

# The characteristics of atmospheric phthalates in Shanghai: A haze case study and human exposure assessment

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## ABSTRACT

While phthalates in indoor environments are extensively studied, reports on phthalates in outdoor air, particularly their associations with haze weather events are rare. Phthalates, especially dimethyl phthalate, are known to react with criteria air pollutants contributing to the formation of secondary organic aerosols. This study investigated phthalates levels in the atmosphere in Shanghai with a focus on their associations with different air quality weather events. The air quality during the study period was classified into three levels: non-haze, light pollution and moderate pollution. Phthalates levels were found to be lower in non-haze weather events (236 ng/m<sup>3</sup>) and higher in moderate pollution weather events (up to 700 ng/m<sup>3</sup>). Meteorological factors of relative humidity and wind speed had an inverse relationship with phthalates levels. Particulate matter had a positive correlation with phthalates levels. Hydroxyl radical initiated photo-reaction of dimethyl phthalate was evident by its inverse relationship with total atmospheric oxidant (O<sub>3</sub> + NO<sub>2</sub>), indicating that dimethyl phthalate could be one of the precursors of secondary organic aerosol causing haze weather events. Daily intake of phthalates through exposure to outdoor air is estimated to be relatively minor; children intake remains higher on a body weight basis. This is the first study demonstrating the relationship of phthalates and different air quality conditions in haze weather events. The knowledge contributes to our understanding on the cause of haze weather events in China and elsewhere.

## 1. Introduction

Phthalates are one of major chemicals used in commerce, with several million tons produced every year. Phthalates have been mainly used as plasticizers to improve flexibility and workability of polymeric materials in consumer products and building materials. They are also used as emulsifiers in cosmetics (Feng et al., 2013), or as additives in various products and they are not chemically bound to the product matrix. Therefore, they can escape from the products into the environment. As such, phthalates have become ubiquitous environmental contaminants (Bertelsen et al., 2013) that are also present in humans (Guo et al., 2011). Phthalates are endocrine disruptors showing estrogenic activity in humans including effects on male reproductive disorders like infertility, reduced sperm motility and decreased sperm counts (Bang et al., 2012). They could also cause asthma and allergic symptoms in humans (Bornehag et al., 2004). Some phthalates are

classified as priority pollutants by the United States Environmental Protection Agency (US EPA) based on their carcinogenicity. For example, di(2-ethylhexyl) phthalate (DEHP) is classified as a probable human carcinogen (class B2), butylbenzyl phthalate (BBP) as a possible carcinogen (class C); di-*n*-butyl phthalate (DnBP), diethyl phthalate (DEP) and dimethyl phthalate (DMP) are not classifiable as to human carcinogenicity (Class D) because of inadequate human and animal evidence of carcinogenicity (Staples et al., 1997; Sampath et al., 2017).

Haze weather events are frequently occurring in recent years and are a public health concern in China. Haze can be largely attributed to the formation of the suspended fine particulate matter (PM) in the atmosphere, and organic compounds are one of the most important compositions in atmospheric PM (Sun et al., 2011; Xu et al., 2017). While some criteria air pollutants, as defined by Environmental Protection Agency of the United States (<https://www.epa.gov/criteria-air-pollutants>) such as atmospheric PM, ground level ozone (O<sub>3</sub>), sulfur

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dioxide (SO<sub>2</sub>), carbon monoxide (CO) and nitrogen dioxide (NO<sub>2</sub>) are routinely monitored (He et al., 2017), measurements of organic compounds in haze weather events are largely limited to a general organic content in PM, while measurements of individual organic pollutants are focused on polycyclic aromatic hydrocarbons (PAHs) (Zhao et al., 2014). Only limited information about the characteristics of airborne phthalates, especially during haze events in China (Ma et al., 2014; Zhang et al., 2014; Wang et al., 2008) is available.

It is known that some phthalates such as DMP in the atmosphere can undergo photochemical reactions in the presence of atmospheric free radicals such as hydroxyl (OH) (Ma et al., 2014; Han et al., 2014; An et al., 2014). Thus, a better understanding of phthalates in the atmosphere and its possible contribution to the formation of haze weather events would help inform potential impact on environmental and human health issues. Shanghai is one of the major metropolitan cities in the world with a high population density and, like other cities in China, has frequent occurrence of haze weathers. This provides an opportunity to study phthalates in the atmosphere in both haze and non-haze weather events.

The aims of the study were (1) to measure temporal variations of phthalates with changing haze weathers in an urban area in Shanghai, (2) to analyze the correlation of phthalates with meteorological data such as air temperature, relative humidity and wind speed, and with criteria air pollutants like PM, O<sub>3</sub>, and NO<sub>2</sub>, and (3) to estimate inhalation exposure to phthalates for the general population exposed to atmospheric phthalates in urban areas in Shanghai. Six commonly monitored phthalates, namely DMP, DEP, DnBP, BBP, DEHP and di-*n*-octyl phthalates (DnOP) were included in the study (Table 1).

