



## Technical Note

# Phthalate Ester Concentrations, Sources, and Risks in the Ambient Air of Tianjin, China

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## ABSTRACT

Phthalate esters (PAEs) are excessively used in industries, which have posed a serious threat to human health. In this study, PAEs concentrations, sources, and risks in the ambient air of Tianjin, China were studied. The average concentrations of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di (2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DOP) in PM<sub>10</sub> were 0.18, 0.08, 2.24, 0.02, 10.79, and 0.10 ng m<sup>-3</sup>, respectively; in PM<sub>2.5</sub> the average concentrations were 0.14, 0.07, 1.93, 0.02, 6.26, and 0.05 ng m<sup>-3</sup>, respectively. DEHP and DBP were the predominant compounds identified, and the concentrations of PAEs in summer were significantly higher than those in winter. A coefficient of divergence analysis indicated that the PAE composition profiles in PM<sub>10</sub> and PM<sub>2.5</sub> were significantly different at the HD (Hedong) and HB (Hebei) sites; however, they were similar to each other at the NK (Nankai) and TT (Tieta) sites. A principal component analysis indicated that the emissions from cosmetics, personal care products, industrial processes, plasticizers, and medical devices may be major sources of PAEs in ambient PM in Tianjin. The daily intake (DI) of six PAEs from ambient air inhalation in Tianjin was estimated for five age groups. The results showed that the highest exposure dose was DMP in all age groups. Infants experienced the highest total DI of all six PAEs, whereas adults experienced the lowest total DI. The cancer risks from ambient air inhalation exposure were also estimated on the basis of DEHP concentrations. Although the risks for all population groups were below the U.S. Environmental Protection Agency threshold of 10<sup>-6</sup>, our result underestimates the actual health risk because only ambient air inhalation exposure to DEHP was considered in this study. Additional studies are necessary to investigate the effects of long-term exposure to air pollution in Tianjin.

**Keywords:** Phthalate esters; Particulate matter; Principal component analysis; The cancer risks.

## INTRODUCTION

With its rapid economic development, China is facing severe air pollution problems, particularly concerning particulate matter (PM). PM<sub>10</sub> can penetrate deep into the respiratory system when inhaled, whereas PM<sub>2.5</sub> can penetrate farther into the lungs and reach blood circulation. Because of the severe health effects caused by PM, World Health Organization guidelines address the risks of PM exposure. The exact mechanisms of injury and the health risks of PM are unclear. Some studies found that the surface area and adsorption of organic compounds can increase the toxicity of PM, leading to inflammation, oxidative stress, and the activation of the innate immune system (Yang and Holgate, 2013); however, the biological mechanisms behind

underlying these factors require further research.

On their surface adsorbed contaminants may be dispersed in the air by particles (Gu *et al.*, 2010). Therefore, it is important and interesting to determine the concentrations of Phthalate esters (PAEs) in particles.

PAEs are mainly used as plasticizers for improving the flexibility and workability of polymeric materials. They are used in numerous polymer products and other consumer products such as flooring, wallpaper, toys, cosmetics, medical products, electronics, and auto parts (Afshari *et al.*, 2004; Duty *et al.*, 2004). Because of the weak intermolecular forces between PAEs and polymer products, PAEs can continuously leach and be released from products into the environment over time. Consequently, PAEs pose a considerable threat to human health because they are ubiquitous in food, soil, dust, air, and drinking water (Ji *et al.*, 2014).

Kong *et al.* (2013a) conducted detailed comparison of six PAE levels in ambient PM<sub>10</sub> and PM<sub>2.5</sub> of Tianjin in three seasons and focused on the influence of ambient temperature. Zhang *et al.* (2014) investigated the concentrations, characteristics and the daily intake of six PAE in indoor

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PM<sub>10</sub> and PM<sub>2.5</sub> from thirteen homes in Tianjin, China.

This study targeted six PAE compounds: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di (2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DOP). The aims of this study were to 1) determine the PAE concentrations in ambient PM<sub>10</sub> and PM<sub>2.5</sub> in Tianjin, China; 2) identify the differences in PAE composition in ambient PM<sub>10</sub> and PM<sub>2.5</sub> at different sites; 3) identify the possible sources of PAEs in ambient PM<sub>10</sub> and PM<sub>2.5</sub>; 4) estimate inhalation exposure to PAEs in ambient air in Tianjin, China; and 5) estimate the cancer risks of inhalation exposure to DEHP in ambient air in Tianjin, China.

