



Airborne particulate endocrine disrupting compounds in China: Compositions, size distributions and seasonal variations of phthalate esters and bisphenol A



Jianjun Li, Gehui Wang*

State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

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ABSTRACT

Phthalate esters and bisphenol A (BPA) are endocrine disrupting compounds (EDCs) and ubiquitously occur in the environment. In the past decade we have characterized atmospheric organic aerosols from various environments (e.g., urban, rural, mountain and marine) of East Asia on a molecular level, but not investigated EDCs in the samples. In the current study we re-analyzed our database for concentrations, compositions and size distributions of phthalates and BPA and compared with those in the literature to improve the understanding on air pollution status in China. Our results showed that airborne particulate phthalates and BPA are 63–1162 ng m⁻³ and 1.0–20 ng m⁻³ in the urban regions in China, respectively, being one to two orders of magnitude higher than those in the developed countries. Among the detected phthalates in Chinese urban areas, bis(2-ethylhexyl) phthalate (BEHP) is the predominant congener, contributing to 23–79% (ave. 53 ± 15%) of the total phthalates. Concentrations of phthalates and bisphenol A in Shanghai and Xi'an (two mega-cities in China) in 2009 were 3–84% lower than those in 2003, probably indicating a positive effect of the government's air pollution control in the recent years. Phthalates are higher in summer than in winter, because they are not chemically bonded to the polymeric matrix and more easily evaporate into the air under higher temperature conditions. Based on the size distribution observation, we found that diisobutyl and dibutyl phthalates mainly exist in coarse particles because of high volatilities, in contrast to BEHP and BPA, which are dominant in fine particles due to less volatility. Our results also indicate that BPA is mostly derived from the open burning of solid waste while phthalates are derived from both direct evaporation from the matrix and solid waste combustion.

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1. Introduction

The rapid development of polymeric substances in new building materials, food and beverage containers, and other consumer products over the past fifty years has resulted in a corresponding increase of new chemicals in the living environment (Cohen, 2003; Weschler, 2009). Epidemiological and laboratory studies pointed out that some of these chemicals have a severe disturbance to endocrine system of humans and

wildlife (Collins, 2008; Harris et al., 1997; Hunt et al., 2003). At the present, around 100 of industrial chemicals are suspected as endocrine disrupting compounds (EDCs) (Falconer et al., 2006; Rudel and Perovich, 2009). They can emit into the environment and contaminate air, water and soil, attracting much public attention in recent years (Chen et al., 2012; Fromme et al., 2013; Li et al., 2010; Pojana et al., 2007).

Phthalate esters and bisphenol A (BPA) are two important categories of EDCs, which are widely used in people's daily lives (Singh and Li, 2012) and ubiquitous in aquatic environment, soil and sediment, air and food (Flint et al., 2012; Huang et al., 2012). Phthalate esters are mainly used as plasticizers for

* Corresponding author. Tel.: +86 29 8832 9320; fax: +86 29 8832 0456.
E-mail addresses: wanggh@ieecas.cn, gehuiwang@yahoo.com.cn (G. Wang).

improving the flexibility and workability of polymeric materials. Epidemiological, clinical, and experimental data have demonstrated that phthalates have a significant effect on male reproductive disorders, such as infertility, reduced sperm motility, and decreased sperm (Bang et al., 2012). The other chemical, bisphenol A, was first synthesized in 1891 (Dianin, 1891) and has been widely used since the 1950s in epoxy resins, polycarbonates, and other polymeric materials. Recent studies found that it also has potential association with adverse health effects, such as prostate cancer, obesity, neuro-behavioral and reproductive problems (Howdeshell et al., 1999; Hunt et al., 2003; Vandenberg et al., 2007).

China is the biggest developing country in the world with huge resource consumption and severe environment problems. There is an increasing demand for phthalates and bisphenol A products in the country. Bing and Li (2009, 2011) reported that China is the biggest manufacturer of polyvinyl chloride (PVC) in the world, a mainly phthalate product, which increased from 2.9 million tons in 2000 to 12.9 million tons in 2010. China is also the main BPA producer in Asia, which has grown at an annual rate of 13% in the past decade (Huang et al., 2012). Moreover, China has annually generated a total of 1000–3300 million tons of industry solid waste and 150–170 million tons of household garbage since 2003 (NBSC, 2001–2012), which can also release massive phthalates and bisphenol A into the environment.

In China public concern about potential health risk of toxic organic compounds in the atmosphere has been arising dramatically in the past years. However, in most cases people only focused on polycyclic aromatic hydrocarbons (PAHs) and their derivatives (Li et al., 2013b; Wang et al., 2008b, 2009a, 2011), because these compounds are highly carcinogenic. In contrast, EDCs in the atmosphere have not been given much attention. Although phthalates and bisphenol A in various environmental media in China were reported by a few researchers (Chen et al., 2012; Fu and Kawamura, 2010; Wang et al., 2006b, 2008a), very few studies have investigated the temporal and spatial distributions of phthalates and bisphenol A in the atmosphere across the whole country. Our previous studies had reported over one hundred organic compounds in aerosols from mainland China and its surrounding regions (Li et al., 2013a, 2014; Wang and Kawamura, 2005; Wang et al., 2006a,b, 2009b), but we didn't give much attention for those endocrine disrupting compounds (EDCs), especially for bisphenol A. In the current work, we firstly quantified the two classes of EDCs from the GC/MS database of the atmospheric aerosol samples collected from various environments of China and its surrounding areas including urban, rural, mountain and marine regions. Then we discussed their spatial and temporal variations, sources and size distributions.