## 2. Material and methods

### 2.1. Chemicals and materials

A standard solution of EPA 506 phthalate mix (1000 µg/ml, in iso-octane) was purchased from Sigma-Aldrich (Shanghai, China). All calibration standard solutions were prepared by series dilutions in hexane (HPLC graded, Sigma-Aldrich). Nitrogen gas (99.999% purity) was used for dispersing chemicals spiked in the thermal desorption (TD) tubes, and for conditioning thermal desorption tubes and for operating switching valves of the thermal desorption unit. Helium gas (99.999% purity) was used for dry purging, thermal desorption and GC/MS analysis.

TD tubes (6 mm internal diameter (I.D.) × 100 mm length) that contained (from weak to strong absorbent) 10 mm of Quartz wool, 10 mm of Tenax TA (35/60 mesh) and 10 mm of Carbograph 5TD (40/60 mesh) were bought from Markes International Ltd (Liantrisant, UK). Prior to their initial use, tubes were conditioned at 320 °C for 5 h under nitrogen gas, at a flow rate of 100 ml/min, using a tube conditioning system (BTH-10, TSKM Ltd, Beijing, China). For subsequent uses, tubes were subjected to a clean-up at 320 °C for 1 h at a flow rate of 100 ml/min. Once cleaned, the tubes were sealed with long-term storage caps, wrapped in aluminum foil, and stored in a refrigerator at 4 °C.

**Table 1**

Target phthalates with their retention time (RT) on GC, quantitation ion (T) and qualifier ion (Q), along with instrument detection limit (IDL), repeatability (RSD, %, n = 6), and desorption recovery (DR, %).

Compounds (abbreviation)	RT (min)	T (m/z)	Q (m/z)	IDL (ng/tube)	RSD (%)		
					5 ng/tube	125 ng/tube	125 ng/tube
Dimethyl phthalate (DMP)	18.79	163.0	77.0	0.19	6.3	1.1	99.8
Diethyl phthalate (DEP)	19.63	149.0	105.1	0.75	25.2	9.7	96.8
Di- <i>n</i> -butyl phthalate (DnBP)	22.07	149.0	105.1	0.18	6.0	2.3	97.8
Benzyl butyl Phthalate (BBP)	26.43	149.0	91.0	0.41	13.7	1.6	100
Di-2-ethylhexyl phthalate (DEHP)	28.08	149.0	167.0	0.27	9.1	3.4	100
Di- <i>n</i> -octyl phthalate (DnOP)	30.13	149.0	207.0	0.25	8.5	2.1	100

### 2.2. Sampling of outdoor air

Airborne phthalates (gas phase + particulate phase) were collected from December 5 to December 15, 2016. The TD tube was placed about 1 m outside an 8th floor window (approximately 20 m above ground level) of a building at Shanghai Academy of Environment and Sciences (SAES) in Shanghai (latitude 31°17' N, longitude 121°44' E). The building is situated an urban area of mixed residential and office buildings and traffic routes in the city and there is no known industrial pollution sources nearby. Pocket air sampling pumps (210–1000 MH, SKC, Houston, TX, USA) were used for sample collection at a nominal flow rate of 100 ml/min. The actual flow rate of the pump was calibrated using a digital flow meter (Sensidyne Gilian Gilibrator, Petersburg, FL, USA) before and after sampling. All samples were analyzed within a few hours after sampling.

Meteorological data and criteria pollutants data of NO<sub>2</sub>, O<sub>3</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> were downloaded from the closest monitoring station of China Environmental Monitor Center (CEMC) that is located in the same area (latitude 31°19' N, longitude 121°44' E).

### 2.3. TD-GC/MS analysis

All analyses were performed on a TD-GC/MS system consisted of a thermal desorber equipped with a multi-tube auto sampler (TD-100, Liantrisant, UK), a gas chromatograph (Trace 1300, Thermo Fisher Scientific Inc., Waltham, MA, USA) and a mass spectrometer (BenchTOF-Evolve, Liantrisant, UK). Primary thermal desorption was carried out at 320 °C at a flow rate of 50 ml/min for 20 min. The desorbed analytes were collected in a cold trap set at –10 °C for retaining the desorbed analytes. When the primary desorption was completed, the trapped analytes were released to GC column by rapidly heating the cold trap to 320 °C and hold for 8 min at 12 ml/min. The chromatographic separation of phthalates was carried out in a HP-ULTRA 2 capillary column (50 m length × 0.32 mm I.D. × 0.5 µm film thickness, Agilent Technologies, Folsom, CA, USA). Helium was used as carrier gas. The GC column was operated at a constant flow of 3 ml/min. The MS was operated in the electron impact (EI, 70 eV) ionization mode. The ion source and transfer line temperatures were both set at 300 °C. Signals of MS were recorded in full scan mode with a scan range of 35 m/z to 500 m/z. The GC oven temperature was first set at 50 °C for 8 min during heating of cold trap, then increased to 100 °C at 15 °C/min, and further to 260 °C at 20 °C/min and hold for 6 min, the temperature was further raised to 300 °C at 50 °C/min and hold for 10 min. Ion m/z 163 was used for the quantification of DMP, and m/z 149 for DEP, DnBP, BBP, DEHP and DnOP (Table 1). External standard quantification method was used to determine the amount of phthalates in the samples.

