer season than within samples collected in colder season (Zhang et al., 2019b). It has come to our attention that only one study in China has reported on vertical distribution patterns of PAEs (Wang et al., 2008).

With the current state of knowledge on outdoor PM$_{2.5}$-PAE in China, concentrations (Lu et al., 2018; Ouyang et al., 2019), sources (Li et al., 2019; Zhen et al., 2019), seasonal variation (Huo et al., 2023; Li and Wang, 2015) and relation between concentration and meteorological factors (Ma et al., 2020; Zhen et al., 2019) or carbonaceous species (Li et al., 2022) have been reported. However, some information regarding PM$_{2.5}$-PAEs in Shanghai have not been reported yet. For instance, Shanghai possesses secluded islands which have been singled out when assessing PM$_{2.5}$-bound PAEs. In addition, the sources of PM$_{2.5}$-PAEs in Shanghai were not discussed in previous reports. Thus, this study was primarily oriented to 1) deeply demonstrate spatial and seasonal profiles of PM$_{2.5}$-PAEs in samples from urban, sub-urban, and coastal locations in Shanghai, 2) identify potential sources of PAEs-PM$_{2.5}$ in atmosphere of Shanghai, 3) assess the influence of meteorological factors on PAEs concentrations, and 4) determine the inhalation exposure risks to Shanghainese people. The results from this study were compared with previous
reports on PM$_{2.5}$-PAEs in China and abroad, so as to assess the city's efforts with regard to curbing health risks associated with inhalation of airborne chemical pollutants.

2. Material and methods

2.1 Reagents and materials

16 PAE congeners were analyzed in this study. The CAS numbers of these compounds are shown in Table S1. A stock solution (1 ppm) used to prepare working solutions was prepared with a mixture of diethyl phthalate (DEP), DMP, DnBP, diisononylphthalate (DINP), diisobutyl phthalate (DIBP), di (2-propylheptyl) phthalate (DPHP), butylbenzylphthalate (BBzP), dicyclohexyl phthalate (DCHP), dihexyl phthalate (DHxP), dipentyl phthalate (DPeP), diallylphthalate (DAIP), diphenyl phthalate (DPHP), di (2-methoxyethyl)phthalate (DMEP), bis (2-etoxyethyl) phthalate (DEEP), bis (2-butoxybutyl) phthalate (DBEP) and bis (4-methyl,2-pentyl) phthalate (BMPP) provided by accustandard,Inc. (New Haven, CT, USA). The solvents used for extraction (methanol and dichloromethane) were of HPLC grade, and they were purchased from Alladin Biochemical Technology Co.,Ltd (Shanghai, China). Deuterated PAE standards (DEP-d4, DBzP-d4, DBP-d4, DHxP-d4, and DEHP-d4 ) were obtained from Accustandard, Inc. (New Haven, CT, USA). The optima grade mobile phase solvents (Methanol and formic acid) were obtained from Thermo Fischer Scientific, Waltham, Massachusetts, USA.

2.2 Sampling campaign

Nine sampling sites comprising urban (PT, XUH and PD), suburban (FX, HU) and coastal sites (QP, JSH, TH and CH) were considered in the present study (locations are illustrated by Fig. 1). Ambient PM$_{2.5}$ samples were intermittently collected between February 3$^{rd}$ (2015) and September 2$^{nd}$ (2021) using medium volume air samplers (TH-
150C, China) operating continuously for 24 hrs at flow rates of 100 L/min for two sites (XUH and TH) and at 16.67 L/min for other sites. Prior to sampling, quartz membrane filters (Whatman, grade QM-A, pore size: 2.2 mm, 90 mm, UK) were baked (450ºC for about 6 hours) using a muffle furnace (Thermo scientific TM Lindberg/Blue M™, USA) so as to remove background PAEs. Altogether, 128 samples were collected throughout the campaign from XUH (n = 49), TH (n = 11), JSH (n = 13), FX (n = 16), HU (n = 8), PD (n = 9), PT (n = 5), CM (n = 9), and QP (n = 8). The damages likely to occur during sample collection were minimized by enveloping within aluminum foils which were afterwards wrapped in polyethylene bags, and ultimately, the bags were kept within a medium at a temperature beneath 20ºC until the extraction.

2.3 Extraction

Initially, each quartz fiber filter sample (QFF) was weighed (CPA-26P, Sartorius, German) and then cut into tiny pieces (1×1cm) which were subsequently transferred into 15 mL cylindrical glass tubes. Next, the filters were spiked with a volume of 100 μL taken from each of three deuterated surrogate solution (DEP-d4, DBzP-d4, and DHXP-d4) solutions. Subsequently, a volume of 5ml dichloromethane (DCM) was poured into each of glass tubes, and samples were sonicated (water bath temperature: 30°C) for 15 min and then shaken in ES-20/60 orbital shaker (T: 30°C, 200 rpm) for 30 minutes. This was followed by centrifuging (Hermle Labnet model Z383K, Hemle labotechnik, Wehingen, Germany) for five minutes at 4000 rpm. The supernatants were isolated from residues using pipettes and then transferred into clean 15ml glasses. Samples were subjected to the same procedure twice, combining all the extracts in the corresponding tubes. Afterwards, the extracts were concentrated to nearly dryness using a gentle stream of N2. Residues were reconstituted with methanol to 1ml, then cleansed with 0.2 μm GPH filters (Waters, Milford, USA) before being transferred to vials. Finally, 50 μL was pipetted from each of deuterated internal standards (DBP-d4 and DEHP-d4) solutions, and spiked into extracts prior to vortex mixing followed by LC-MS/MS analysis.

2.4 LC-MS/MS analysis

The quantification was performed using liquid chromatography coupled to triple quadrupole mass spectrometry (LC-MS/MS) in multiple reaction monitoring (MRM) mode (LCMS8050 Shimadzu, Kyoto, Japan). The separation was conducted by CSHC18 chromatographic column (2.1 mm × 100 mm, 1.7μm inner packing diameter). The column
temperature, injection volume and flow rate were 40°C, 1μL, and 0.3 ml/min, respectively. The mobile phase consisted of aqueous phase A (0.1% formic acid) and organic phase B (methanol containing 0% formic acid). Gradient elution mobile phase conditions were set as following: Starting at 70% (v/v) B and held for 1 min, then taken to 100% (v/v) B at 7th min and held for 3 min, then returned to 70% (v/v) B at 10.1th min and retained for 2.9 min for an overall run time of 13 min. The MS/MS system was operated in multiple reaction monitoring (MRM) negative ion mode using a heated electrospray ionization source (ESI). The spray voltage was KV, capillary temperature was 250°C, and vaporization temperature was 300°C. The atomizing gas and heating gas flow rates were 3 and 10 L/min, respectively.