2. Experimental section

2.1. Sample collection

More than 330 TSP/PM₁₀/PM_{2.5} samples were collected at urban, mountain and remote areas during winter and summer from 2003 to 2010. Detail sample information including sampling location, period and aerosol type (TSP/PM₁₀/PM_{2.5}) is summarized in Table 1. 24 sets of size-resolved (9 stages) aerosol samples were collected in Xi'an (3 sets in winter and 5

sets in summer), Nanjing (4 sets in summer), Baoji (3 sets in winter), Mt. Hua (3 sets in winter and 3 sets in summer) and Mt. Tai (3 sets in winter) during 2006–2009. All the size-segregated samples were collected using Andersen 9-stage air sampler (Thermo electronic Company, USA) with the cutoff points at 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4 μm under an airflow rate of 28.3 L min⁻¹. In addition, marine aerosols were also collected during spring in Gosan, Korea (21 TSP samples, 2005) and Okinawa, Japan (3 sets of size-resolved samples, 2008). All samples were collected on pre-baked (450 °C for 8 h) quartz microfiber filters (Whatman). After sampling, the filter was sealed in an aluminum bag and stored at -18 °C prior to analysis.

2.2. Extraction and derivatization

For each sample, a filter aliquot (3–50 cm²) of the sample/blank filter was cut in pieces and extracted three times with a mixture of dichloromethane and methanol (2:1, v/v) under ultrasonication for 15 min. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated using a rotary evaporator under a vacuum condition, and then blown down to dryness with pure nitrogen stream. The extracts were reacted with 60 mL mixture of N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and pyridine (5:1, v/v) at 70 °C for 3 h. During the derivatization, OH groups of bisphenol A convert to the corresponding trimethylsilyl (TMS) esters. After the reaction, derivatives were diluted with 40 or 140 μL of *n*-hexane containing the internal standard (Tridecane, 1.51–3.02 ng μL⁻¹), and then determined by gas chromatography–mass spectrometry (GC/MS).

2.3. GC/MS quantification

Gas chromatography–mass spectrometry analysis of the derivatized fraction was performed using an Agilent 7890A GC coupled with an Agilent 5975C MSD. The GC separation was carried out on a DB-5MS fused silica capillary column with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ and then to 300 °C at 5 °C min⁻¹ with a final isothermal holds at 300 °C for 16 min. The sample was injected in a splitless mode at an injector temperature of 280 °C, and scanned from 50 to 650 Da using electron impact (EI) mode at 70 eV. GC/MS response factors were determined using authentic standards.

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

During each sampling campaign, field blank samples (*n* = 15) were collected before and after sampling by mounting the filters onto the sampler for about 10 min without sucking any air. Field blank samples were extracted and analyzed in the same way as ambient samples. Results showed no serious contamination (less than 5% of those in the real samples) was found in the blanks. The limits of detection (LOD) of the GC/MS instrument were 0.01, 0.09, 0.15, 0.06, 0.21, 0.30, 0.33 and 0.01 ng μL⁻¹ (*S/N* = 3) for dimethyl, diethyl, diisobutyl, isobutyl butyl, dibutyl, benzyl butyl and bis(2-ethylhexyl) phthalates and bisphenol A, respectively. Recoveries of the target compounds were better than 80%. Data presented here were corrected for the field blanks but not corrected for the recoveries. Relative

Table 1

Detail information on the aerosols samples and concentrations of phthalates and bisphenol A.