### 2.4. Quality assurance and quality control

All plastic equipment and tools were avoided during the whole sampling and analysis process. Instrument detection limit (IDL, ng/

tube) was estimated using replicates spiked at 1 ng/tube and at 5 ng/tube. Detection of a peak in the samples was based on a signal to noise ratio of 3 or greater. IDLs were below 0.5 ng/tube for all phthalates, except for DEP (0.75 ng/tube). Repeatability was evaluated by assessing the relative standard deviation (RSD) of replicate tubes spiked at two different levels (5 ng/tube and 125 ng/tube) per individual phthalate (Table 1). RSD values at 5 ng/tube level were below 14%, while RSD values at high spiking level of 125 ng/tube were below 4%, except for DEP, whose RSD was at 25% and 10%, respectively. To check if there was any background contamination during the storage, sampling and preparation of samples, seven blanks were brought to the sampling site, connected to and then disconnected from the pump without flow and analyzed throughout the study. Among target phthalates, no detected levels were observed for BBP, DEHP and DnOP in the blanks. The average blank level of DMP and DnBP was 0.69 and 2.69 ng/tube respectively, while the blank level of DEP had a higher average level of 24.5 ng/tube (ranging from 6.9 to 105 ng/tube). Reported values in the samples were blank corrected for these three phthalates by subtracting the values with the average blank value.

To determine desorption recovery (DR), the same sample tube that was spiked at high level (125 ng/tube) was analyzed two times. There was no residue detected for BBP, DEHP and DnOP in the second run, and only a small quantity was detected for DMP, DEP and DnBP in the second run. DR in Table 1 therefore was defined as the percentage of amount detected from the first sample run divided by the sum of amount from the first and second sample runs, which was in the range of 96.8%–100%. Calibration was performed in a linear range of 0.2–125 ng/tube for each analyte (0.2, 1, 5, 25, 125 ng/tube) with a coefficient of determination ( $r^2$ ) values of the regression greater than 0.9807 for all target compounds, except for DEP ( $r^2 = 0.9035$ ).

### 3. Results and discussion

#### 3.1. Levels of phthalates in outdoor air under different air quality weathers

Ambient air quality in cities across China is monitored and reported daily using the air quality index (AQI) that has been officially used since 2012. AQI was reported based on the highest individual air quality index (IAQI) among the following criteria air pollutants: SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, CO, PM<sub>2.5</sub> and PM<sub>10</sub>. AQI in China defines pollution levels with the following scale: 0–50: excellent, 51–100: good, 101–150: light pollution, 151–200: moderate pollution, 201–300: severe pollution and > 300: very serious pollution (<http://kjs.mep.gov.cn/hjbhzbz/bzwb/dqjhjbh/jcgfffbz/201203/W020120410332725219541.pdf>). For the purpose of the discussion in this paper, we combined the AQI values of 0–50 and 51–100 into a non-haze category. Between December 5 and December 15, 2016, the AQI values in Shanghai varied between 50 and 200, the corresponding weather was (1) non-haze, (2) light pollution and (3) moderate pollution. On some days, pollution levels were in

transition from one level to another, while on other days the pollution level stayed in the same haze category (Fig. 1).

Phthalates in both gaseous and particle phases were collected in a single TD tube. Therefore, the total amount of airborne phthalates (amount in gaseous and particle phases) was determined and reported. The sum of the six measured phthalates ( $\Sigma$ PAAE) varied from 236 ng/m<sup>3</sup> in non-haze weather to 700 ng/m<sup>3</sup> in moderate pollution weather (Fig. 1). Individual phthalates followed a similar trend. The average percentage of individual phthalates in the samples varied quite a lot among the air samples; they were 9–46%, 8–38%, 8–33%, 10–26%, 7–24% and 0–20% for DEHP, DEP, DMP, DnBP, DnOP and BBP, respectively.