2.5 Quality assurance and quality control

Glassware (pipettes, volumetric flasks) utilized throughout the procedure were rinsed three times with tap water, pure water and methanol before their baking using a muffle furnace set at 450°C for 8 hrs. The calibration curves used during the quantification were constructed by means of internal standards and target PAEs solutions prepared at concentrations varying from 15.625 ppb to 1 ppm. Moreover, all correlation coefficients (R²) surpassed a value of 0.99. Field blanks (baked filters introduced in the sampler for a minute without filtering the air, n = 9) and procedural laboratory blanks (baked filters not containing PM₂.₅, n = 14) were utilized following the same protocol used for the actual PM₂.₅ samples. Together with solvent blanks (methanol, n = 12), they were analyzed for every batch of 10 samples so as to monitor the pollution that might arise from extraction and analysis procedures. The average recoveries for deuterated PAE standards spiked in samples prior to analysis ranged from 80.5% (DCHP) to 94.7% (DBEP) (Table S2). The negligible trace amount of target compounds (all below LOD) was found in blank samples
at concentrations ranging from 0.006 (BMPP) to 0.21 ng/m³ (DIBP), and it was subtracted from the concentrations of actual samples. The detection limits (LODs) which varied from 0.01 (DEP) to 0.54 ng/m³ (DIBP) (Table S2) were determined as S/N (signal- to noise) ratio of 3. The samples with concentrations below LOD were assigned a value of zero for statistical analysis.

2.6 Estimation of exposure risks

Hazard quotients (HQs) were determined for concentrations of major congeners, and they helped to evaluate the probable harm to humans as a result of inhaling PM2.5-PAEs. Numerically, HQs (Eq. 2) are determined as ratios between daily intakes, EDIs (ng kgBWt⁻¹day⁻¹) and reference doses (Zhang et al., 2019b). The combined threat caused by inhaled PAEs which is known as hazard index (HI) (Eq. 3) was calculated by aggregating HQs for individual congeners. Basically, the inhaled dose of PAE-PM2.5 is considered a potential threat to exposed individuals in case either of calculated HQs or HIs exceeds one. The calculation of EDI (Eq. 1) provided values which were compared to benchmark doses (tolerable daily intakes (TDIs) and reference doses (RfDs)) as suggested by the European food safety authority (EFSA) and the United States Environmental protection agency (U.S. EPA), respectively. At the time, there is no reference doses associated with the inhalation of PAEs, and the aforesaid doses (TDIs and RfDs) help to determine HIs and HQs (Table S7). DEHP which is solely evidenced to be carcinogenic among PAE species was not part of target species in this study, which is attributable to its maximal concentration that exceeded the instrumental capability. Thus, the evaluation of cancer risks attributable to inhaling PM2.5-PAEs wasn't performed. The previously reported population groupings
(Table S7) for Shanghai (Zhang et al., 2019b) were utilized as a reference to determine the exposure magnitude for different age categories.

\[ \text{EDIs} = \frac{[\text{PAEs}] \times \text{IR} \times f_1}{BWt} \]  

(1)

\[ \text{HQs} = \frac{\text{EDIs}}{\text{Reference limits}} \]  

(2)

\[ \text{HI} = \sum_{i=1}^{n} \text{HQs} \]  

(3)

[\text{PAEs}] represents the combined concentrations (ng/m³) of particle and gas phase (Cₐ + Cₚ) for a specific congener (Table S8). IR stands for the inhalation rate (m³/day), f₁ (Unitless) is the exposure fraction in ambient milieu, whereas BWt (kg) is the body weight.

2.7 Statistical analysis

IBM SPSS software version 29.0.0.0 (214) and Microsoft excel (2013) were utilized for the statistical analysis. The comparison of mean concentrations for different sampling sites and seasons was performed using one-way analysis of variance (ANOVA) and student t-test. The checking of normality of data was carried out using both Shapiro Wilk and Kolmogorov Smirnov tests. To evaluate the relationship between PAE congeners, Spearman correlation analysis was utilized as the results from the normality testing did not demonstrate normal distributions following log-transformations of concentration data. The significance (alpha) level was set at p < 0.05.

3. Results and discussion

3.1. Detection, concentration and distribution

3.1.1. Detection frequencies (DF)
Considering the campaign as a whole and different sampling venues, \( \sum 6 \text{PAEs} \) were highly identified (DF: 44.5% to 85.9%) (Fig. S1, Fig. S2). In general, DBP and DIBP were the most predominant (DF: 85.9% and 71.1%, respectively) species (Fig. S1). The decreasing order of DF values for the rest of species were 71.1%, 63.3%, 60.9%, and 44.5% for DINP, DPHP, DEP, and DMP, respectively, and the cause of least DF of DMP may be associated with its lower molar weight (194) as well as its substantial occurrence in gas phase (Weschler et al., 2008). Besides, DHxP and BBZP dominated the least detected cluster accounting for 21.9% and 10.2% of total DF, respectively. Considering the samples from each site, two species (DBP and DIBP) were uniformly predominant in samples from all sites except those from PT where DINP (DF: 80%) was the most identified compound (Fig. S2). This may indicate a widespread occurrence of these PAEs in air particulates from Shanghai. At PT, DINP was detected in 4 of 5 samples, when the highly detected species (DBP and DIBP) were only detected in 3 samples. This might have originated from slight mistakes done during sample preparation or analysis. This might possibly be caused by the instrumental artifacts during the analysis. The highest DF values for both species were observed in samples from XUH (DF: 98 and 95.9%, respectively), JSH (92.3%), and PD (77.8%). Remarkably, detection levels for both species were levelled in samples from four locations namely JSH, PD, QP and FX (Fig. S2). This certainly corroborates the presence of these PAEs in environmental samples from Shanghai. The previous reports in China have also documented some of our key species as major PAEs. For instance, three PAEs (DMP, DEP and DBP) were frequently detected in PM\(_{2.5}\) samples collected in summer and winter periods from 14 cities across China (Wang et al., 2006), in TSP samples collected from an urban location in Shanghai (Li et al., 2018), and within PM\(_{2.5}\) samples collected
from four Chinese metropolis (Zhang et al., 2019b). Four species (DBP, DMP, DIBP and DEP) were frequently found in PM$_{2.5}$ samples from Shanghai (Ma et al., 2014).