Location	Period	Type	Phthalates								BPA	
			DMP	DEP	DiBP	iBBP	DBP	BBP	BEHP	Subtotal		
<i>(I) Unban sites</i>												
Hong Kong ^a	Winter 2003	PM _{2.5}	2.9 ± 1.3	12 ± 7.0	20 ± 5.6	1.2 ± 1.0	42 ± 8.4	nd ^g	96 ± 25	174 ± 33	3.8 ± 1.5	
	Summer 2003	PM _{2.5}	0.8 ± 0.3	6.6 ± 0.2	36 ± 2.8	5.0 ± 0.6	117 ± 4.0	0.8 ± 0.1	241 ± 87	407 ± 24	2.3 ± 0.1	
Guangzhou ^a	Winter 2003	PM _{2.5}	0.5 ± 0.2	1.1 ± 1.1	31 ± 1.0	3.0 ± 0.03	37 ± 1.0	nd	262 ± 2.5	335 ± 0.41	20 ± 2.7	
	Summer 2003	PM _{2.5}	1.1 ± 0.3	3.8 ± 0.3	104 ± 2.1	7.8 ± 0.4	121 ± 6.3	nd	202 ± 25	440 ± 29	5.9 ± 1.4	
Xiamen ^a	Winter 2003	PM _{2.5}	3.9 ± 0.8	7.1 ± 0.3	30 ± 7.6	2.2 ± 0.4	31 ± 1.2	nd	76 ± 23	150 ± 29	7.7 ± 0.2	
	Summer 2003	PM _{2.5}	0.4 ± 0.03	2.1 ± 0.4	43 ± 0.5	3.1 ± 0.2	52 ± 4.6	2.2 ± 0.3	102 ± 10	205 ± 4.5	1.8 ± 0.8	
Chongqing ^a	Winter 2003	PM _{2.5}	0.9 ± 0.7	2.1 ± 2.1	35 ± 1.3	nd	53 ± 12	nd	244 ± 81	335 ± 91	18 ± 7.4	
	Summer 2003	PM _{2.5}	1.0	5.4	120	11	167	1.9	856	1162	11	
Hangzhou ^a	Winter 2003	PM _{2.5}	5.1 ± 0.7	5.4 ± 0.9	45 ± 6.0	2.5 ± 0.2	34 ± 0.8	nd	115 ± 3.5	207 ± 1.7	11 ± 0.09	
	Summer 2003	PM _{2.5}	1.1 ± 0.2	6.8 ± 1.9	137 ± 34	6.0 ± 1.6	165 ± 34	nd	266 ± 29	582 ± 100	5.4 ± 1.3	
Wuhan ^a	Winter 2003	PM _{2.5}	1.9 ± 0.1	5.4 ± 0.01	37 ± 4.0	3.4 ± 0.9	29 ± 5.9	nd	63 ± 27	140 ± 28	6.9 ± 1.4	
	Summer 2003	PM _{2.5}	1.3 ± 0.5	6.6 ± 1.7	130 ± 55	7.3 ± 1.6	131 ± 26	2.6 ± 0.4	198 ± 10	477 ± 95	3.3 ± 2.9	
Shanghai ^a	Winter 2003	PM _{2.5}	1.9 ± 1.0	5.1 ± 0.3	43 ± 18	3.2 ± 1.4	32 ± 11	nd	258 ± 170	343 ± 200	9.1 ± 6.6	
	Summer 2003	PM _{2.5}	1.4 ± 0.3	13 ± 7.0	164 ± 15	9.4 ± 1.0	158 ± 13	nd	277 ± 2.6	623 ± 19	4.2 ± 0.9	
	Summer 2009	PM ₁₀	5.7 ± 3.6	nd	100 ± 22	9.8 ± 13	64 ± 17	8.7 ± 3.0	130 ± 57	317 ± 116	1.0 ± 1.2	
Nanjing ^b	Winter 2005	PM _{2.5}	nd	nd	29 ± 14	nd	26 ± 13	nd	155 ± 77	210 ± 102	3.9 ± 2.5	
	Summer 2004	PM _{2.5}	nd	nd	21 ± 27	nd	33 ± 44	nd	160 ± 100	214 ± 108	3.0 ± 1.9	
Xi'an ^{a,c}	Winter 2003	PM _{2.5}	0.3 ± 0.04	5.6 ± 4.0	79 ± 30	4.7 ± 2.1	48 ± 1.0	nd	313 ± 21	451 ± 14	18 ± 3.4	
	Summer 2003	PM _{2.5}	1.6 ± 0.2	14 ± 3.2	236 ± 39	11 ± 1.8	185 ± 22	1.1 ± 1.1	225 ± 30	673 ± 97	6.9 ± 0.02	
	Winter 2009	TSP	nd	nd	47 ± 13	3.3 ± 0.9	37 ± 11	17 ± 4.6	164 ± 79	268 ± 98	18 ± 13	
	Summer 2009	PM ₁₀	nd	nd	117 ± 27	21 ± 8.1	69 ± 16	2.5 ± 1.3	134 ± 35	344 ± 80	1.1 ± 1.1	
Baoji ^d	Winter 2008	PM _{2.5}	nd	nd	35 ± 15	3.4 ± 2.0	39 ± 19	nd	242 ± 69	325 ± 103	3.3 ± 1.7	
Qingdao ^a	Winter 2003	PM _{2.5}	2.6 ± 0.9	4.7 ± 1.4	19 ± 3.8	1.1 ± 0.4	28 ± 8.2	nd	44 ± 5.4	99 ± 20	6.0 ± 0.6	
	Summer 2003	PM _{2.5}	0.7 ± 0.0	4.1 ± 1.6	44 ± 7.5	2.6 ± 0.3	64 ± 0.8	nd	55 ± 2.1	170 ± 5.5	2.2 ± 0.1	
Yulin ^a	Winter 2003	PM _{2.5}	1.5 ± 0.3	4.1 ± 0.8	17 ± 0.9	1.7 ± 0.3	14 ± 1.9	nd	25 ± 3.7	63 ± 3.9	3.8 ± 3.5	
	Summer 2003	PM _{2.5}	1.3 ± 0.4	23 ± 5.8	57 ± 12	2.5 ± 0.3	60 ± 9.4	nd	119 ± 17	263 ± 11	8.2 ± 0.7	
Jinchang ^a	Winter 2003	PM _{2.5}	2.1 ± 0.1	3.9 ± 0.3	23 ± 5.6	1.7 ± 0.3	19 ± 0.2	nd	39 ± 4.6	89 ± 1.5	2.0 ± 0.2	
	Summer 2003	PM _{2.5}	2.1 ± 0.01	14 ± 0.5	64 ± 4.2	2.7 ± 0.0	97 ± 1.0	nd	110 ± 8.3	290 ± 4.6	4.2 ± 0.6	
Tianjin ^a	Winter 2003	PM _{2.5}	1.3 ± 0.1	3.9 ± 0.5	24 ± 5.0	1.88 ± 0.1	21 ± 1.1	nd	75 ± 16	127 ± 9.1	10 ± 4.3	
	Summer 2003	PM _{2.5}	0.9 ± 0.3	9.0 ± 1.5	281 ± 11	17 ± 5.8	269 ± 28	1.2 ± 1.2	394 ± 144	972 ± 132	3.8 ± 3.0	
Beijing ^a	Winter 2003	PM _{2.5}	1.5 ± 0.3	3.5 ± 0.3	22 ± 2.5	1.4 ± 0.4	21 ± 2.9	nd	130 ± 107	179 ± 113	6.6 ± 3.7	
	Summer 2003	PM _{2.5}	1.7 ± 0.6	11 ± 0.9	122 ± 12	5.9 ± 0.4	135 ± 16	2.6 ± 1.1	130 ± 32	408 ± 63	4.9 ± 0.7	
Changchun ^a	Winter 2003	PM _{2.5}	1.9 ± 0.6	4.3 ± 0.3	28 ± 2.1	2.2 ± 0.1	18 ± 0.4	nd	63 ± 18	117 ± 20	11 ± 1.2	
	Summer 2003	PM _{2.5}	2.2 ± 0.3	15 ± 3.9	118 ± 22	5.1 ± 1.4	143 ± 33	nd	133 ± 36	416 ± 97	8.6 ± 3.1	
<i>(II) Mountain, remote and marine sites</i>												
Mt. Hua	Winter 2009	PM ₁₀	nd	nd	24 ± 9.5	nd	7.2 ± 5.8	nd	4.1 ± 2.1	35 ± 17	0.03 ± 0.02	
	Summer 2009	PM ₁₀	nd	nd	28 ± 7.	nd	12 ± 4.4	nd	10 ± 5.2	50 ± 17	0.01 ± 0.01	
Mt. Tai	Summer 2006	PM _{2.5}	nd	nd	11 ± 5.6	1.3 ± 0.5	17 ± 7.5	nd	19 ± 11	49 ± 22	0.05 ± 0.04	
Qinghai Lake ^e	Summer 2010	PM _{2.5}	nd	nd	0.88 ± 0.59	nd	0.38 ± 0.27	nd	0.67 ± 0.42	1.9 ± 1.2	nd	
Gosan, Korea ^f	Spring 2005	TSP	2.1 ± 2.5	0.7 ± 0.4	0.3 ± 0.2	nd	1.7 ± 2.5	nd	23 ± 9.1	29 ± 13	0.14 ± 0.11	
Okinawa, Japan ^d	Spring 2008	TSP	nd	nd	0.46 ± 0.21	nd	2.4 ± 1.01	nd	29 ± 4.7	32 ± 5.4	nd	