A positive relationship between airborne phthalate levels and pollution levels in air was noticed. For example, during the study period there were two changing weather events in air quality, both from moderate pollution to non-haze, where phthalates levels decreased in both cases (Fig. 1, indicated by arrows). A Spearman's rank-order correlation test was used to examine correlations between phthalate levels and air quality. For transit weather from one haze level to another level (for example, light pollution to moderate pollution), average AQI values of the two was used in the correlation. Among all pollutants, DnBP ( $r = 0.76$ ,  $p = 0.028$ ) and  $\Sigma$ PAAE ( $r = 0.78$ ,  $p = 0.021$ ) showed statistically significant correlation, and DEHP ( $r = 0.64$ ,  $p = 0.086$ ) a weak correlation. The absolute levels of phthalates in these two events were not the same, but both exhibited similar decreasing trend of phthalate levels. The difference in absolute levels could be attributed to the fact that AQI was reported considering all monitored criteria air pollutants for computing the AQI values and therefore similar AQI values may have different levels of individual criteria air pollutants that could affect the levels of airborne phthalates (see sections 3.2 and 3.3).

Phthalates in atmosphere in different cities were also reported by others. A brief comparison of the mean values and range of concentrations of our results to the reported values is summarized in Table 2. The levels of the monitored six phthalates in this study were comparable to the levels in Chennai, India (Sampath et al., 2017), but higher than levels observed in other cities such as Nanjing (China) (Wang et al., 2008), Seoul (Korea) (Jo et al., 2016) and Paris (France) (Teil et al., 2006). Phthalates levels in this study included light to moderate pollution weathers contributing to a higher phthalate level in the atmosphere. Many other factors including geographic area, season, local sources and different sample collection and analysis methods among studies could also influence the values. Ma et al. (2014) reported a higher level of DEHP and lower levels for the more volatile phthalates, compared to the levels determined in this study. However, only the particulate bound phthalates collected on filters were determined in Ma et al. study; phthalates in gaseous phase were calculated using air-particle partition coefficient.

In general, among measured phthalates, DEHP levels in this study agreed best with values reported by others. Noticeably is that levels of

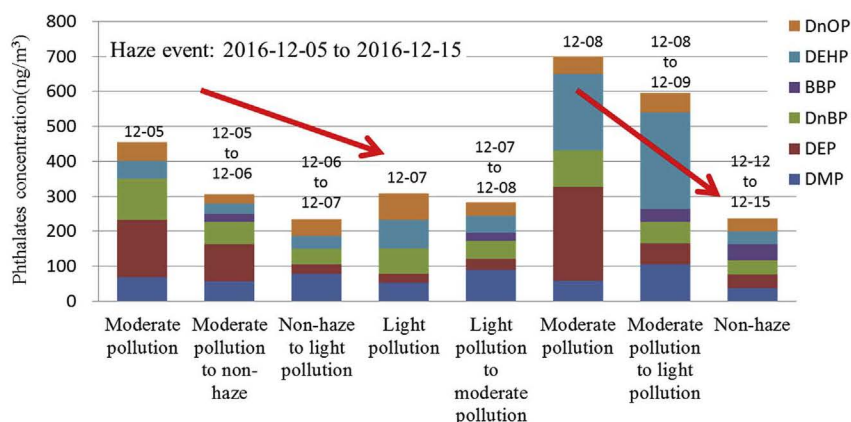


Fig. 1. Variations of phthalates concentrations with changing of air quality weather events in Shanghai. DnBP ( $r = 0.76$ ,  $p = 0.028$ ),  $\Sigma$ PAAE ( $r = 0.78$ ,  $p = 0.021$ ), DEHP ( $r = 0.64$ ,  $p = 0.086$ ),  $p$  values for other phthalates were  $> 0.1$ .

Table 2

Comparisons of mean concentrations and range of concentrations (in parentheses) of phthalates in outdoor air among different cities (ng/m<sup>3</sup>).

Compound		DMP	DEP	DnBP	BBP	DEHP	DnOP
Shanghai, China (This study)		68 (37–105)	90 (26–268)	70 (39–119)	16 (0–46)	96 (29–276)	49 (28–76)
Baoshan district, Shanghai, China (Ma et al., 2014), <sup>a</sup>		1.5	0.71	33	1.4	279	NM
Nanjing, China (Wang et al., 2008)		10.1 (0.6–4.8)	3.4 (0.4–9.6)	58.8 (33.7–94.7)	3.2 (1.3–10.3)	20.3 (9.6–133.8)	1.2 (ND–3.6)
Chennai, India (Sampath et al., 2017)	Summer	5	39	212	4	662	5
	Pre-monsoon	18	103	215	101	369	18
	Monsoon	0	4	26	5	142	10
Seoul, Korea (Jo et al., 2016)		1.62	2.54	ND	ND	58.3	ND
Paris, France (Teil et al., 2006)		0.5	10.7	22.2	4.6	18.9	0.7

<sup>a</sup> Total airborne (gaseous plus particle phases) level, in which levels in gaseous phase were estimated from measured levels in particle phase considering partition coefficient; ND: Not detected; NM: Not monitored.

both DMP and DEP, two phthalates that are predominantly in gaseous phase, were much higher in this study compared to values reported by others. This is likely due to the fact that in this study, the adsorbent used in the tube captured volatile species such as DMP and DEP more effectively. The discrepancy of BBP levels however could not be explained.