## METHODS

### *Sampling Area and Methods*

In this study, four sites were selected to sample ambient PM<sub>10</sub> and PM<sub>2.5</sub> for measuring PAE concentrations (Fig. S1). Sampling was conducted January 21–30, 2014 and July 6–14, 2014. A total of 16 PM<sub>10</sub> and 16 PM<sub>2.5</sub> valid samples were collected at each sampling site during the two periods.

PM<sub>10</sub> and PM<sub>2.5</sub> samples were collected onto quartz filters (Ø = 90 mm, Pall Gelman Laboratory, Ann Arbor, MI, USA) by medium-volume samplers (model TH-15S, Tianhong Instrument Co., Ltd., Wuhan, China). The sampling time was a continuous 24-h period and the samplers operated at a flow rate of 100 L min<sup>-1</sup> with a 10-µm cut-point for PM<sub>10</sub> and a 2.5-µm cut-point for PM<sub>2.5</sub>. The samplers were carefully cleaned in a clean laboratory and placed on the rooftop of selected buildings.

Prior to sampling, the quartz filters were baked in an oven at 600°C for 2 h to remove any organic compounds that may have been present; they were then equilibrated in a temperature (22 ± 2°C) and relative-humidity-controlled (35 ± 1%) environment for 48 h before gravimetric analysis. The filters were weighed with a microbalance (Mettler Toledo, Co., Ltd., Switzerland) with a balance sensitivity of ± 0.010 mg. After sampling, the filters were folded in half, wrapped in aluminum foil, equilibrated, and weighed, after which the filters were stored in a refrigerator at -4°C before chemical analysis. Blank filters were assessed in the same way.

### *Chemical Extraction*

The use of any plastic instruments was prohibited in the process of this experiment. Milli-Q water was generated with an ultrapure water system (Millipore Express, Co., Ltd., USA). A KQ-300DE ultrasonic extractor (Shumei, Co., Ltd., Kunshan, China) and a WD-12 water bath nitrogen evaporator (Aosheng, Co., Ltd., Hangzhou, China) were used. All glassware were initially soaked in a mixture of potassium dichromate and sulfuric acid for 12 h, rinsed with Milli-Q water, baked at 400°C for 8 h, and rinsed with dichloromethane prior to use.

PAE standards, DMP, DEP, DBP, BBP, DEHP, and DOP, and the internal standards (benzyl benzoate) were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). The solutions of the six PAEs were prepared in dichloromethane at a concentration of 200 mg L<sup>-1</sup>, and the solutions of the internal

standards were prepared in dichloromethane at a concentration of 50 mg L<sup>-1</sup>. Filters were cut into pieces, inserted into a clean centrifuge tube with 10 mL of dichloromethane, and then extracted with an ultrasonic extractor for 15 min. The extracts were filtered into a clean, 25-mL centrifuge tube. The filter pieces were then extracted a second time with an additional 10 mL of dichloromethane. All extracts were collected in centrifuge tubes and transferred into concentration tubes after the volumes were reduced to approximately 5 mL by purified nitrogen; they were then concentrated to below 2 mL by purified nitrogen. After the internal standard solution was added, the volume was adjusted to 2 mL with dichloromethane. The extracts were finally transferred into autoinjection vials and stored in a refrigerator at -4°C.