3.1.2. Concentrations

Fig. 2 depicts the concentrations of $\sum_6$PAEs, the concentrations of the least identified PAEs (minor species) along with the proportions (%) contributed by different sampling locations to the total concentrations of major species for all the campaign. Fig. S4 illustrates the concentration magnitude for 16 target species. The spatial concentration profiles of $\sum_6$PAEs are illustrated in Table 2. In view of the campaign as a whole, two species (DBP and DIBP) contributed significantly (79.4%) to the cumulative concentration (4181.6 ng/m$^3$) of PAEs in all samples. They also exhibited a strong positive correlation ($r = 0.876, p < 0.001$) (Table 3) which reiterates the previous finding by Wang et al. (2006). This indicates a common utilization of these PAEs in China. The aggregate concentrations of $\sum_6$PAEs contributed 99.1% of the overall concentration. Spatially, the samples from Xuhui (ECUST) contributed higher (38.97%) to the cumulative concentration of PAEs in the campaign, and also to the total concentrations of $\sum_6$PAEs (Figure 2, B). However, it was noted that the fluctuating site profiles may have largely depended on sample size rather than the emission magnitude of PAE sources at sampling sites. The range (mean, median) of $\sum_{16}$PAEs were from below detection limit to 127 ng/m$^3$ (32.7; 29.4 ng/m$^3$). The ranges (mean, median) for $\sum_6$PAEs were: DMP: 0.07 to 1.48 ng/m$^3$ (0.80 ng/m$^3$, 0.82 ng/m$^3$); DEP: 0.02 to 0.76 ng/m$^3$ (0.34 ng/m$^3$, 0.40 ng/m$^3$); DBP: 0.05 to 55.00 ng/m$^3$ (13.47 ng/m$^3$, 11.97 ng/m$^3$); DIBP: 0.90 to 61.00 ng/m$^3$ (18.40 ng/m$^3$, 17.29 ng/m$^3$); DINP: 0.06 to 19.90 ng/m$^3$ (5.99 ng/m$^3$, 4.75 ng/m$^3$), and DPHP: 0.02 to 14.26 ng/m$^3$ (2.55 ng/m$^3$, 1.31 ng/m$^3$). The relatively higher mean concentration of DBP might be attributed to its potentially
higher emission to atmosphere brought by its extensive utilization alongside diethylhexyl phthalate (DEHP) in plastics, cosmetics, personal care products and latex adhesives, together with its resistance to the covalent bonding with a polymeric matrix. In China, the use of DBP as plasticizer mounted to > 47.7Kt in 2006 (Zhang et al., 2019a), and as it was previously stated by Wang et al. (2010), DBP and DEHP are the most utilized plasticizers in China. The comparison of total concentrations has been frequently impractical due to inconsistency with respect to PAEs species of interest among various studies. Therefore, a comparison with previously reported individual congeners in China and elsewhere was undertaken (Table 1). The mean concentrations of DMP (1.4 and 1.9 ng/m³), DEP (5.1 and 13 ng/m³), DBP (32 and 158 ng/m³), and DIBP (43 and 164 ng/m³) in PM₂.₅ samples collected nearly two decades ago in Shanghai (Wang et al., 2006) were significantly higher than the concentrations in this study. Same trend was observed in a study on combined gas and particle phase samples collected in 2016, where reported ranges (means) of DMP: 37-105 ng/m³ (68 ng/m³), DEP: 26-268 ng/m³ (90 ng/m³), and DBP: 39-119 ng/m³ (70 ng/m³) surpassed by far the measured concentrations in this study (Li et al., 2018). This substantiates a relatively decreasing loading of PAEs in the atmosphere of Shanghai following a modernization of handling plastic wastes as stated by Ma et al. (2014).
Fig. 2. Concentrations of major (A) and minor (B) PAE species, (C): Spatial distribution of campaign's total concentration (%) for each of major species.
308 Table 1 Comparison of measured mean concentrations (ng/m³) with previously reported outdoor air PAEs data.

<table>
<thead>
<tr>
<th>Country</th>
<th>Location</th>
<th>Sampling period (Year)</th>
<th>Type</th>
<th>PAE congeners</th>
<th>Source</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DMP</td>
<td>DEP</td>
</tr>
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<td>China</td>
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<td>PM₁₀</td>
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<td></td>
<td>Lake Chaohu</td>
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<td>PM₁₀</td>
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</table>

G: Gas phase, ND: Not detected, TSP: Total suspended particles. For locations with the symbol (*), the maximum concentration was reported. NS: Not specified.
Nonetheless, the mean concentrations of DMP (0.32 ng/m$^3$), DEP (0.19 ng/m$^3$), DIBP (12.6 ng/m$^3$) and DBP (6.72 ng/m$^3$) in PM$_{2.5}$ samples collected in Shanghai between 2011 and 2012 (Ma et al., 2014), as well as the maximum (mean) concentrations of DMP: 0.43 ng/m$^3$ (0.06 ng/m$^3$), DEP: 0.51 ng/m$^3$ (0.02 ng/m$^3$), and DBP: 52 ng/m$^3$ (9.26 ng/m$^3$) in particulate (PM$_{2.5}$) samples collected between 2015 and 2017 in Shanghai (Zhang et al., 2019b) are marginally below our observations. A number of previous research works across China and abroad have similarly pinpointed some of our major species as their priority compounds, and three target PAEs (DMP, DEP, and DBP) were commonly measured in almost all studies. Generally, it is well apparent that the atmospheric environment in several Chinese megacities has been highly loaded with the aforementioned PAEs as compared to the atmosphere of Shanghai (Table 1). The mean concentration of DBP was one order of magnitude higher than the concentrations found in PM$_{2.5}$ samples from Shenzhen and Mount Tai. However, it is in the same order of magnitude as the reported concentrations in PM$_{2.5}$ from Tianjin, Xi'an and Pearl River Delta (Table 1). The mean concentrations of PAEs (DMP, DEP, and DBP) in this study are relatively higher than the concentrations measured in air particulates from France (0.1 ≤ Mean Conc. ≤ 1.9), but lower than concentrations found in air particulates from India (0.009 ≤ Mean Conc. ≤ 42.4) (Table 1). This enlightens the elevated emission of air pollutants accompanying a glittering rapid development in world's most developing countries.