Phthalates are man-made chemicals used as additives in consumer products and therefore have mainly indoor sources (Shi et al., 2012; Kim et al., 2013). Sources for outdoor phthalates may include emission of phthalates from indoors through ventilation and exchange of indoor and outdoor air and from phthalate-containing products in waste disposal. Emissions from transportation, where phthalate are used in many interior parts of the vehicles, could also be an important source (Haddad et al., 2009). Both high density of residence in urban Shanghai and large volume of transportation vehicles per surface area, particularly personal cars, in Shanghai could be the main contributors of phthalates in outdoor air.

### 3.2. The relations between phthalates and meteorological conditions

Meteorological conditions, such as temperature, relative humidity (RH) and wind speed, are primary factors that can influence pollutant levels in the atmosphere (He et al., 2016). A weak but statistically significant inverse relationship (Spearman's rank-order correlation) between RH and  $\Sigma$ PAE levels ( $r = -0.71$ ,  $p = 0.050$ ) was observed in this study (Fig. 2). An inverse relationship between the levels of air pollutants and RH, which was varied from < 10% to 70%, in the majority cities of south China was reported (He et al., 2017). Levels of phthalates reported in an India study were lower in the monsoon season, when RH is usually high, than in the pre-monsoon season; one of the explanations was that a higher RH can limit the vaporization of phthalates in air (Sampath et al., 2017). Temperature effects on levels of airborne phthalates were also reported by others, showing that levels

of phthalates were higher in summer months when temperature is higher than levels in the winter months (Wang et al., 2008; Melymuk et al., 2012). However the impact of temperature on the levels of phthalates was not observed in this study (Fig. 2) due to short period of sampling time, in which the outdoor temperature only changed slightly (11–19 °C) and such a small change in temperature was likely not sufficient to demonstrate the impact in the presence of other influencing factors such as wind speed, RH, as well as other pollutants.

It is known that a higher wind speed can help disperse pollutants trapped in the atmosphere in a haze event thereby improving the air quality (He et al., 2017). Average wind speed and wind direction during each sample collection period were calculated from original weather data. There were two distinguished wind speed ranges that had a different impact on phthalate levels: a wind speed range of 1.5–2.2 m/s (5–10 km/h) where phthalate levels had an inverse relationship with the wind speed and a wind speed range of 2.2 m/s and above where there was no clear changes in phthalate levels (Fig. 3). There was one exception however at the low wind speed of 1.6 m/s where the phthalate level was also low. This low wind had a wind direction of 105°, while wind directions of the rest were all within 180°–270°. As Shanghai is a coastal city, south-east wind (105°) that brings clean air from the Pacific Ocean will help dilute the pollution even with a relatively low wind speed. This showed that not only the wind speed, but also wind direction is important.

The three high phthalate levels (in the circle in Fig. 3) were all associated with either the moderate pollution level or the weather in the transition from moderate to light pollution. Haze weather is usually associated with lack of wind to disperse the pollutants in addition to the inverse temperature in the atmosphere (Xu et al., 2016a, 2016b).

### 3.3. Relationships between phthalates and other airborne pollutants

Besides meteorological conditions that can influence the levels of

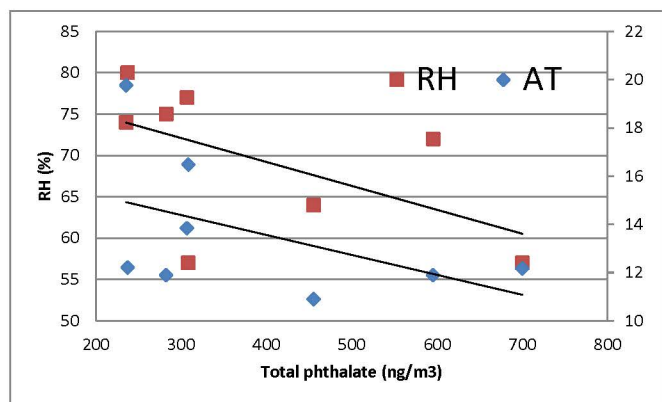


Fig. 2. Correlation of total phthalates ( $\Sigma$ PAE) and meteorological parameters of atmospheric temperature (AT,  $r = 0.46$ ,  $p = 0.25$ ) and relative humidity (RH,  $r = 0.71$ ,  $p = 0.050$ ).

