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Phthalate Esters in Sediments from Guanting Reservoir and the Yongding River, Beijing, People's Republic of China

X. T. Wang, L. L. Ma, Y. Z. Sun, X. B. Xu

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 10085, People's Republic of China

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Phthalate esters (PAEs) are a class of high production volume synthetic chemicals with a wide range of chemical and toxicological characteristics. The worldwide production of PAEs approximates 2.7 million metric tons a year (Bauer and Herrmann, 1997). PAEs are widely used in different industrial applications, mainly as plasticizers for PVC and to a lesser extent other resins. The content of phthalate in a finished plastic product is in the range 10-60% by weight. Six PAE compounds including dimethyl (DMP), diethyl (DEP), dibutyl (DBP), butylbenzyl (BBP), di(2-ethylhexyl) (DEHP) and di-n-octyl phthalate (DnOP) are classified as priority pollutants by US EPA.

Because phthalates are not chemically bound in the finished products, they can release into the environment throughout the cycle of their production, use, and disposal. Phthalates are ubiquitous in today's environment. The widespread presence of phthalates results in multiple human exposure routes. Phthalates are a concern in environmental public health because of the high potential for human exposure to phthalates and their demonstrated toxicity in animals. Endocrine-disruptive effects were observed in vivo for DBP, DEHP, BBP, DEP and DHP with relative potency ranging from 10^{-4} to 10^{-7} (relative to 17β-estradiol) (Law, 1991; van Wezel, 2000). Human studies are scarce, but recent studies have indicated that PAE compounds can induce the premature breast development (Colón et al., 2000), short pregnancy duration (Latini et al., 2003), increase the risk of cancer (Melnick, 2001) and stimulate the proliferation of human breast cell (MCF-7) (Blom et al., 1998). In addition, monoethyl phthalate (MEP) has shown an association with sperm DNA damage (Duty et al. 2003). Phthalate congeners with more than two and fewer than eight carbon atoms are reproductive and developmental toxicants of varying potencies (Gray et al. 2000; Heindel et al. 1989).

In recent years, several results about the level and distribution of PAEs in soil from China have been reported (Hu et al., 2003; Ma et al., 2003). However, no information on pollution of PAEs in surface sediment in China is available. The work is a part of a continuous research program on the pollution of Guanting Reservoir and the Yongding River in Beijing. The objectives of this study were to determine the levels and distribution of PAE residues in sediments collected from

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Correspondence to: X. B. Xu

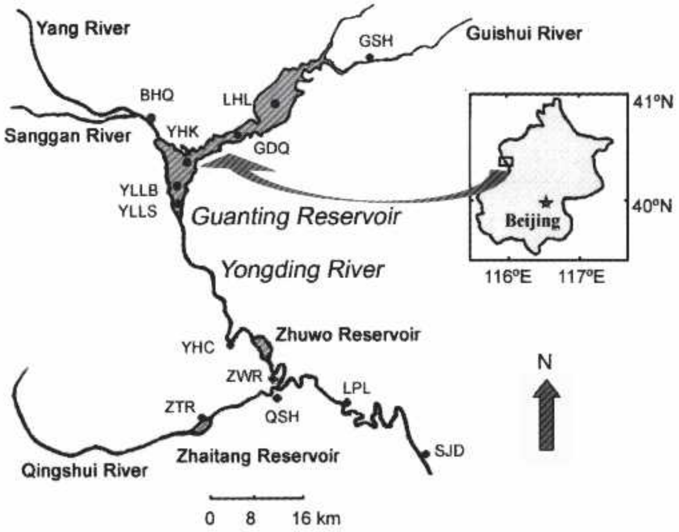

Figure1. Geographical position of Guanting Reservoir and the Yongding River and sampling stations

Guanting Reservoir and the Yongding River.

MATERIALS AND METHODS

The stock standard solutions of 16 phthalate esters (listed in Table1) at a concentration of 1000 μg/mL, and diphenyl phthalate (DPP) (used as surrogate) were purchased from Chem Service Inc. The desired concentration solution of PAEs was obtained by diluting the standard solution with iso-octane. Neutral alumina (heated at 400°C at least 16 hr prior to use.) and Florisil cartridge (1g) were from Supelco (Bellfonte, PA, USA). All solvents used in the study were from Merk (Darmstadt, Germany). In order to avoid contamination by PAEs in whole procedure, plastic containers were abstained; all solvents were redistilled in all-glass system before use. Glassware was detergent washed; rinsed with organic-free reagent water, then soaked in 5% $K_2Cr_2O_7$ sulfuric acid solution overnight; then re-rinsed with water, then acetone, hexane, and dichloromethane, respectively; finally baked at 450 °C at least 5 hr. Mortar and pestle were also cleaned using the similar procedure mentioned above, but heated at 250 °C for 12 hr. Anhydrous sodium sulfate (Beijing Chemical Factory) was baked at 500°C for 12 hr to remove all organic interferences.