3.1.3 Spatial and seasonal profiles

Seasonal profiles are represented by Fig. 3, Fig. 4 and Fig. S3, while concentrations found in studied sites are shown in Table 2. Specifically, Fig. 3 depicts the concentrations of $\sum$6PAEs measured for warm (April to October) and cold (November to March) seasons.
In addition, the concentrations of $\sum_6$PAEs for samples collected in winter (December to February) and spring (March to May) were determined Fig. 4. With Fig. S4, the concentrations of $\sum_6$PAEs for samples collected in summer (June to August) were also illustrated. The range (mean, median) concentrations of $\sum_{16}$PAEs for both warm periods were from $< \text{LOQ}$ to 127 ng/m$^3$ (28.5 ng/m$^3$, 15.1 ng/m$^3$) in 2015 and from $< \text{LOQ}$ to 82.3 ng/m$^3$ (32.7 ng/m$^3$, 31.8 ng/m$^3$) in 2021, whereas the range (mean, median) for cold periods were from 2 to 67.3 ng/m$^3$ (37.0 ng/m$^3$, 41.5 ng/m$^3$) in 2015 and from $< \text{LOQ}$ to 85.8 ng/m$^3$ (38.5 ng/m$^3$, 36 ng/m$^3$) in 2021. The range (mean, median) concentrations of $\sum_{16}$PAEs measured for Spring and winter seasons were from $< \text{LOQ}$ to 85.83 ng/m$^3$ (37.29 ng/m$^3$, 35.47 ng/m$^3$) and from 4.59 to 82.21 ng/m$^3$ (51.14 ng/m$^3$, 65.08 ng/m$^3$), respectively, in 2021, and from 7.30 to 18.73 ng/m$^3$ (14.69 ng/m$^3$, 16.37 ng/m$^3$) and 2.04 to 67.26 ng/m$^3$ (36.95 ng/m$^3$, 41.55 ng/m$^3$), respectively, in 2015. This could suggest that PM$_{2.5}$ samples collected during colder months contained higher concentration of PAEs than PM$_{2.5}$ samples collected in hotter months, even though there wasn't a statistically significant difference between mean concentrations (ANOVA: $p > 0.05$, F stat. $< F$ critical). This is not in accordance with the previous reports in Shanghai, where the concentrations of PM$_{2.5}$-PAEs in warmer periods were significantly higher (Li and Wang, 2015; Ma et al., 2014; Zhang et al., 2019b). A non-simultaneous sampling campaign as well as the disproportional sample sizes (60 to 24 samples in 2021, and 40 to 3 samples in 2015) may be part of the factors impeding the results in this study to match with those in the previous studies. However, the higher concentrations of PM$_{2.5}$-PAEs in colder periods were found at times in other cities across China (Ma et al., 2020; Wang et al., 2008). In fact, PAEs are semi-volatile compounds released from the polymeric matrix, and the rise in temperature...
leads to their higher emission to atmosphere in warmer periods (Clausen et al., 2012; Ma et al., 2014). But, the intense photochemical degradation with free radicals in air, which potentially occurs in hotter months, may bring about a decrease in PAE concentrations in warmer periods (Wang et al., 2008). Comparing $\sum_{6}$PAEs in warm and cold seasons of 2021 and 2015, there weren't statistically significant differences between mean concentrations (ANOVA for warm seasons, $p$: 0.15, 0.67, 0.60, 0.20, 0.32 and 0.85, respectively, for DMP, DEP, DBP, DIBP, DINP and DPHP; ANOVA for cold seasons, $p$: 0.61, 0.98, 0.30, 0.31, 0.64 and 0.57, respectively, for DMP, DEP, DBP, DIBP, DINP and DPHP).

Fig. 3. Distribution of concentrations (ng/m$^3$) of $\sum_{6}$PAEs for warm and cold seasons.
Fig. 4. Distribution of concentrations (ng/m³) of ∑6PAEs for spring and winter seasons.

Fig. 5 demonstrates the mean concentrations of ∑6PAEs and ∑16PAEs for various sites through heat map visualization. There wasn't a statistically significant difference in means of total concentrations (∑16PAEs) between the sites (ANOVA: p = 0.10, F stat. = 1.74, F crit. = 2.02), and their magnitudes were not necessarily the highest for the sites renowned to have a bulk of plastic manufacturing plants (e.g. FX, PD) as it is depicted in Fig. 5. But, the mean concentrations of ∑6PAEs in various sites were significantly different (ANOVA: p = 0.006, 4.4x10⁻⁵, 0.04, 2.4x10⁻⁶, and 0.007 for DBP, DIBP, DMP, DEP and DPHP, respectively) except concentrations of DINP (ANOVA: p = 0.13). The highest
overall concentration of $\sum_{16}$PAEs was determined in samples from XUH (1629.6 ng/m$^3$) followed in decreasing order by JSH (643.5 ng/m$^3$) > FX (520.7 ng/m$^3$) > CM (359.8 ng/m$^3$) > PD (354 ng/m$^3$) > QP (334.7 ng/m$^3$) PT (212.4 ng/m$^3$) > HN (75.7 ng/m$^3$) and TH (51.3 ng/m$^3$) (Fig. 1). In fact, sample size for XUH was considerably larger than the sample sizes for other sites, and this resulted in a sizable discrepancy within overall concentrations. Measurable concentrations for three species (DMP, DIHP and DIBP) were not found in all samples from TH (Table 2). As TH is a small island with a relatively small population, there may be a lower load of plastic wastes, which are known to be part of major generators of airborne PAEs. Moreover, the location is relatively well distanced from the industrial emissions, and during the sampling campaign, the island may have experienced stronger wind episodes which might disperse air pollutants. The ranges (mean, median) of $\sum_{16}$PAEs were: XUH, from < LOQ to 70.4 ng/m$^3$ (33.3 ng/m$^3$, 29.2 ng/m$^3$); TH, from < LOQ to 14.5 ng/m$^3$ (4.7 ng/m$^3$, 2 ng/m$^3$); JSH, from 2 to 85.8 ng/m$^3$ (49.5 ng/m$^3$, 50.8 ng/m$^3$); FX, from < LOQ to 82.2 (32.5 ng/m$^3$, 32.4 ng/m$^3$); HN, from < LOQ to 21.7 ng/m$^3$ (9.5 ng/m$^3$, 10.7 ng/m$^3$); PD from < LOQ to 113 ng/m$^3$ (39.3 ng/m$^3$, 34.6 ng/m$^3$); PT, from < LOQ to 72.5 ng/m$^3$ (42.5 ng/m$^3$, 65.4 ng/m$^3$); CH, from < LOQ to 75.5 ng/m$^3$ (40 ng/m$^3$, 48.4 ng/m$^3$) and QP, from < LOQ to 127 ng/m$^3$ (41.8 ng/m$^3$, 38.9 ng/m$^3$).

The highest mean concentration of DBP was found in samples from PT (22.67 ng/m$^3$) followed by QP > PD > JSH > CH > FX > XUH > TH, and HU, whereas for DIBP, the decreasing order for mean concentrations was PT > PD > FX > JSH > QP > CH > XUH, and HU (Table 2). PT is categorized among urban areas with an elevated population density (15000-30000 people/km$^2$) (Cui and Shi, 2012), which may potentially be aligned with a higher consumption of PCPCs renowned as a source of DBP and DIBP.
In general, the location of sampling sites did not demonstrate a significant influence on the magnitude of data as it is literally noticeable from Fig. 5 and Table 2. For instance, the mean concentrations of $\sum_{16}$PAEs are relatively higher at JSH which is a coastal area, CH which is marine (island) area as well as PT which is an inland area (Fig. 5). Moreover, taking a look at mean concentrations of the most significant PAE species (DBP and DIBP) Table 2, it is clear that the locations renowned to have plastic manufacturing plants in Shanghai (e.g. PD and FX) did not exhibit the highest values as compared to other sites (e.g. PT and QP).