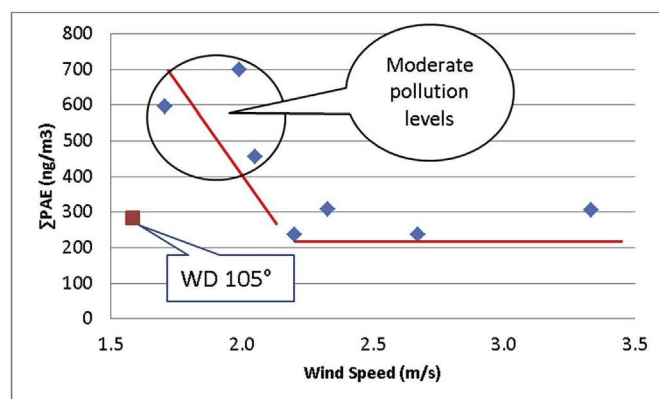


Fig. 3. Phthalate levels in atmosphere as a function of wind speed. WD = wind direction (0° = north, 90° = east, 180° = south, and 270° = west).

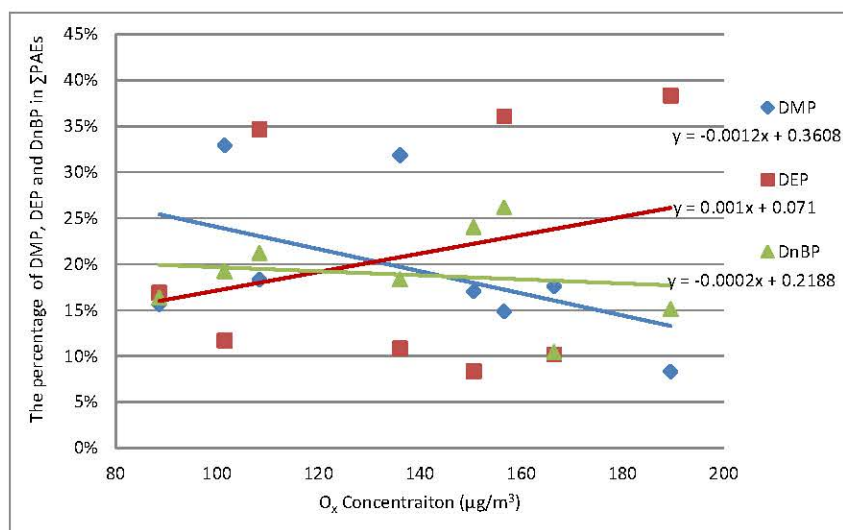


Fig. 4. Comparison of percentage of DMP, DEP and DnBP against total airborne oxidant (O<sub>x</sub>). The slope of the regression lines is -0.001, 0.001 and -0.0002 for DMP, DEP and DnBP, respectively. P values were > 0.1 in all cases.

phthalates in the atmosphere, other pollutants present in the atmosphere can react with organic compounds like phthalates. For example, Han et al. (2014) theoretically predicted the mechanism and kinetics of hydroxyl radical (OH<sup>•</sup>)-initiated photo-oxidation of DMP in the atmosphere, based on quantum calculation. The abstraction of a hydrogen atom from the methyl group and addition of OH radical to the aromatic ring were identified as the two major mechanisms of the oxidation. OH<sup>•</sup>-initiated photo-oxidations of DMP, DEP and DnBP in aqueous solutions were also reported (An et al., 2014; Gao et al., 2015).

OH<sup>•</sup> in the atmosphere could be formed as a result of photoreaction of ozone and sun radiation in the presence of water: O<sub>3</sub> + H<sub>2</sub>O + hv → OH<sup>•</sup>. Levels of OH<sup>•</sup> were reported to have a positive relationship with atmospheric oxidant (O<sub>x</sub>), which is the sum of O<sub>3</sub> and NO<sub>2</sub> (Notario et al., 2012, 2013). Fig. 4 shows the relationships between O<sub>x</sub> and the percentage of three relatively more volatile phthalates (DMP, DEP and DnBP). Although not statistically significant (Spearman's rank-order correlation, p > 0.1 for all three relationships), the largest decrease of the percentage against the O<sub>x</sub> was observed for DMP (slope = -0.0012). This phenomenon can be ascribed to the photo-oxidation by OH<sup>•</sup> in the atmosphere (An et al., 2014; Gao et al., 2015; Notario et al., 2012, 2013), DMP is the most volatile one and has the largest proportion in gas phase among measured phthalates and therefore could be the most reactive one in OH<sup>•</sup> initiated photo-oxidation in the atmosphere.