### *Analytical Procedures*

The quantification of PAEs was performed with an Agilent 6890N gas chromatograph and an Agilent 5975B mass spectrometer (GC-MS). The ChemStation software package was used for data processing. Detected ions were generated by electron impact ionization and monitored in the EI-SIM selective mode. A 30 m × 0.25 mm fused silica capillary column (95% dimethyl-5% diphenylpolysiloxane) with a 0.25-µm-thick film was used for separation. The injector temperature was 250°C. The flow rate of the helium carrier gas (> 99.999% pure) was kept constant at 1.0 mL min<sup>-1</sup>. The oven temperature program was as follows: 100°C for 1 min, an increase of 8 °C min<sup>-1</sup> to 300°C, and then maintained at 300°C for 5 min. The interface, ion source, and quadrupole temperatures were maintained at 280°C, 250°C, and 150°C, respectively. The ionization mode was electron impact (70 eV). One microliter of the sample was injected into the GC-MS under the pulsed splitless mode with an inlet temperature of 250°C. For quantification, the GC-MS was operated in the selective ion monitoring mode to detect the following masses: m/z = 77.163 (DMP), m/z = 149.177 (DEP), m/z = 149.223 (DBP), m/z = 91.149 (BBP), m/z = 149.167 (DEHP), and m/z = 149.279 (DOP). Quantification was performed using calibration curves based on the response factor to the internal standard benzyl benzoate. The calibration curves were created with concentrations ranging from 0.05 to 1.0 mg L<sup>-1</sup>. The correlation coefficients for the six PAEs ranged from 0.99923 for DOP to 0.99988 for DBP. The recovery of PAEs in samples was evaluated by spiking a known amount of standard mixture with a concentration similar to those in real samples onto the blank sampling filter, and passing this mixture through the entire analytical procedure. The overall recoveries of standard mixtures for DMP, DEP, DBP, BBP, DEHP, and DOP in the spiked blank matrices ranged from 77.62% to 116.41%. Instrumental limits of detection (LODs) were set on the basis of a signal-to-noise ratio of 3:1. The LODs for DMP, DEP, DBP, BBP, DEHP, and DOP were 0.016, 0.004, 0.002, 0.007, 0.003, and 0.003 ng m<sup>-3</sup>, respectively.

## RESULTS AND DISCUSSION

### *PAE Concentrations in PM<sub>10</sub> and PM<sub>2.5</sub>*

The PAE concentrations in ambient PM<sub>10</sub> and PM<sub>2.5</sub> in Tianjin are shown in Table 1. The average concentrations

**Table 1.** PAEs concentrations in ambient PM<sub>10</sub> and PM<sub>2.5</sub> in Tianjin (ng m<sup>-3</sup>).

Periods	PAEs	PM <sub>10</sub>				PM <sub>2.5</sub>			
		Mean ± S.D.	Median	Min	Max	Mean ± S.D.	Median	Min	Max
Winter	DMP	0.174 ± 0.151	0.121	0.041	1.321	0.136 ± 0.201	0.098	0.030	0.896
	DEP	0.056 ± 0.042	0.048	0.024	0.270	0.052 ± 0.026	0.044	0.018	0.147
	DBP	1.446 ± 0.867	1.193	0.641	4.077	1.327 ± 0.643	1.128	0.508	3.149
	BBP	0.006 ± 0.006	0.004	0.001	0.031	0.005 ± 0.004	0.003	0.001	0.017
	DEHP	3.704 ± 3.865	2.635	0.786	19.138	2.630 ± 1.455	2.537	0.256	6.137
	DOP	0.046 ± 0.183	0.012	0.003	1.169	0.013 ± 0.007	0.012	0.001	0.031
	∑ <sub>6</sub> PAEs	5.431 ± 4.574	3.946	2.371	23.953	4.163 ± 1.927	3.879	1.669	9.782
Summer	DMP	0.144 ± 0.043	0.137	0.078	0.230	0.192 ± 0.063	0.195	0.079	0.285
	DEP	0.084 ± 0.032	0.070	0.046	0.166	0.113 ± 0.039	0.114	0.046	0.197
	DBP	2.680 ± 1.678	2.192	0.573	6.382	3.221 ± 1.720	2.810	0.965	7.643
	BBP	0.049 ± 0.117	0.016	0.005	0.663	0.029 ± 0.062	0.018	0.008	0.366
	DEHP	10.805 ± 3.784	10.747	2.656	21.621	19.65 ± 12.348	15.695	5.584	52.503
	DOP	0.090 ± 0.119	0.039	0.010	0.431	0.177 ± 0.190	0.067	0.008	0.602
	∑ <sub>6</sub> PAEs	13.851 ± 3.994	13.530	5.137	24.201	23.38 ± 12.330	19.054	9.432	54.874