**Fig. 5.** Heat map showing the average concentrations of major and all congeners ($\sum$PAEs) for various sampling sites
### Table 2: Spatial profiles (ng/m³) of target PAEs with significant concentrations.

<table>
<thead>
<tr>
<th>PAEs</th>
<th>TH</th>
<th>CH</th>
<th>QP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Av ± SD</td>
<td>Median</td>
</tr>
<tr>
<td>DMP</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEP</td>
<td>0.02 - 0.05</td>
<td>0.03 ± 0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>DBP</td>
<td>0.07 - 14.37</td>
<td>6.34 ± 5.46</td>
<td>5.03</td>
</tr>
<tr>
<td>DIBP</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DINP</td>
<td>0.06 - 0.16</td>
<td>0.11 ± 0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>DPHP</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RANGE</td>
<td>Av ± SD</td>
<td>Median</td>
</tr>
<tr>
<td>DMP</td>
<td>1.05 - 1.17</td>
<td>1.11 ± 1.06</td>
<td>1.11</td>
</tr>
<tr>
<td>DEP</td>
<td>0.22 - 0.45</td>
<td>0.33 ± 0.12</td>
<td>0.33</td>
</tr>
<tr>
<td>DBP</td>
<td>0.21 - 1.86</td>
<td>1.20 ± 0.60</td>
<td>1.29</td>
</tr>
<tr>
<td>DIBP</td>
<td>0.90 - 2.46</td>
<td>1.78 ± 0.60</td>
<td>1.90</td>
</tr>
<tr>
<td>DINP</td>
<td>2.51 - 11.35</td>
<td>5.84 ± 3.35</td>
<td>4.75</td>
</tr>
<tr>
<td>DPHP</td>
<td>0.34 - 11.58</td>
<td>4.84 ± 4.86</td>
<td>2.58</td>
</tr>
</tbody>
</table>

Note: Av: Mean; SD: Standard deviation; <LOQ: The concentration was found below quantification limit.
Thus, in order to obtain more reliable information regarding the influence of sampling locations on PAEs' concentrations, we suggest a simultaneous sampling across the city, with the same number of collected samples at all sites.

### 3.2 Concentrations of PM2.5, EC/OC and their correlations with PM2.5-PAEs

#### 3.2.1 Profile of PM2.5 and its relationship with PAEs

Following a normality testing (Table S5 and Table S6), the datasets were not normally distributed, and so, the correlation analysis referred to calculated Spearman correlation ranks and p values (Table 3). By reason of a small number of samples for other sites, the analysis was restricted to data from XUH where a relatively sizeable number of samples (n = 49) was collected. Consistent with the results, there wasn't a significant correlation between concentrations of PAE and those of PM2.5 (Table 3). Alike this study, Zhang et al. (2019b) also did not find concentrations of PAEs (ΣPAEs, DEP, DBP, and DMP) significantly related with concentrations of PM2.5 samples from Shanghai. But, a positive correlation was found between concentrations of PAEs and those of PM2.5 during an hourly monitoring of PAEs characteristics in Beijing. It was concluded that PAEs tend to adsorb and condense onto the carrying particles (Li et al., 2022). Similarly in Xi'an, a significant relationship was found between concentrations of PM2.5 and those of ΣPAEs, which led to a conclusion that a removal of PM2.5 from the atmosphere, would concomitantly lessen PAEs concentrations (Ma et al., 2020). Taking into account the campaign holistically, the mean (range) concentrations of PM2.5 were 38.06 μg/m³ (1.62 to 120.83 μg/m³), and a slight difference in mean concentrations (0.71 μg/m³) was observed between samples collected in 2015 and those collected in 2021 (Table S4). The average concentration is higher than
the lately unveiled annual mean concentration of PM$_{2.5}$ in China (35 μg/m$^3$) as set by air quality standard of China (Lu et al., 2018; Wang et al., 2015). Nevertheless, it is below the mean concentrations found earlier in outdoor PM$_{2.5}$ samples from Beijing (68.5 μg/m$^3$) and Shenzhen (65.5 μg/m$^3$) (Chen et al., 2018; Lu et al., 2018). In outdoor air samples from Chinese cities of Xi’an and Hangzhou, the concentrations of PM$_{2.5}$ were found in ranges of 11.4 - 596 μg/m$^3$ and 17-190 μg/m$^3$, respectively (Lu et al., 2018; Ouyang et al., 2019), and they surpass the concentration range in this study.

### 3.2.2 Profile of carbonaceous species (EC & OC) and their relationships with PAEs

EC and OC play a vital role when tracing the source of air pollutants. They are also renowned to pose significant effects on human health owing to their chemical and physical characteristics (Pio et al., 2011). The mean OC and EC concentrations for the campaign were 1.70 and 0.94 μg/m$^3$ respectively (Table S4). They are one order of magnitude inferior to their previously reported average concentrations in PM$_{2.5}$ collected in sub-urban areas of Shanghai (Ma et al., 2013). The study by Duan et al. (2016) which reported a sharp decrease of EC in PM$_{2.5}$ from Shanghai between 2009 and 2012, may corroborate an observed decline in mean concentrations of EC in this study as compared to concentrations reported by Ma et al. (2013). The total concentration of organic carbon (TOC: OC+EC) ranged between 0.43 μg/m$^3$ and 8.73 μg/m$^3$. The burning of biomass and fossil fuels may be part of local sources of OC and EC, when SOC (secondary OC) is traced from the atmospheric gas-particle conversion. The tracing of carbonaceous matter's source has been based on OC/EC ratio (Castro et al., 1999). The ratio increases when there is a continuous regional contribution of aged particles with higher SOC content (Ma et al., 2013; Pio et al., 2011). Given a small difference in mean concentrations of OC and EC in this study, a lower
ratio (1.82) of OC/EC was found which excludes secondary organic aerosols (SOA) transported to sampling site among potential sources of PM$_{2.5}$-PAEs. The lower ratio also indicates that local sources may be actual contributors to PM-bound organic matter. As depicted in Table 3, OC significantly correlated with $\sum_{16}$PAE concentrations ($p < 0.05, r = 0.470$), but it is not related with individual PAEs. This relationship infers a potential adsorption of PM$_{2.5}$-PAEs on organic matter.