^a Phthalates in the PM_{2.5} samples of the 14 urban sites during winter and summer, 2003 have been reported by Wang et al. (2006a) and recalculated in this study.^b Phthalates in the Nanjing aerosols have been reported by Wang and Kawamura (2005).^c Phthalates and bisphenol A in TSP in Xi'an during winter, 2009 have been reported by Li et al. (2014).^d The concentration of phthalates and bisphenol A in TSP in Baoji and Okinawa were calculated as the sum concentrations of 9-stage samples.^e Phthalates and bisphenol A in PM_{2.5} in Qinghai Lake during winter, 2010 have been reported by Li et al. (2013a).^f Phthalates in TSP in Gosan, Korea during spring, 2005 have been reported by Wang et al. (2009b).^g nd: not determined.

standard deviation of the target compound concentrations, based on a triplicate analysis, was <5% (N = 10).

3. Results and discussion

3.1. Spatial distribution

3.1.1. Phthalate esters

Seven phthalate esters were detected in the urban, mountain, remote and marine regions in mainland China and its

surrounding regions. Their molecular and spatial distributions were shown in Table 1 and Fig. 1. Bis(2-ethylhexyl) phthalate (BEHP) is the predominant congener, contributing to 23–79% (ave. 53 ± 15%) of the total phthalates in the urban areas. The second most abundant phthalate ester is diisobutyl (DiBP) or dibutyl (DBP) phthalate, accounting for 7.9–38% (ave. 21 ± 7.7%) of the total.