of DMP, DEP, DBP, BBP, DEHP, and DOP in Tianjin were 0.18, 0.08, 2.24, 0.02, 10.79, and 0.10 ng m<sup>-3</sup> in PM<sub>10</sub> and 0.14, 0.07, 1.93, 0.02, 6.26, and 0.05 ng m<sup>-3</sup> in PM<sub>2.5</sub>, respectively. Among the six PAEs analyzed, DEHP and DBP were the dominant compounds found in PM<sub>10</sub> and PM<sub>2.5</sub> (Fig. S2), which can be attributed to their high level of use; DEHP and DBP are the main additives used in industrial production (Wang *et al.*, 2008). Many studies have shown that DEHP and DBP were the most abundant PAEs in ambient PM (Zeng *et al.*, 2006; Wang *et al.*, 2008; Shao *et al.*, 2009; Kong *et al.*, 2013a). Table S1 shows a comparison of PAE concentrations in Tianjin among different studies. The total PAE concentration of indoor PM<sub>10</sub> was 32 times higher than that of the ambient PM<sub>10</sub> measured in this study, indicating that sources of PAEs exist mainly in indoor environments. The values determined in the study conducted by Kong *et al.* (2013a) in ambient air in Tianjin were much higher than those measured in this study. Thus, a detailed emission inventory for PAEs is needed to better understand the diversities of their levels in the atmosphere.

PAE concentrations in summer were significantly higher than those in winter (Fig. 1). A similar pattern was reported for other cities in China (Wang *et al.*, 2006). PAEs are semivolatile compounds not covalently bound to polymeric matrixes. Therefore, elevated temperatures in ambient air can result in an increased release from plastic products, thus contributing to high levels of PAEs during summer (Clausen *et al.*, 2012; Zhang *et al.*, 2014).

#### Coefficient of Divergence Analysis

The similarities between PAE composition profiles in PM<sub>10</sub> and PM<sub>2.5</sub> at different sites could be identified according to the coefficient of divergence (CD), a self-normalizing parameter used to measure the spread of data points for two datasets. The parameter was determined as follows:

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left( \frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}} \right)^2} \quad (1)$$

where  $j$  and  $k$  are the two profiles for the sampling sites,  $p$  is the number of investigated components, and  $x_{ij}$  and  $x_{ik}$  represent the average mass concentrations of chemical component  $i$  for  $j$  and  $k$ . If  $CD_{jk}$  approaches zero, the two compared composition profiles are determined to be significantly similar; and if  $CD_{jk}$  approaches one, the profiles are deemed significantly different (Zhang and Friedlander, 2000; Kong *et al.*, 2013b). Wongphatarakul *et al.* (1998) suggested that a CD value of 0.269 reflected the similarity between particles of two cities.

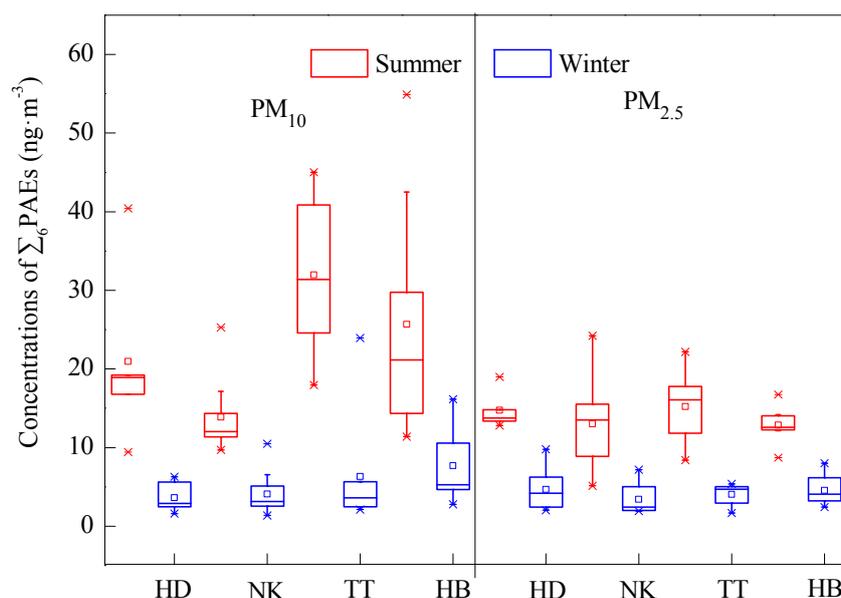
Scatter plots of PAE component mass concentrations for  $j$  against  $k$  are shown in Fig. S3. For both PM<sub>10</sub> and PM<sub>2.5</sub>, the  $CD_{jk}$  values for the HD and HB sites were all higher than 0.30, indicating significant differences in PAE compositions among the two sizes of ambient PM. By contrast, the  $CD_{jk}$  values for the NK and TT sites were all lower than 0.20, indicating that the PAE compositions in PM<sub>10</sub> and PM<sub>2.5</sub> were similar at the two sites. Therefore, the PAE compositions in PM<sub>10</sub> and PM<sub>2.5</sub> at different sites were different, indicating the influence of different sources.