3.2.3 Relationship between PAE concentrations and meteorological factors

Spearman correlation analysis results depicted in Table 3 demonstrate relationships between concentrations of PM$_{2.5}$-PAEs and meteorological factors. In fact, the atmospheric level of a pollutant is substantially influenced by factors such as relative humidity, temperature and wind speed (He et al., 2017). Significant positive correlations were found between concentrations of DBP and those of $\sum$PAEs with temperature ($p < 0.05, r = 0.345$ and 0.352, respectively). In general, the rise of temperature prompts a transformation of PAEs to gas phase from particle phase, and thus, the increased concentrations of low molecular weight congeners which primarily occur in gas phase. Besides, the higher temperature may trigger an increase of emission from sources (e.g. plastic products) in case strong radiations lead to the degradation of PAEs (Ma et al., 2020). By clustering the concentrations of samples from XUH, some relationships were demonstrated for different sampling days, and they were stronger between samples labelled S20 and S39 along with S14 and S19 (Fig. S5). Generally, these samples exhibited the highest concentration of DBP and one of $\sum$PAEs. In addition, they were collected on days with a relatively higher average temperature which may underline the correlations found between concentrations of both DBP and $\sum$PAEs with temperature (Table 3). Previously in Shanghai, temperature
was not found significantly related to PAE concentrations owing to the slight temperature fluctuation throughout the sampling period (Li et al., 2018). However, relative humidity and wind speed were significantly correlated with concentrations of PAEs. The rise of humidity brings about the adsorption of PAEs on particles, when strong wind tend to scatter and dilute PM in atmosphere (Ma et al., 2020). In northwestern Chinese city of Xi’an, Ma et al. (2020) found significant correlations between ∑PAEs and DBP concentrations with temperature, relative humidity and visibility. The lower is the visibility, the higher is the atmospheric load of PM, and the higher are concentrations of PAEs. It was noted that on a highly polluted day (20-05-2021) among samples from XUH, the strong wind arriving at the site was dominated by air mass coming from NW, when the average temperature reached the peak level (Fig. S6). This may reflect a predominant occurrence of PAE sources at NW direction of the site, but this needs a further verification.

**Table 3** Spearman correlation ranks between concentrations of major PAEs, PM$_{2.5}$, EC/OC, and meteorological factors.

<table>
<thead>
<tr>
<th></th>
<th>DMP</th>
<th>DEP</th>
<th>DBP</th>
<th>DIBP</th>
<th>DINP</th>
<th>DPHP</th>
<th>∑16PAEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEP</td>
<td>0.431$^a$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DBP</td>
<td>-0.071</td>
<td>0.181$^b$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIBP</td>
<td>0.028</td>
<td>0.155</td>
<td>0.876$^a$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DINP</td>
<td>0.037</td>
<td>0.236$^a$</td>
<td>0.514$^a$</td>
<td>0.544$^a$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPHP</td>
<td>0.201$^b$</td>
<td>0.453$^a$</td>
<td>0.284$^a$</td>
<td>0.368$^a$</td>
<td>0.475$^a$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>∑16PAEs</td>
<td>0.037</td>
<td>0.237$^a$</td>
<td>0.929$^a$</td>
<td>0.952$^a$</td>
<td>0.684$^a$</td>
<td>0.491$^a$</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>PM$_{2.5}$</th>
<th>-0.005</th>
<th>-0.092</th>
<th>-0.141</th>
<th>-0.174</th>
<th>0.037</th>
<th>-0.014</th>
<th>-0.199</th>
</tr>
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<tbody>
<tr>
<td>OC</td>
<td>-0.094</td>
<td>0.069</td>
<td>-0.004</td>
<td>-0.061</td>
<td>-0.011</td>
<td>0.0139</td>
<td>0.470$^b$</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>-0.051</td>
<td>-0.147</td>
<td>0.030</td>
<td>0.121</td>
<td>0.013</td>
<td>-0.0173</td>
<td>0.266</td>
<td></td>
</tr>
<tr>
<td>T ($^\circ$)</td>
<td>-0.068</td>
<td>-0.015</td>
<td>0.345$^b$</td>
<td>0.274</td>
<td>0.169</td>
<td>-0.129</td>
<td>0.352$^b$</td>
<td></td>
</tr>
<tr>
<td>WS (Km/h)</td>
<td>0.258</td>
<td>0.121</td>
<td>0.038</td>
<td>-0.148</td>
<td>0.109</td>
<td>-0.061</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>RH (%)</td>
<td>-0.171</td>
<td>0.166</td>
<td>0.085</td>
<td>0.042</td>
<td>-0.180</td>
<td>-0.076</td>
<td>0.051</td>
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<tr>
<td>AP (Pa)</td>
<td>0.005</td>
<td>0.146</td>
<td>-0.207</td>
<td>-0.253</td>
<td>-0.254</td>
<td>-0.045</td>
<td>-0.274</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: denotes a very significant correlation with $p < 0.01$, $^b$: denotes a significant correlation set at $p < 0.05$; WS: Wind speed; RH: Relative humidity; AP: Atmospheric pressure.

3.3 Source identification by principal component analysis (PCA)
To identify the probable sources of PAEs in ambient PM$_{2.5}$ samples, principal component analysis (PCA) performed using IBM SPSS was performed. The software has extracted the principal components for the whole campaign as well as various sampling locations (Table 4). Previously, studies reported that principal components are deemed relevant when the cumulative variances of their factors surpass 80% following a varimax rotation (Chen et al., 2018). In this study, PCA-returned factors which changed within the sites, reflected the spatial discrepancy of PAE sources. Higher factor loadings provided by the software were regarded as pertinent to affirm the local origin for PAEs. As illustrated in Table 4, two factors with a cumulative variance of 91.35% were determined for the campaign as a whole. Regarding sampling locations, two loading factors were determined for XUH, FX, CH, TH and QP, when three factors were found for PD, JSH, PT and HU. The cumulative variances were found equal to 67.95%, 91.41%, 74.23%, 86.62%, 75.44%, 77.78%, 97.09%, 80.49% and 91.44% for XUH, PD, FX, JSH, CH, TH, PT, QP and HU, respectively. Thus, in accordance with Chen et al. (2018), the factors found for PD, JSH, PT, QP and Hu could solely be relied upon when pinpointing PAEs sources. However, the study by Ma et al. (2020) also considered principal components with cumulative variance > 70%, and in this line, principal components for FX, TH and CH may also be considered during the analysis.