Total phthalates were 63–425 ng m⁻³ and 170–1162 ng m⁻³ during winter and summer in the urban regions of China, respectively. In winter the highest concentration (451 ±

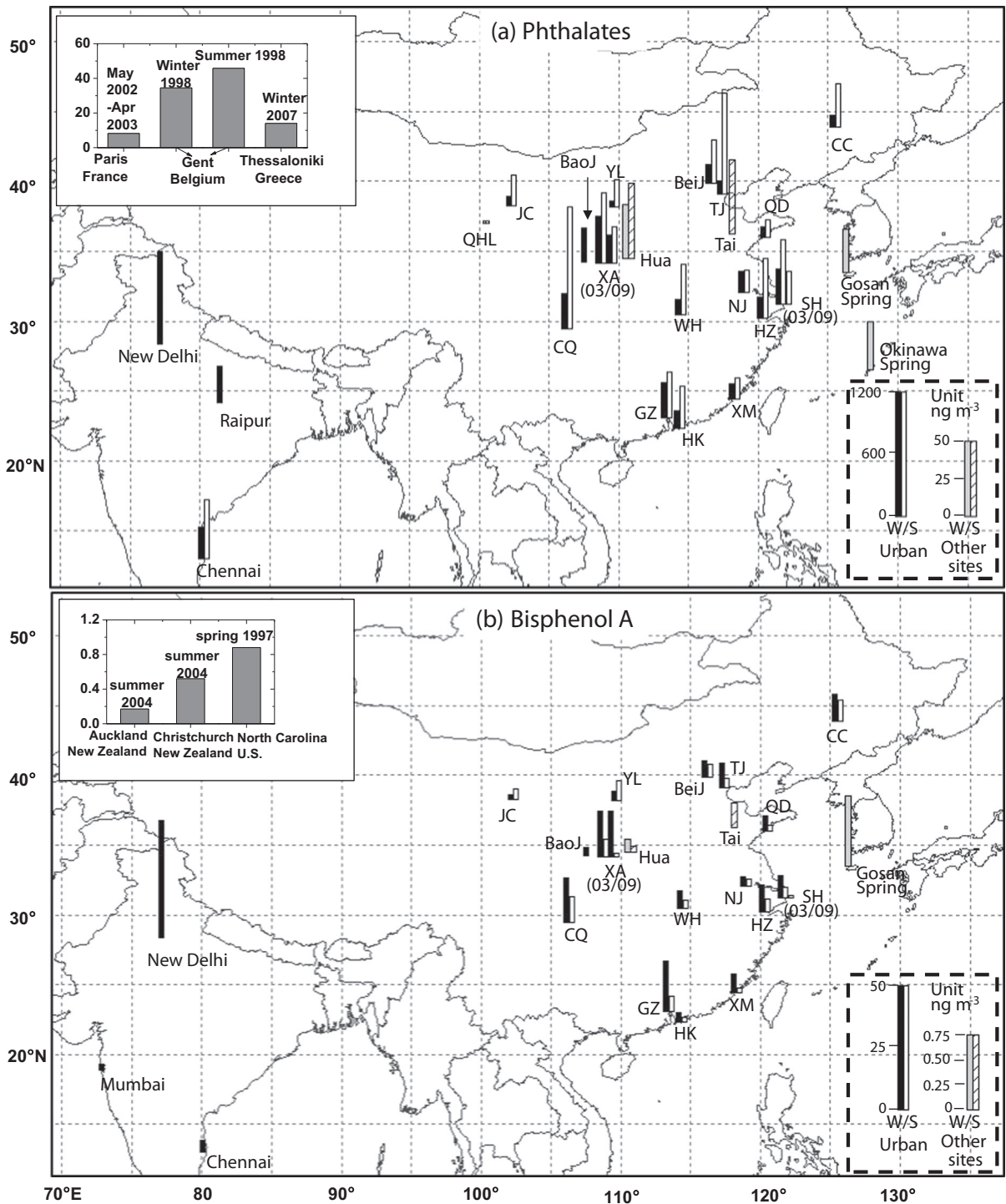


Fig. 1. Spatial distribution of phthalates and bisphenol A in aerosols in China and its surrounding regions. Sampling site names (from east to west): CC, Changchun; SH, Shanghai; QD, Qingdao; HZ, Hangzhou; NJ, Nanjing; XM, Xiamen; Tai, Mt. Tai; TJ, Tianjin; BeiJ, Beijing; HK, Hong Kong; WH, Wuhan; GZ, Guangzhou; Hua, Mt. Hua; YL, Yulin; XA, Xi'an; BaoJ, Baoji; CQ, Chongqing; JC, Jinchang; QHL, Qinghai Lake. W/S means winter/summer.