#### Source Identification by Principal Component Analysis

To identify the possible sources of PAEs in ambient PM in Tianjin, a principal component analysis (PCA) was performed using SPSS software. PCA can simplify the interpretation of complex systems and reduce a large set of variables to a few new factors. Each of these factors can be identified as either an emission source or a chemical interaction (Wang *et al.*, 2012; Wu *et al.*, 2014).

In this study, a PCA with a varimax normalized rotation was performed. Considering that  $n > 30 + (V + 3)/2$  (where  $n$  is the number of samples and  $V$  is the number of variables) (Callén *et al.*, 2009) and the relatively limited numbers of samples available for each period and at each site in this study, the samples of PM<sub>10</sub> and PM<sub>2.5</sub> from all sites were combined for the analysis.

For PM<sub>10</sub>, two factors explaining 61.45% of the data variance were obtained (Fig. 2(a)). Factor 1, including DMP and DEP, accounted for 34.22% of the variance. DMP and DEP may have come from emissions of cosmetic and personal



**Fig. 1.** Concentrations of  $\Sigma_6$ PAEs in ambient  $PM_{10}$  and  $PM_{2.5}$  in summer and winter. Box-whisker plots representing the 5th, 25th, 50th, 75th and 95th percentiles, as well as the mean (open squares).

care products (Kong *et al.*, 2013a). Factor 2 showed a higher load of DEHP and DOP, which are tracers for thermal power stations, power plants, industrial boilers, cement plants, and coke ovens (Kong *et al.*, 2013a).

For  $PM_{2.5}$ , three factors were extracted that explained 34.26%, 21.57%, and 17.44% of the total variance (Fig. 2(b)). The loads of the first factor corresponded to those for  $PM_{10}$ . Factor 2 was loaded heavily with DOP, indicating the influence of plasticizers in the polymer industry and the production of vinyl flooring, synthetic leather, inks, adhesives, and food products (Hens and Caballos, 2003). Factor 3 was associated with DEHP, which is used for producing medical devices such as bags and tubing used for blood transfusion, kidney dialysis, or antibiotics delivered intravenously.

Tianjin, the largest harbor of Northern China, is a fast-growing and economically developed city. It has built a comprehensive industrial system including integrated machinery, electronics, petroleum and chemicals, metallurgy, textiles and vehicles. Emissions from cosmetics, personal care products, industrial processes, plasticizers, and medical devices may be major sources of PAEs in ambient PM in Tianjin.

#### Human Exposure to PAEs via Inhalation

PAE concentrations in the gas phase,  $c_{g,10}$  ( $ng\ m^{-3}$ ), can be calculated from the PAE concentrations in the particle phase by using Eq. (2) from our previous study (Zhang *et al.*, 2013):

$$c_{g,10} = \frac{F_{10} / PM_{10}}{K_p} \quad (2)$$

where  $F_{10}$  is the PAE concentration in  $PM_{10}$  ( $ng\ m^{-3}$ ),  $PM_{10}$  is the median concentration of ambient  $PM_{10}$  during the sampling period ( $214.29\ \mu g\ m^{-3}$ ),  $K_p$  is the particle-gas

partition coefficient ( $m^3\ \mu g^{-1}$ ).