Sediment samples were collected in October 2003 in Guanting Reservoir and in November 2003 in Yongding River. Twelve sampling sites were selected in the areas investigated, seven (BHQ, GSH, LHL, GDQ, YHK, YLLB and YLLS, among them BHQ and GSH are two inlets situated in Yang River and Guishui River, respectively) at Guanting Reservoir and five (YHC, ZTR, QSH, LPL and SJD) at Yongding River, respectively, were selected in the areas for investigation.

The geographical location of Guanting Reservoir, the Yongding River and the sampling sites are shown in Figure1.

The extraction and analysis of PAEs were performed according to USEPA SW-846 method 8061A with slight modification. Briefly, about 10 g of dry sediment sample was ground with 20 g of anhydrous sodium sulfate, then Soxhlet extracted with dichloride methane for 24 hr. 1 ml of DPP solution at a concentration of 2 μg/mL was added before extraction as a surrogate standard. The extract was concentrated in a rotary vacuum evaporator to about 5 mL; residual water was removed by an anhydrous sodium sulfate column chromatography; and then the clean-up was achieved by using neutral alumina (10 g) chromatographic column (30 cm×1 cm id). The eluate was concentrated to 2 mL, and the coextracted sulphur was removed by addition of mercury. Further cleanup was done by a 1-g Florisil cartridge (pre-conditioned with hexane), the eluate was placed in Kuderna-Danish tube and blown under a gentle stream of nitrogen to exactly 1mL for GC injection.

Quantification of 16 PAEs were carried out on an Agilient 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector (GC6890-μECD and a DB-5 fused silica capillary column (30 m × 0.25 mm id, and 0.25 μm film thickness). 1 μL of sample was injected in splitless mode and the purge time was 0.75 min. Nitrogen was used as carrier gas and make-up gas. The injector and detector temperature were 225°C and 300°C, respectively. The GC oven temperature was programmed as follows: initial temperature of 100 °C was held for 2 min, increased at a rate of 10°C /min to 280°C, and then held for 10 min. The quantification of the analytes was performed by external standard method. The identification of 16 phthalates was made by comparing the retention times with corresponding standards and confirmed on an Agilient 6890 GC /5973 (MSD) equipped with a HP-5 fused silica capillary column (30 m × 0.25 mm id, and 0.25 μm film thickness). Helium was used as carrier gas with a flow rate of 1 mL/min. The GC parameters were the same as described above. The mass spectrometer was operated in full scan mode using the electron impact (EI) mode (70 eV). The transfer line and ion-trap manifold were set at 280°C and 300°C, respectively. The mass range scanned was from 50 to 550 amu.

Blank and recovery experiments were run for sediment. For recovery experiments, PAE mixture in iso-octane was added to the PAE-free matrix. The method detection limits (MDLs) of 16 PAEs were determined as the concentrations of analytes in a blank sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. Detection limits varied for the different PAEs and ranged from 0.35 to 3.05 ng/g-dry weight. For every set of 6 samples, a procedural blank and spiked sample consisting of all reagents were run to check for interference and cross-contamination. The recoveries of PAEs spiked in matrix were in the range of 76-103%, and RSD (n=7) was 2.7-18.6%. The recoveries of surrogate standard (DPP) spiked in blank, matrix, samples were above 85%. These results indicated that the analytical protocols used in this study are effective for determination of phthalate residues in sediments. All samples were analyzed in duplicate, both for

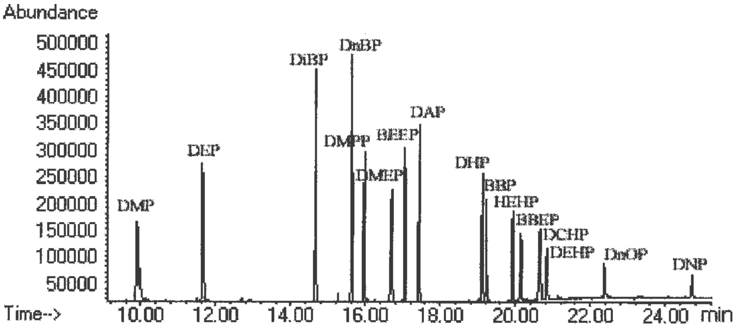

Figure.2 GC-MS (SIM) chromatogram of 16 PAE standards

qualitative and quantitative analysis. All residue concentrations below method detection limits were expressed as ND and regarded to be equal to zero in calculation of sum, means and so on. All results were expressed in ng/g on a dry weight basis and all results were not corrected for recoveries.