14 ng m⁻³, Fig. 1) occurred in Xi'an, followed by Shanghai, Chongqing, Guangzhou and Baoji. In contrast, during summer the most abundant phthalates (1162 ng m⁻³, Fig. 1) were

found in Chongqing, followed by Tianjin, Xi'an and Shanghai. Higher concentrations of phthalates in Chongqing (located in Sichuan Basin), Xi'an and Baoji (located in Guanzhong Basin)

are consistent with the high loadings of fine particles ($PM_{2.5}$, particles with aerodynamic diameter less than $2.5 \mu m$) in the atmospheres (van Donkelaar et al., 2010) and can in part be ascribed to the local topography, which is basin-like and favorable for pollutant accumulation. However, the abundant phthalates in the atmosphere of some developed cities (i.e., Shanghai, Tianjian and Guangzhou) has resulted from more significant anthropogenic activities and industry emissions. Due to the lower concentration of OC, relative abundances of phthalates (i.e., phthalates/OC) (18% in winter and 52–66% in summer, Fig. 2) in Shanghai are higher than those (3.4–4.9% in winter and 11–24% in summer, Fig. 2) in Xi'an. The lowest concentrations in urban areas during winter and summer were found in Yulin and Qingdao, respectively. As shown in Fig. 1a, phthalate ester concentrations are comparable and even higher in India ($351\text{--}884 \text{ ng m}^{-3}$) than in China (Fu et al., 2010; Giri et al., 2013; Li et al., 2014). Phthalates in India and China, the two biggest developing countries in the world, are 1.0–100 times higher than those in the developed countries, e.g. France (Paris, 8.2 ng m^{-3} during 2002–2003, TSP) (Teil et al., 2006), Belgium (Gent, 35 ng m^{-3} in winter and 46 ng m^{-3} in summer 1998, TSP) (Kubátová et al., 2002) and Greece (Thessaloniki, 14 ng m^{-3} in winter 2007, PM_{10}) (Salapasideou et al., 2011) (Fig. 1a), indicating the severe air pollution problem in both countries.

Total phthalate esters are $1.9\text{--}50 \text{ ng m}^{-3}$ in the atmospheres over Mt. Hua, central China and Mt. Tai, east China, Qinghai Lake in Tibet Plateau and East China Sea, which are 1–4 orders of magnitude lower than those in urban areas (Table 1). Qinghai Lake is located in the northeastern part of Tibetan Plateau, where population is very low and industrial activity is insignificant. Our previous studies found that atmospheric aerosols in Qinghai Lake are almost entirely derived from natural sources and impact of anthropogenic activities on the atmospheric environment is negligible (Li et al., 2013a). As shown in Table 1, fine particulate phthalates in the Qinghai Lake atmosphere are $1.9 \pm 1.2 \text{ ng m}^{-3}$ during summer, which is two orders of magnitude lower than in Chinese urban regions, again demonstrating the pristine nature of the Qinghai Lake atmosphere. On contrast, phthalates in Gosan, Korea ($29 \pm 12 \text{ ng m}^{-3}$ in TSP during 2005) (Wang et al., 2009b) and Okinawa, Japan ($32 \pm 5.4 \text{ ng m}^{-3}$ in TSP during 2005) (Table 1) are about one order of magnitude

higher than in Qinghai Lake, demonstrating a significant impact of Chinese air pollution on the Asian continental outflow regions.

3.1.2. Bisphenol A

Similar to phthalates, the highest concentrations of bisphenol A were observed in Guangzhou during winter and Chongqing during summer (Fig. 1b). The concentrations of bisphenol A (BPA) are $2.0\text{--}20$ and $1.0\text{--}10 \text{ ng m}^{-3}$ in the urban areas of China during winter and summer, respectively, which are lower than those in India ($2.5\text{--}47 \text{ ng m}^{-3}$) but around 10 times higher than those in urban areas of New Zealand (Auckland, 0.17 ng m^{-3} , and Christchurch, 0.52 ng m^{-3} in summer 2004, PM_{10}) (Fu and Kawamura, 2010) and USA (North Carolina, 0.88 ng m^{-3} in spring 1997, PM_{10}) (Wilson et al., 2001). BPA was not found in the aerosol samples collected at Qinghai Lake and Okinawa sites. BPA at other non-urban sites ranged from 0.01 to 0.05 ng m^{-3} , being 2–3 orders of magnitude lower than those in urban areas.

Chen et al. (2012) and Huang et al. (2012) assessed the exposure of phthalates and bisphenol A in various environmental media in China, such as water, air and food, and found that the single effect of the compounds by intake from air are much lower than those from foods and water. However, airborne particulate EDCs are usually mixed with other pollutants and thus may have a synergistic effect with other toxic species. For instance, Xu (2009) found that the joint adverse effect of bis(2-ethylhexyl) phthalate (BEHP) and benzo(a)pyrene (BaP) are much higher than that predicted from the known individual effects of each. Besides, the EDCs can be accumulated in human body, which would sharply increase their cumulative risk to human health (Zeng et al., 2013). Thus, the health effect of EDCs in the atmosphere of China should not be ignored.