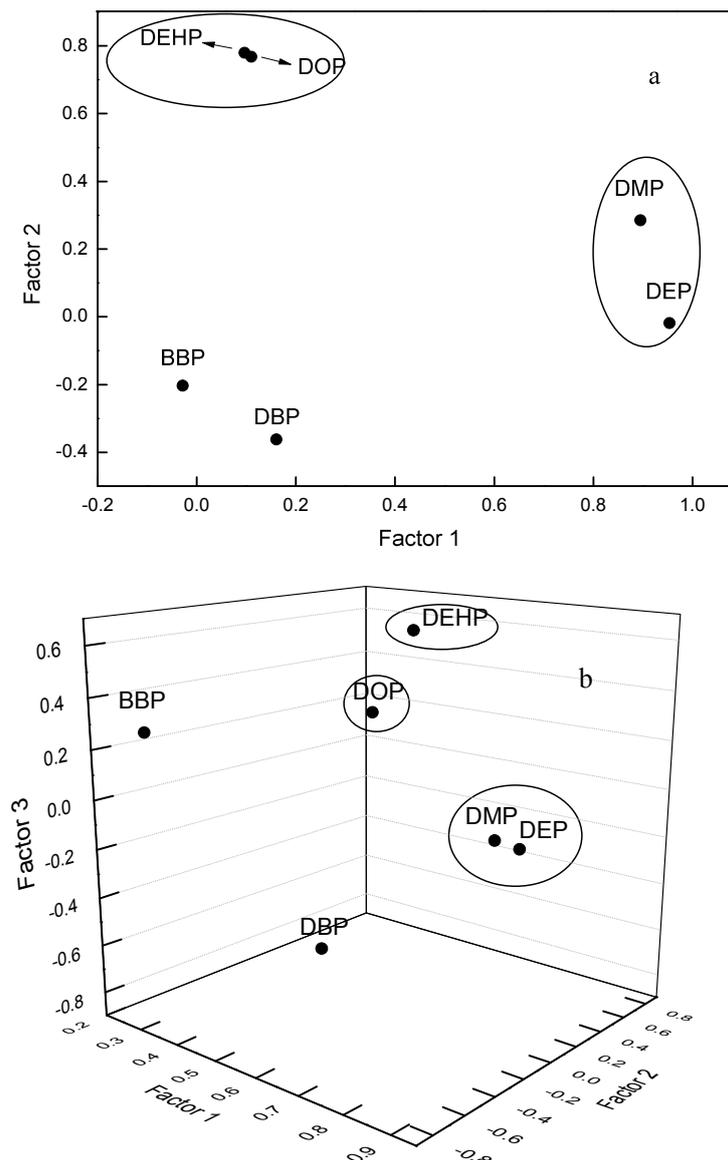
The measured median concentrations of the six PAEs in the particle phase ( $PM_{10}$ ) and the calculated values of the six PAEs in the gas phase are listed in Table S2.

The daily intake (DI,  $ng\ kg^{-1}\ day^{-1}$ ) of PAEs through ambient air inhalation can be estimated using Eq. (3) (Zhang *et al.*, 2013). Because body weight and inhalation rates vary with age, the DIs of PAEs were estimated over five age groups: infants (< 1 year), toddlers (1–3 years), children (4–10 years), adolescents (11–17 years), and adults ( $\geq 18$  years) (Zhang *et al.*, 2013).

$$DI = \frac{C_{air} \cdot IR \cdot ET}{BW} \quad (3)$$

where  $C_{air}$  is the median concentration (particle-phase + gas-phase) of PAEs in air ( $ng\ m^{-3}$ ),  $IR$  is the inhalation rate ( $m^3\ day^{-1}$ ),  $ET$  is the exposure fraction, and  $BW$  is body weight (kg) (Zhang *et al.*, 2013).

