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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^3) and higher in moderate pollution weather events (up to 700 ng/m^3). 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_3 + NO_2), 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_3), sulfur

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dioxide (SO_2), carbon monoxide (CO) and nitrogen dioxide (NO_2) 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_3, and NO_2, 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 isooctane) 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.

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_2, O_3, $PM_{2.5}$ and PM_{10} 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/

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 (%)		DR (%)
					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-*n*-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-*n*-octyl phthalate (DnOP)	30.13	149.0	207.0	0.25	8.5	2.1	100