3.2. Seasonal variation

As shown in Table 1 and Fig. 1a, the concentrations of phthalate esters in summer are 2.0–7.7 times higher than those in winter in the urban and mountain regions. A similar seasonal variation was also reported in Tianjin (Zhu et al., 2010), where phthalates in summer are 1.1–10 times higher than those in winter. Phthalates are used mainly in the manufacture of polyvinyl chloride polymer (PVC), resins, plasticizers for building materials and home furniture, food packaging and insect repellents (Fromme et al., 2004). Since phthalates are not chemically bond to the polymeric matrix, they can enter the environment by escaping from manufacturing processes and by leaching from final products (Stales et al., 1997). On the other hand, plastic waste incineration is an important source of phthalates in the atmosphere. Teil et al. (2006) reported that 65–94% of phthalates in the atmosphere of Paris is in the gas phase and volatilization from the matrix is probably the important origin. Given that sources are relatively stable in whole year, the higher concentration of phthalate esters in summer could be caused by the enhance volatilization of plastics under high temperature conditions.

Unlike phthalates, bisphenol A is used mostly as a monomer for manufacturing polycarbonates and epoxy resins, as well as unsaturated polyester–styrene resins and flame retardants (Fromme et al., 2004; Staples et al., 1998). The chemical

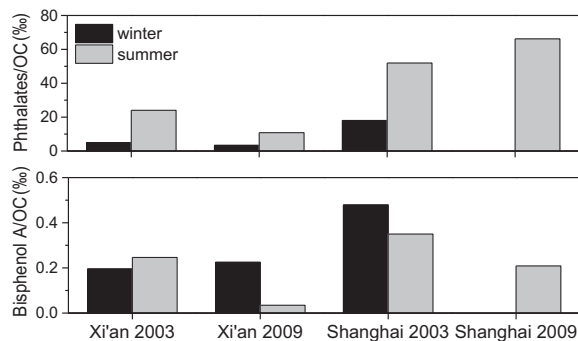
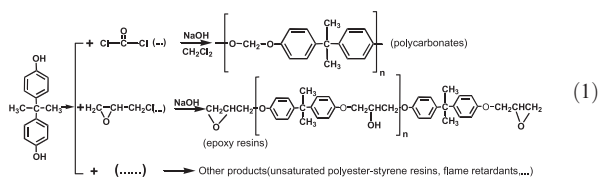


Fig. 2. Relative contribution of phthalates and bisphenol A to OC in Xi'an and Shanghai.

processes of bisphenol A in manufacturing the polymers are shown briefly in Eq. (1):



Bisphenol A is chemically bonded to the polymeric matrix, and thus hardly evaporates directly to the air. Instead, bisphenol A in the atmosphere is largely derived from combustion processes especially open burning of solid wastes (Fu and Kawamura, 2010). Thus it is reasonable that bisphenol A did not display seasonal variation similar to phthalates (Fig. 1). As shown in Fig. 3, bisphenol A and phthalates showed a better correlation in winter than in summer, confirming that the direct volatilization is an important origin of phthalates but not for bisphenol A.

In addition, concentrations of phthalates and bisphenol A in Shanghai and Xi'an (two mega-cities in China) in 2009 were 3–84% lower than those in 2003 (Table 1 and Fig. 1). This may suggest that air pollution control by Chinese government in recent years is effective.

3.3. Size distribution

Size distribution patterns of three major phthalates (i.e., diisobutyl (DiBP), dibutyl (DBP), and bis(2-ethylhexyl) (BEHP) phthalates) and bisphenol A (BPA) were plotted in Fig. 4. Diisobutyl phthalate showed a unimodal size distribution in winter and summer, peaking at the range of 4.7–5.8 μm (Fig. 4a and e). In contrast, dibutyl phthalate presented a bimodal pattern in both seasons with a major peak in coarse particles ($>2.1 \mu\text{m}$) and a minor peak in fine particles ($<2.1 \mu\text{m}$). Bis(2-ethylhexyl) phthalate was mostly enriched in the fine particles with a relative increase in the coarse particle during summer. Teil et al. (2006) also found that more amount of DBP exists in the gas phase than bis(2-ethylhexyl) phthalate in the atmosphere of Paris, France. DiBP and DBP are lower molecular weight compounds and thus more volatile than BEHP. For example, vapor pressure of DiBP is 0.01 KPa at 20 °C and one order of magnitude higher than BEHP (0.001 KPa at 20 °C) (NIOSH, <http://www.cdc.gov/niosh/ipcs/icstart.html>). Thus, in comparison with BEHP the more abundant DiBP and

DBP in coarse particles ($>2.1 \mu\text{m}$, Fig. 4) can be ascribed to more significant evaporation of DiBP and DBP from fine particles and subsequent adsorption onto pre-existing coarse particles (Teil et al., 2006; Wang et al., 2009a). However, the vapor pressure of BPA is very low ($1.2\text{E}-10$ to $5.3\text{E}-8$ KPa at 20 to 25 °C) (Staples et al., 1998), indicating that it is preferably enriched in fine particles after entering into the air via combustion process (Fu and Kawamura, 2010). Thus BPA presented a unimodal pattern and dominated in fine particles ($<2.1 \mu\text{m}$, Fig. 4d and h).