RESULTS AND DISCUSSION

The phthalate ester pollution in sediments from different sampling sites in Guanting Reservoir and the Yongding river was investigated and the results of the analyses, including range, arithmetic mean, and standard deviation (SD) of the concentrations on dry weight base, are presented in Table 1. Organic carbon contents in sediment samples analyzed by redox titration according to the previous method (Li, 1989) ranged from 0.03% to 4.47%, with a mean of 1.59%. Among the 16 PAEs detected in sediments, DEP, DiBP, DnBP and DEHP were detected in all samples (100%), followed by HEHP with a detection frequency of 91%. DOP was detected only one in 12 sediment samples. While the concentrations of DMPP, BBP, BBEP and DNP were below their detection limits in all sediment samples from Guanting Reservoir and the Yongding River.

The distribution of 16 PAEs (ΣPAEs) investigated and 6 US EPA priority PAEs (6 PAEs) in sediments from different sampling sites in Guanting Reservoir and the Yongding River was shown in Figure 3. The concentrations of ΣPAEs varied from 478.54-2118.91 ng/g, with an average of 1053.34 ng/g. The highest total concentration of PAEs (ΣPAEs) was found in SJD, followed by YHK and ZTR, with concentration of 1923.58 and 1374.61 ng/g, respectively. The lowest concentration was found in YHC (487.5 ng/g), followed by GSH (525.76 ng/g) and GDQ (592.7 ng/g).

The total concentrations of 6 US EPA priority PAEs (6 PAEs) including DMP, DEP, DiBP, DnBP, DEHP and DnOP ranged from 348.78 ng/g in GDQ to 1974.82 ng/g in SJD, with a mean of 845.40 ng/g. The contribution of 6 PAEs to the total PAEs was in the range of 58.85% to 97.79% with a mean of 88.43 %.The distribution patterns of 6 PAEs in each sediment samples from Guanting reservoir

Table 1. Concentrations (ng/g, dw) of 16 PAEs in sediment samples from Guanting Reservoir and Yongding River

Compound name	Abbreviation	Range	Mean	SD[a]
Dimethyl phthalate	DMP	ND-20.67	9.42	4.15
Diethyl phthalate	DEP	9.34-53.96	22.09	13.87
Diisobutyl phthalate	DiBP	49.54-749.89	368.51	335.38
Di-n-butyl phthalate	DnBP	95.34-165.25	129.93	46.09
Bis(4-methyl-2-pentyl) phthalate	DMPP	ND	ND	ND
Bis(2-methoxyethyl) phthalate	DMEP	ND-229.42	76.32	ND
Bis(2-ethoxyethyl) phthalate	BEEP	ND-60.95	24.13	23.40
Diamyl phthalate	DAP	ND-49.09	10.99	16.94
Dihexyl phthalate	DHP	ND-81.90	16.86	ND
Butyl benzyl phthalate	BBP	ND	ND	ND
Hexyl 2-ethylhexyl phthalate	HEHP	ND-86.83	26.63	27.46
Bis(2-n-butoxyethyl) phthalate	BBEP	ND	ND	ND
Dicyclohexyl phthalate	DCHP	ND-90.29	18.85	23.07
Di(2-ethylhexyl) phthalate	DEHP	169.82-1087.02	347.93	529.94
Di-n-octyl phthalate	DnOP	ND-20.23	1.69	14.30
Dinonyl phthalate	DNP	ND	ND	ND
ΣPAEs		478.54-2118.91	1136.92	998.56
6 PAEs		348.78-1974.82	879.56	907.70

[a] SD-standard deviation (n=12)

and Yongding river were similar to ΣPAEs.

In present study, the levels of DMPP, BBP, BBEP and DNP were lower than their MDLs in all samples, while DMEP, DAP, DCP and DCHP either their detection frequencies were lower or they were occurred at lower concentration, and therefore their contribution to the total PAEs were lower, the further discussion here will focus on the 8 PAEs including DMP, DEP, DiBP, DnBP, DEHP, BEEP, HEHP and DHP for convenience.