The median values of estimated DIs of six PAEs from the inhalation of ambient air for five age groups are shown in Table 2. The DI values for DMP and DBP were higher than for DEP, BBP, DEHP, and DOP in all age groups. The DIs in decreasing order were: DMP, DBP, DEP, DEHP, BBP, and DOP. The total DI of the sum of the six PAEs ( $\Sigma_6$ PAEs) for infants, toddlers, children, adolescents, and adults were 5.975, 4.647, 4.367, 1.754, and 1.402  $ng\ kg^{-1}\ day^{-1}$ , respectively. In contrast, the DI of the  $\Sigma_6$ PAEs from the inhalation of indoor air for the five age groups were 664.332, 265.062, 249.067, 194.982, and 155.850  $ng\ kg^{-1}\ day^{-1}$ , respectively (Zhang *et al.*, 2013). The DIs of the  $\Sigma_6$ PAEs from the inhalation of air (indoor and ambient) for the five age groups were 670.307, 269.709, 253.434, 196.736, and 157.252  $ng\ kg^{-1}\ day^{-1}$ , respectively. The DIs of the  $\Sigma_6$ PAEs from the inhalation of air (indoor and ambient) decreased in the



**Fig. 2.** Principal component analysis results for PAEs in ambient PM<sub>10</sub> (a) and PM<sub>2.5</sub> (b) of Tianjin. From PCA analysis, two factors were extracted for data about PAEs in PM<sub>10</sub> while three factors were extracted for data about PAEs in PM<sub>2.5</sub>.

**Table 2.** Estimated daily intakes of six PAEs from ambient air inhalation (median values as ng kg<sup>-1</sup> day<sup>-1</sup>) for various age groups in Tianjin, China.

Age groups	DMP	DEP	DBP	BBP	DEHP	DOP	Total
infants	3.875	0.422	1.338	0.002	0.337	0.002	5.975
toddlers	3.014	0.328	1.041	0.002	0.262	0.002	4.647
children	2.832	0.308	0.978	0.002	0.246	0.001	4.367
adolescents	1.137	0.124	0.393	0.001	0.099	0.001	1.754
adults	0.909	0.099	0.314	0.001	0.079	0.000	1.402

following order: infants, toddlers, children, adolescents, and adults. There was also a downward trend in the median DI values from infants to adults for all six PAEs.

Reference doses (RfDs) for DIs established by the United States Environmental Protection Agency (U.S. EPA) are 800, 100, 200, 20, and 400 μg kg<sup>-1</sup> day<sup>-1</sup> for DEP, DBP, BBP, DEHP, and DOP, respectively (Guo *et al.*, 2011; Zhang *et*

*al.*, 2013). The tolerable daily intake (TDI) suggested by the European Food Safety Authority for DBP, BBP, DEHP, and DOP are 100, 200, 50, and 370 μg kg<sup>-1</sup> day<sup>-1</sup>, respectively (Guo *et al.*, 2011; Zhang *et al.*, 2013). The estimated DI values for the PAEs (except for DBP) of all five age groups from the inhalation of air (indoor and ambient) in Tianjin were lower than the RfD and TDI values.