4. Conclusion

Airborne particulate phthalates and bisphenol A in mainland China and its surrounding regions were investigated. In general, bis(2-ethylhexyl) phthalate is the dominant congener. More abundant phthalates and BPA were presented in basin-like regions or developed cities, because of their geographic features or high industry emissions and anthropogenic activities. However, their abundances relative to particle loadings are more abundant in Shanghai than in Xi'an. Higher concentrations of phthalates and BPA in the Gosan Korea and Okinawa Island, Japan samples, compared with those in the Qinghai Lake samples, suggests that the high loadings of pollutants in mainland China have a significant impact on the downwind marine atmosphere. Phthalates showed higher concentrations in summer than in winter. In contrast, bisphenol A, which showed higher concentrations in winter, because direct evaporation from the matrix is the major origin of phthalates in the atmosphere and more significant in summer. However, atmospheric bisphenol A is largely derived from open burning urban solid wastes in China and can be significantly accumulated under wintertime meteorological conditions (such as stagnation conditions). Due to their much higher volatilities, diisobutyl and dibutyl phthalates mainly exist in coarse particles. In contrast, bis(2-ethylhexyl) phthalate and bisphenol A are much less volatile and thus mostly enriched in fine particles. The high levels of phthalates and bisphenol A in the atmosphere of China indicate that health effects of these EDCs should not be ignored because of their synergistic effect with other harmful species and their cumulative effect in human body.

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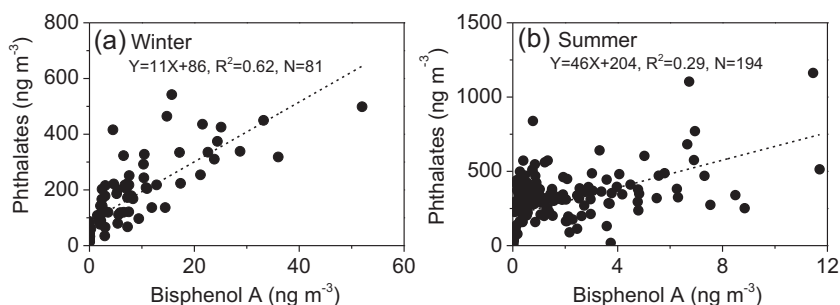


Fig. 3. Linear correlation between phthalates and bisphenol A in the wintertime and summertime aerosols of China.

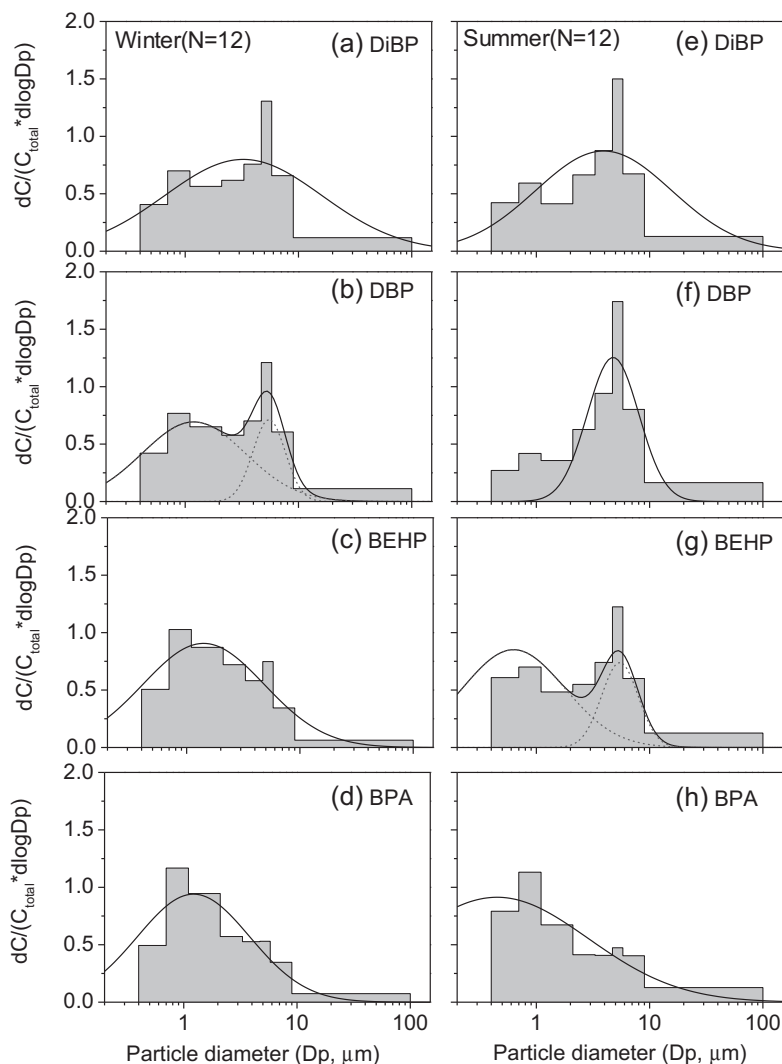


Fig. 4. Size distributions of diisobutyl, dibutyl, bis(2-ethylhexyl) phthalates and bisphenol A in winter and summer.

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