The individual PAE concentrations of 8 PAEs at each site were shown in Figure 4. Among the 8 PAEs, DMP, DEP, DiBP, DnBP and DEHP were detected in all sampling sites. DMP and DEP occurred in lower concentration. The predominate phthalates among the 8 PAEs were DEHP, DiBP and DnBP in all sampling sites, which accounted for 12.77-51.30%, 8.36-53.73% and 7.29-25.4%, and with means of 33.22, 30.74 and 14.54% of total PAEs, respectively. The sum of DEHP, DiBP and DnBP accounted for 56.40-90.23% with a mean of 78.50% of total PAEs. The results were similar to those observed in greenhouse soils from Beijing suburbs (Ma et al., 2003), in which the three PAEs were the most frequently identified compounds and accounted for more than 97% of total 6 EPA priority

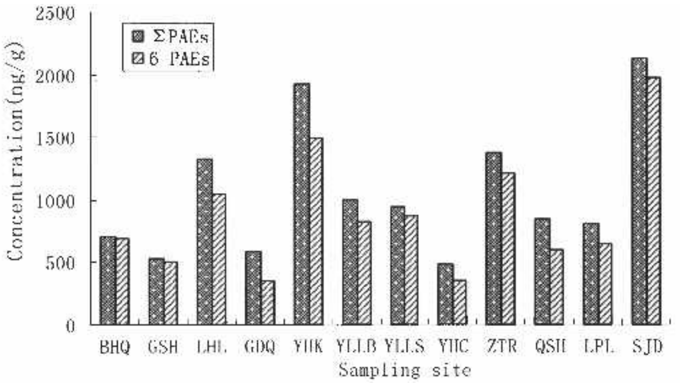

Figure 3. Distributions of 16 PAEs and 6 EPA PAEs in sediment samples

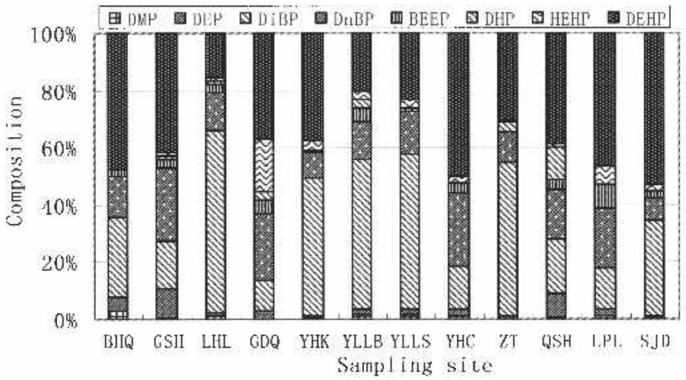

Figure 4. The distribution pattern of 8 selected PAEs

PAEs. Their concentrations were in the range of 69.82 (LHL) to 1087.02 ng/g (SJD), 49.54 (GDQ) to 749.89 ng/g (YHK) and 95.34 (YHC) to 165.25 ng/g (SJD) with averages of 347.10, 335.18 and 129.93 ng/g, respectively. DnBP and DEHP are important and popular addictives in many industrial products including flexible PVC materials and household products such as paint and glues (Madsen et al., 1999). DEHP is difficult to degrade under both aerobic conditions and anaerobic conditions. Therefore, the contribution of DEHP to total PAEs was higher than that of other PAE congeners in most sediment samples. DiBP was the second highest PAE congener on average in abundance, which is similar to that of greenhouse soil in Beijing suburbs (Ma et al., 2003). Unfortunately, related information on DiBP was scarce.

Due to lack of quality guideline for freshwater surface sediment, to evaluate the potential for adverse effects of phthalate esters, marine sediment quality standards-chemical criteria in WAC173-204-320 (Washington State Department of Ecology, 1995) was used. The sediment quality standards correspond to a sediment quality that will result in no adverse effects, including no acute or chronic adverse effects on biological resources and no significant health risk to humans. The criteria values are 53, 61, 220, 4.9, 47 and 58 mg/kg organic carbon for DMP, DEP, DnBP, BBP, DEHP and DnOP, respectively. The concentrations of DMP, DEP, DnBP, and DEHP were 1.52, 1.21, 1.03 and 16.19 times higher than these chemical criteria at BHQ. PAE levels at other sites were lower compared to these chemical criteria. Van Wezel et al. (2000) derived the environmental risk limits (ERLs) for DBP and DEHP with emphasis on endocrine disruptive properties. The ERLs in soil and sediment normalized based on 10% organic matter are 0.7 mg/kg for DnBP and 1 mg/kg for DEHP, respectively. According to the ERLs, the concentrations of DnBP in sediment samples were lower than the ERL, and DEHP in sediments exceeded the value only one (0.76 mg/kg at BHQ) in twelve sampling sites.

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