Considering the whole sampling campaign, factor one (F1) accounted for 25.9% of the total variance when factor two (F2) accounted for 65.4%. Congeners DBP, DIBP and DINP loaded sizably together with F1, when DEP, DMP and DPHP loaded well together with F2 (Table 4). This may indicate a similar environmental behavior and/or sources for the co-loading PAEs. Looking at different sampling sites, DBP and DIBP loaded well together
with F1 among all sampling sites except TH. This may absolutely confirm similar sources for these PAEs in Shanghai. In addition, DBP, DIBP and DINP loaded together within 5 of 9 sampling sites which implies a widespread co-emission of PAEs from their sources across Shanghai. DINP and DPHP loaded well together with F2 in 6 of 9 sampling sites which may designate the probable common sources for these PAEs. DEP and DMP loaded very well together with F2 for PD, F3 for JSH, and F2 for HU which may indicate the similar sources of these PAEs in these locations. DIBP and DBP are renowned to originate from personal care products (PCPs), adhesives, cosmetics and paints (Duan et al., 2022). DBP is also utilized in special adhesives formulations, epoxy resins and cellulose esters (Abdel daiem et al., 2012; Ma et al., 2020). High molecular weight (MWt) PAEs including DINP are extensively used in clothing, polymer industry, building materials, children's products, medical devices and food packaging (Abdel daiem et al., 2012; Heudorf et al., 2007; Wormuth et al., 2006). PAEs with lower MWt like DEP, DBP and DMP are broadly used in PCPCs (Ma et al., 2020). DEP is also used broadly in air fresheners (Velázquez-Gómez and Lacorte, 2019). Given the limited samples collected from each site (apart from XUH site), we suggest future research works to revisit PCA analysis for PAEs across Shanghai in order to corroborate the common factor loadings of PAE congeners as it was observed in this study.
### Table 4 PCA factor loadings for major PAE congeners

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>All</th>
<th>XUH</th>
<th>PD</th>
<th>FX</th>
<th>JSH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F1</td>
<td>F2</td>
<td>F1</td>
<td>F2</td>
<td>F3</td>
</tr>
<tr>
<td>DMP</td>
<td>-1.51</td>
<td>0.74</td>
<td>-0.75</td>
<td>0.07</td>
<td>0.18</td>
</tr>
<tr>
<td>DEP</td>
<td>0.11</td>
<td>0.76</td>
<td>-0.31</td>
<td>0.61</td>
<td>-0.27</td>
</tr>
<tr>
<td>DBP</td>
<td>0.94</td>
<td>-0.60</td>
<td>0.90</td>
<td>0.07</td>
<td>0.97</td>
</tr>
<tr>
<td>DIBP</td>
<td>0.92</td>
<td>0.20</td>
<td>0.88</td>
<td>0.86</td>
<td>0.96</td>
</tr>
<tr>
<td>DINP</td>
<td>0.64</td>
<td>0.37</td>
<td>0.32</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td>DPHP</td>
<td>0.22</td>
<td>0.67</td>
<td>0.09</td>
<td>0.86</td>
<td>-0.15</td>
</tr>
<tr>
<td>Variance (%)</td>
<td>25.92</td>
<td>65.40</td>
<td>40.81</td>
<td>27.14</td>
<td>43.93</td>
</tr>
</tbody>
</table>

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### 3.4 Evaluating exposure risks to humans via inhalation

Fig. 6 and Table S3 depict mean EDIs values for nine sampling sites distinctly, when Fig. S7 illustrates mean EDIs for the campaign as a whole. The average concentrations of combined gas and particle phases (Table S8) were calculated for four PAEs (DMP, DEP, DBP and DIBP). These are PAE species for which the risk estimation coefficients were previously reported in literature (Liu et al., 2021; Zhang et al., 2019), and were employed to determine EDIs. The risk assessment was conducted upon different population groups in Shanghai (Table S7). According to Zhang et al. (2019), criteria: infants (0 to 2 years old), toddlers (3 to < 6 years old), adolescent (7 to < 16 years old), and adult (17 to < 70 years old) were uniquely used for Shanghai.

Taking all the samples as a single set, the sum of mean EDIs ranged from 1.04 to 27.95, 0.62 to 18.29, 0.71 to 19.68 and 0.32 to 8.77 ng kgBWt⁻¹day⁻¹ for toddlers, adolescents, infants, and adults, respectively. Thus, toddlers seemed to be highly exposed to PM₂.₅- PAEs among all population strata in Shanghai which aligns with findings from a previous
study by Zhang et al. (2019b). However, a different scenario in which the highest EDI was found for infants was reported before in Shanghai (Li et al., 2018). This could be attributed to the estimation parameters (e.g. population groups, inhalation rates) used by Li et al. (2018) deviate the reference values in this study. Adults demonstrated an exposure level that is relatively 2 to 3 times lower than the combined exposure level for infants, adolescents and toddlers together. The big disparity between groups might be due to young children's smaller body mass (Chen et al., 2018; Li et al., 2018; Zhang et al., 2019). In a study by Lu et al. (2018) in Shenzhen, after taking into consideration PAEs' bioaccessibility in PM$_{2.5}$, the total daily "high" and "typical" intakes dropped to 120 and 29 ng kgBW$^{-1}$, respectively, for female infants, and 113 and 27.3 ng kgBW$^{-1}$, respectively, for male infants (Lu et al., 2018). Site-wise, mean EDIs for DBP and DIBP were significantly higher than those of DMP and DEP in all sites (Fig. 6). The total mean EDIs for DIBP and DBP were roughly 53.45% - 53.48% and 44.15% - 44.18% of the total average EDIs for these four congeners. Previously in Shanghai, Zhang et al. (2019b) found the total EDIs for DBP equal to 23.1% - 62.8% of the total EDIs of the measured species. The most elevated total EDIs ranged from 8.25 to 27.95 ng kgBW$^{-1}$day$^{-1}$ for PT followed by QP (2.73-9.26 ng kgBW$^{-1}$day$^{-1}$) and TH (2.63-8.92 ng kgBW$^{-1}$day$^{-1}$), while the least range was found for HU (0.62-1.07 ng kgBW$^{-1}$day$^{-1}$). For DBP, the highest EDIs were found in samples from PT (9.95-9.96 ng/kg.day).
Fig. 6. Spatial profiles of average estimated daily intake for some major target congeners.
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<th>TH</th>
<th>JSH</th>
<th>FX</th>
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Table 5: Hazard quotients (HQs) and indexes (HIs) calculated for target PAEs possessing reference parameters for various sites. Details on Ref D, TDI and LD50 are presented in Table S7.
followed in decreasing order by TH (8.58-8.86 ng kgBWt\(^{-1}\)day\(^{-1}\)) > QP (3.54-3.65 ng kgBWt\(^{-1}\)day\(^{-1}\)) > JSH (2.73 - 2.82 ng kgBWt\(^{-1}\)day\(^{-1}\)) > PD (2.71-2.80 ng kgBWt\(^{-1}\)day\(^{-1}\)) > FX (2.31- 2.39 ng kgBWt\(^{-1}\)day\(^{-1}\)) > XUH (2.07- 2.14 ng kgBWt\(^{-1}\)day\(^{-1}\)) > CH (2.01-2.08 ng kgBWt\(^{-1}\)day\(^{-1}\)) > HU (0.26 ng kgBWt\(^{-1}\)day\(^{-1}\)), while for DIBP, the highest exposure was found in PT (17.17-17.72 ng kgBWt\(^{-1}\)day\(^{-1}\)) followed by QP (5.29 - 5.46 ng kgBWt\(^{-1}\)day\(^{-1}\)), FX (4.45 - 4.59 ng kgBWt\(^{-1}\)day\(^{-1}\)), JSH (4.32 - 4.46 ng kgBWt\(^{-1}\)day\(^{-1}\)), PD (4.09 - 4.22 ng kgBWt\(^{-1}\)day\(^{-1}\)), CH (2.82 - 2.92 ng kgBWt\(^{-1}\)day\(^{-1}\)), XUH (2.42 - 2.49 ng kgBWt\(^{-1}\)day\(^{-1}\)), HU (0.43-0.44 ng kgBWt\(^{-1}\)day\(^{-1}\)), and TH where DIBP was not detected in PM\(_{2.5}\) samples (Fig. 5, Table S3). EDIs associated with the inhalation of indoor air exceed EDIs related with exposure to outdoor air. The study by Zhang et al. (2014) on indoor PM\(_{2.5}\) samples form Tianjin reported the total EDIs for four PAEs namely DMP, DEP, DBP and DEHP, and the ranges were: infants (6.9-325.9 ng kgBWt\(^{-1}\)day\(^{-1}\)), toddlers (2.7-130 ng kgBWt\(^{-1}\)day\(^{-1}\)), and adults (1.6-76 ng kgBWt\(^{-1}\)day\(^{-1}\)), while the study by Zhang et al.(2019) on outdoor PM\(_{2.5}\) samples from 4 Chinese metropolis reported the total EDIs for the same PAE species, and the ranges were: infants (22.3-52.2 ng kgBWt\(^{-1}\)day\(^{-1}\)), toddlers (30.7-78 ng kgBWt\(^{-1}\)day\(^{-1}\)), and adults (9.3-23.5 ng kgBWt\(^{-1}\)day\(^{-1}\)). This affirms that for each age category, indoor EDIs surpass outdoor EDI values. In fact, owing to the occurrence of several sources of PAEs in indoor environments, the concentrations of some pollutants in air are quite higher as compared to those in outdoor air. Besides, the exposure frequencies are relatively higher for indoor microenvironments (0.88 and 0.79 for adults and children/toddlers, respectively) (EPA, 2002). In a study by Pei et al. (2013), the quantity of PAEs in outdoor air was nearly 125 times less than that in indoor air, which confirmed the presence of numerous sources indoors, and needless to say, a higher exposure and
health risk. In two Chinese cities of Xi’an and Tianjin, EDIs estimated for inhaling indoor 
air were 1.34×10^3 - 3.18×10^3 ng kgBWt^-1 day^-1 (Wang et al., 2014) and 1.55×10^2 - 6.64×10^2 
ng kgBWt^-1 day^-1 (Zhang et al., 2014).