Levels of phthalates had a very similar trend as both PM<sub>10</sub> and PM<sub>2.5</sub>

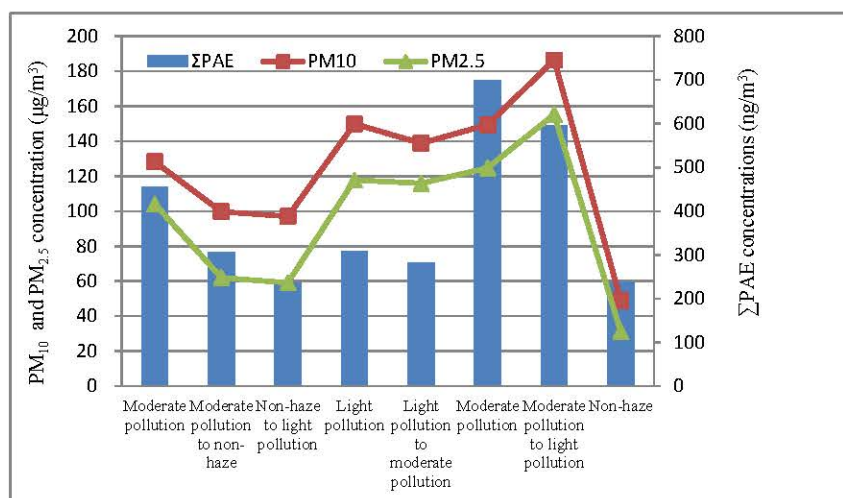


Fig. 5. Positive relationships between ΣPAE and PM<sub>2.5</sub> (p = 0.010) and between ΣPAE and PM<sub>10</sub> (p = 0.028).

had (Fig. 5). Statistically significant, positive relationships, as tested using Spearman's rank-order correlation, between ΣPAE and PM<sub>2.5</sub> (r = 0.83, p = 0.010) and between ΣPAE and PM<sub>10</sub> (r = 0.76, p = 0.028) were observed. The ubiquitous presence of phthalates in airborne PM in the atmosphere in Shanghai was observed in other studies too (Ma et al., 2014). PM was considered to be the main air pollutant contributing to the formation of haze weather. This indicated that phthalates may have played an important role in the formation of haze weathers.

#### 3.4. Human exposure to phthalates in the atmospheric air via inhalation

The higher phthalates levels in outdoor air in the haze weather events implied a greater human exposure to outdoor phthalates in haze weather events, in addition to exposure to other pollutants such as PM. An attempt was made in this study to quantify human exposure to phthalates related to different air quality weather events. Inhaled phthalates in outdoor air is expressed as daily intake (DI, (ng/kg)/(bw/day)) and is described in equation (1) (Sampath et al., 2017; Zhang et al., 2014; Guo and Kannan, 2011).

$$DI = (C_A \times IR \times EF) / (BW) \tag{1}$$

where, C<sub>A</sub> is the total airborne concentration of phthalate (gas phase and particulate phase) in air (ng/m<sup>3</sup>); IR is the inhalation rate (m<sup>3</sup>/day), values of IR for infants, toddlers, children, teenagers and adults

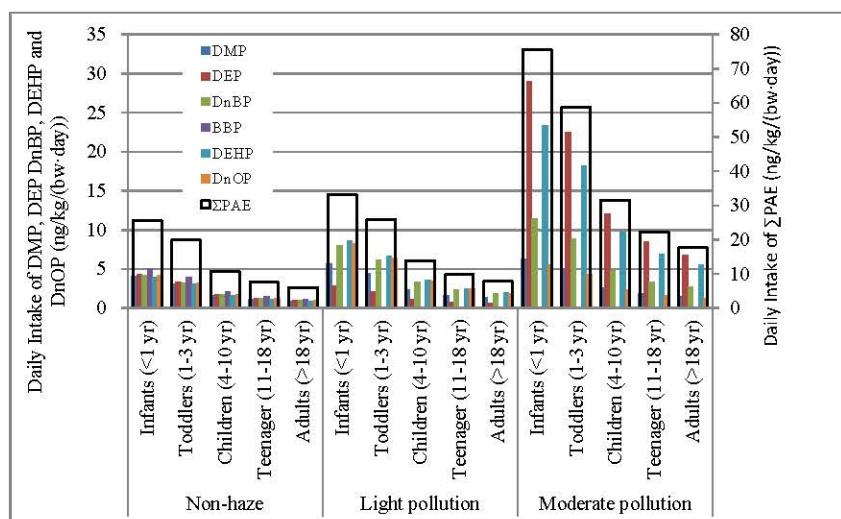


Fig. 6. Daily intake (DI, (ng/kg)/(bw·day)) of phthalates through inhalation to outdoor air, stratified by different age groups under three pollution levels (non-haze, light pollution and moderate pollution). Values for the sum of phthalates ( $\Sigma$ PAEs) were indicated on the y-axis at the right side and individual phthalates at the left side.

were estimated at 4.5, 7.6, 10.9, 14.0 and  $13.3 \text{ m}^3/\text{day}^{-1}$ , respectively (EPA, 2002); EF is the exposure frequency to indicate the time fraction people spend outdoors, the value of EF for the toddler and children was estimated at 0.21, whereas those for infants, teenagers and adults at 0.12 (EPA, 2002); and BW is the body weight, which was assumed to be 5 kg, 19 kg, 29 kg, 53 kg and 63 kg for infants (< 1 year (yr)), toddlers (1–3 yr), children (4–10 yr), teenagers (11–18 yr) and adults (> 18 yr), respectively (US EPA, 1998). Different from oral exposure, not all contaminants in air, especially those attached to the large particles, may be inhaled or deposited in the respiratory system (US EPA, 2000). Therefore, it has to be recognized that the DI value calculated from equation (1) is a more conservative estimation of the actual human inhalation dosimetry of phthalates.