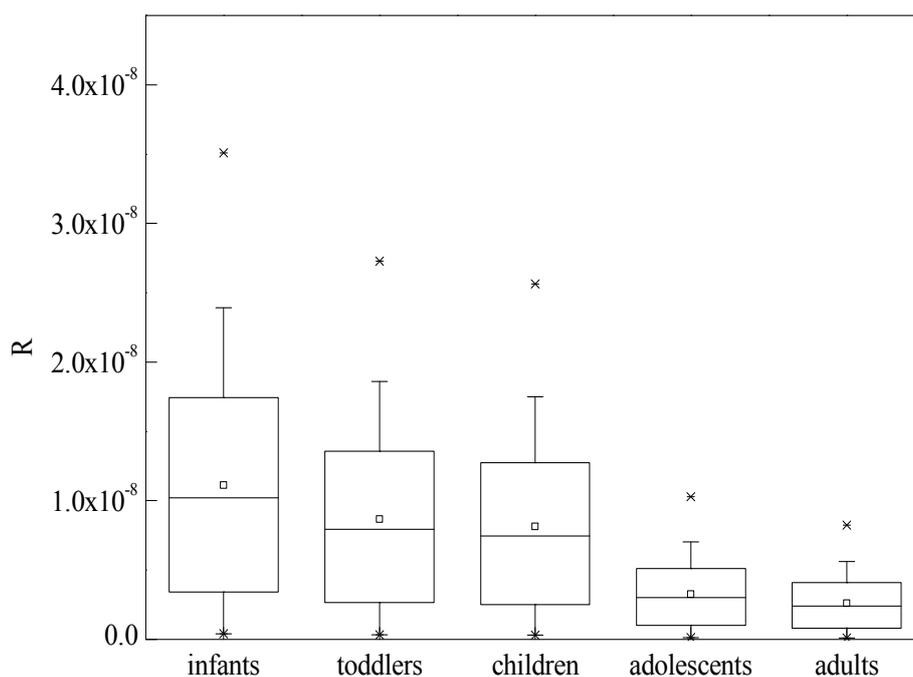


Fig. 3. Cancer risks of DEHP in ambient air exposure on people from different age groups.

### Cancer Risk

The toxicity of PAEs began to receive widespread attention as early as the 1960s. Numerous studies have found that PAEs are a class of endocrine-disrupting chemicals that can affect the reproductive system of laboratory animals (Earl Gray Jr. *et al.*, 2000; Borch *et al.*, 2006). However, only DEHP has been reported to possess carcinogenic potency (Guyton *et al.*, 2009). Studies conducted by the U.S. EPA have shown that DEHP poses a strong cancer risk at low concentrations (U.S. EPA, 1997). The upper-limit incremental cancer risk of DEHP through ambient air inhalation is calculated using Eq. (4) (U.S. EPA, 2000):

$$R = q \times DI \times 10^{-6} \quad (4)$$

where  $q$  is the 95% upper confidence limit of the linearized cancer slope factor of the dose-response function ( $(\text{mg kg}^{-1} \text{ day}^{-1})^{-1}$ ), which is 0.014 for DEHP (U.S. EPA, 1997), and  $DI$  is the DI from ambient air inhalation ( $\text{ng kg}^{-1} \text{ day}^{-1}$ ).

The calculated cancer risks caused by DEHP exposure from ambient air inhalation for the different age groups are presented in Fig. 3. The estimated cancer risks for all population groups were between  $9.75 \times 10^{-11}$  and  $3.51 \times 10^{-8}$ , which are below the human body cancer risk limit of  $1 \times 10^{-6}$  defined by the U.S. EPA. Thus, the cancer risk associated with the inhalation of DEHP in the ambient air in Tianjin is low. The cancer risk values for all population groups in decreasing order were: infants, toddlers, children, adolescents, and adults. Ambient air DEHP exposure was less harmful to adolescents and adults, and the cancer risks decreased gradually with age. A similar trend was also reported for cancer risks associated with PAE exposure from inhalation in Hangzhou (Pei *et al.*, 2013).

### CONCLUSIONS

The PAEs measured in the present study were ubiquitous in ambient  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  in the urban areas of Tianjin, China. DEHP and DBP were the major compounds found in PM samples, and the PAE concentrations in summer were significantly higher than those in winter. PAE compositions in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  at different sites were different, reflecting the influence of different sources.

The major sources of PAEs in ambient air were diverse and may include emissions from cosmetics, personal care products, industrial processes, plasticizers, and medical devices as identified by principal component analysis. Other possibly relevant intake pathways, such as dietary ingestion, settled dust ingestion, and occupational exposure, were not taken into consideration in this study. Diet was reported to be the major source of human exposure to PAEs in the United States, European Union, and Japan (Wormuth *et al.*, 2006; Itoh *et al.*, 2007; Guo and Kannan, 2011). However, air, water, and diet were found to be the main sources of human exposure to PAEs in Tianjin, and the PAE contributions for all exposure sources decreased in the following order: air (43%–50%), drinking water (24%–34%), foodstuffs (19%–24.5%), dust (3%–5.5%), and soil ( $< 0.2\%$ ) (Ji *et al.*, 2014). As inhalation accounted for a large percentage of the total intake, the potential danger for additive or synergistic effects between particles and PAEs must be considered.

The estimated cancer risks for all population groups were below the U.S. EPA threshold of  $10^{-6}$ . Additional studies are necessary to investigate the effects of long-term exposure to air pollution in Tianjin, a rapidly developing economic center in Northern China. Furthermore, the management of PAE sources should be strengthened by the local government.

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## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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