In view of the whole campaign and taking into account all three approaches used to 
estimate HQ, the maximum HQs for infants, toddlers, teenagers and adults ranged from 
1.5×10^-1 for adolescents to 7.5×10^-1 for adults (Table 5). This is one order of magnitude 
higher than HQs reported earlier in Shanghai, where the maximum HQs for adults and 
children equalled to 1.0×10^-2 and 1.5×10^-2, respectively (Zhang et al., 2019b). The 
maximum HIs ranged from 7.5×10^-3 for adults (one order of magnitude less than HI 
reported by Zhang et al. (2019b) to 1.71×10^-2 for infants (Table 5). The dissimilarity 
seems sensible as DEHP that was formerly included in the calculation of HIs was not part 
of target species in this study. Even so, both HQ and HI values in this study were well 
below 1, which indicates that people exposed to these pollutants via inhalation can face no 
or mild health risks. Concerning the individual sampling locations, the highest HQ value 
was estimated for PT (9.9×10^-1) followed downwards by QP (3.7×10^-1) > PD and JSH 
(2.8×10^-1) > CH and XUH (2.1×10^-1) > TH (8.9×10^-2) > HU (8.3×10^-2) and FX (7.5×10^-2), whereas for HIs, the decreasing order was: TH (8.9×10^-2) > HU (8.3×10^-2) > FX (7.5×10^-2) 
> PT (7.0×10^-2) > JSH (5.11×10^-2) > PD (2.81×10^-2) > QP (2.61×10^-2) > XUH (2.1×10^-2) 
and CH (1.5×10^-2) (Table 5). As mentioned earlier in this study, to date, the reference 
values for estimating exposure to PAEs via inhalation are not yet available, and studies 
have been utilizing data for exposure through oral pathway as suggested by different 
entities notably USEPA and EFSA. In addition, some other organizations have proposed a 
consideration of bioavailability factors alongside exposure factors during risk evaluations
(Lu et al., 2018). Therefore, we can affirm that the used approach may overestimate the risk to humans as caused by the inhalation of PAEs. Therefore, we encourage the authorized organizations to determine benchmark values and consensual frameworks, which may be specifically used for assessing risks to humans as a result of exposure to PAEs via inhalation route.

4. Conclusion

A large-scale monitoring of PM$_{2.5}$-PAEs in ambient air from Shanghai was carried out in the current study. LC-MS/MS system was utilized for identification and quantification of 16 PAE species. In general, six compounds (DMP, DEP, DBP, DIBP, DINP, and DPHP) predominated in all samples, with two PAEs (DBP and DIBP) noticeably exhibiting higher concentrations, and four PAEs (DBP, DIBP, DINP, and DPHP) being ubiquitous in samples from all nine investigated site. The sum of aggregated daily concentrations (16$\sum$PAEs) demonstrated a reversed trend as compared to the previous surveys in Shanghai, with higher concentrations found in samples collected in colder periods. A non-simultaneous sampling together with a big discrepancy of sample sizes were primarily considered as the causes. Higher concentrations were relatively found in PM$_{2.5}$ samples collected from sites close to manufacturing plants and higher population density. A strong correlation was found between DBP and DIBP, which aligns with previous reports on outdoor PM$_{2.5}$ from China. Unlike previous studies in which PAE concentrations were correlated with a variety of meteorological factors, temperature was solely correlated with concentrations of DBP and $\sum$16PAEs in this study. The determined totals of daily average intakes (EDIs) unveiled a higher exposure to PM$_{2.5}$-PAEs for toddlers compared to other population groups, which is in accordance with a previous study in Shanghai. The range of
maximums HQs was one order of magnitude higher than the earlier study in Shanghai, and a range of maximum HIs was an order of magnitude inferior to that in the same study. This was attributed to DEHP which was not commonly measured, but, it was involved in calculations during the previous study. Generally, the determined HQs and HIs were quite below the reference benchmark values set by both EFSA and EPA. This could point out that people of Shanghai can face no or mild health threat posed by inhalation of PM$_{2.5}$-PAEs.

CRediT authorship contribution statement

Janvier Munyaneza: Methodology, conceptualization, data analysis, writing the draft; Md Faysal Hossain: Data quality checking, literature compilation, grammar check; Yusen Duan: Sampling, methodology; Xiu Guangli: Project supervision; Fund acquisition; Proof reading.

Conflicts of interest

The authors haven't found any conflict of interest to declare

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