The estimated DI values of six phthalates under three weather qualities (non-haze, light pollution and moderate pollution) and different age groups are presented in Fig. 6. Since the levels of phthalates becomes higher with worsening of weather qualities, DIs of phthalates as a result of inhalation of outdoor air, were the greatest in the moderate pollution weather, followed by light pollution and non-haze weathers. For example, the DI values of  $\Sigma$ PAE in the moderate pollution weather were about three times the DI values in the non-haze weather (Fig. 6). Furthermore, due to smaller body size, small children in general had larger DI values than teenagers and adults. The order of DIs value among different age groups was infants > toddlers > children > teenagers > adults, in a ratio of 1:0.44:0.42:0.29:0.23. This means that when being exposed to the same levels of pollutants, infants' DI was four times higher than adults' on per body weight basis (Sampath et al., 2017; Zhang et al., 2014).

Phthalates are primarily used in indoor products and therefore levels of phthalates in outdoor air are lower than their levels in indoor air in general. Typical phthalate levels in indoor air are in the range of  $0.38\text{--}32.42 \mu\text{g}/\text{m}^3$  for residential (Bu et al., 2016) and  $3.01\text{--}6.7 \mu\text{g}/\text{m}^3$  for office (Song et al., 2015), at least an order of magnitude higher than levels in outdoor air (Rudel and Perovich, 2009). As a result, DIs due to exposure to indoor air are greater than DIs from inhalation from outdoor air due to a combination of higher airborne concentrations and larger exposure frequency (EF) indoors (0.79 and 0.88 for toddler/children and adults, respectively) (EPA, 2002). For example, DIs of phthalates due to exposure to indoor air in two Chinese cities of Tianjin and Xi'an were  $155\text{--}664 \text{ ng}/\text{kg}/(\text{bw}\cdot\text{day})$  (Zhang et al., 2014) and  $1344\text{--}3183 \text{ ng}/\text{kg}/(\text{bw}\cdot\text{day})$  (Wang et al., 2014) respectively. This is about 10 times greater than the DI values from exposure to outdoor air in moderate haze weather observed in this study.

Although phthalates concentrations in atmosphere were comparable between this study and what was reported in India (Sampath et al.,

2017), the DI values in our study were half of theirs. The discrepancy was likely due to the use of different EF values (equation (1)) in the two studies. An EF value of 0.88 and 0.79 was used for toddler/children and adults, respectively, in the Indian study, (Sampath et al., 2017) which we believe is more appropriate for exposure to indoor air.

Reference concentrations (RfC) of phthalates for inhalation exposure have not been established. The tolerable daily intake (TDI) based on oral intake however has been proposed for some common phthalates by various jurisdictions. For example, TDI of 800, 100, 200, 20 and  $400 \mu\text{g}/\text{kg}/(\text{bw}\cdot\text{day})$  for DEP, DBP, BBP, DEHP and DnOP, respectively, were proposed by US EPA (Zhang et al., 2014; Wang et al., 2014). The inhalation dose of individual phthalates derived from this study in all three different air quality weather events were below  $0.03 \mu\text{g}/\text{kg}/(\text{bw}\cdot\text{day})$  (Fig. 6), which is only a tiny fraction of the proposed TDIs.

These analyses results have shown that even in a haze weather event, the contribution of outdoor air phthalates to human exposure remains minor compared to indoor air, and exposure to outdoor air phthalates constitutes only a tiny fraction of the tolerable daily intake.

#### 4. Conclusions

This is the first report on phthalates in the atmosphere with a focus on their associations with different air quality weather events. Haze episodes that occurred frequently in China in the past decades are of great economical, ecological and human health concern. Understanding the pollutants in different haze weather events can help in identifying the cause of haze. The important observations in this study that phthalates levels increase with decreasing weather qualities and the close association between certain phthalates, especially DMP, with some criteria pollutants and with meteorological conditions demonstrated that phthalates in the atmosphere could contribute to the formation of secondary organic aerosol (SOA) causing haze weather events.

Our study also showed that wind speed, which is often closely associated with haze weather events, played an important role on phthalates levels. Low wind speed can result in higher levels of phthalates and other pollutants such as PM in the moderate pollution weather. This is likely a reason for a positive correlation between the two parameters in this study. More research is needed however, to better understand the reactions of phthalates with other air pollutants contributing to the formation of SOA. Interesting observations from this study will inform future study design of the impact of semi-volatile organic compounds and intermediate-volatile organic compounds in the formation of haze weather.

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