



Mapping of phthalate esters in suburban surface and deep soils around a metropolis-Beijing, China



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ARTICLE INFO

Article history:

Received 26 December 2014

Accepted 16 April 2015

Available online 25 April 2015

Keywords:

Mapping
Phthalate esters
Soils
Flux
Modeling

ABSTRACT

For a safety of public health, it is crucial to understand the soil quality in suburban metropolis with rapid urbanization. The levels and compositional patterns of 13 phthalate esters (PAEs) in both surface and deep soil were analyzed in suburban Beijing for the first time. The geochemical distribution was mapped to identify several “hot spots” in the southern and southeastern areas, which could direct the future management and remediation. PAEs were ubiquitous contaminants and di(2-ethylhexyl) phthalate (DEHP), di-isobutyl phthalate (DiBP) together with di-n-butyl phthalate (DBP) were three dominant species in both layers. The total concentrations in the surface and deep soils were 0.02–2.90 mg kg⁻¹ (median: 0.38 mg kg⁻¹) and 0–1.51 mg kg⁻¹ (lower median: 0.12 mg kg⁻¹), respectively. The assessment of eco-toxicological effect of the abundant PAEs suggests that no environmental risk would occur at the present level in suburban Beijing. The modeling volatilization flux of six EPA-PAEs was from 5.07 × 10⁻³ ng h⁻¹ for dimethyl phthalate (DMP) to 1.88 × 10⁻⁶ ng h⁻¹ for di-n-octyl phthalate (DOP). A relationship between volatilization flux (F_v) and octanol-water partition coefficient (K_{ow}) was employed to predict the fluxes of other PAEs from soil to atmosphere. The surface soil could continue to be the source of atmospheric contamination of PAEs in a long term, which deserves further attentions.

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1. Introduction

Recently, the Taiwan food scandal rocked the world since some phthalate esters (PAEs), endocrine disruptors, were found in foods and beverages (Yang et al., 2013). PAEs are widely used as additives in plastics and as non-plasticizers in the manufacturing of cosmetics, insect repellents, insecticide carriers, and propellants (Peakall, 1975). The total global annual production is around several million tons and current consumption of PAEs in China is over 0.87 million tones year⁻¹. Studies have shown that some PAEs and their metabolites elicit reproductive and developmental toxicities in laboratory animals (Boberg et al., 2008; Gray et al., 2000). The United States Environmental Protection Agency (USEPA) and several other countries classified the most commonly occurring PAEs as priority pollutants (Staples et al., 1997). Since only physically incorporated in the polymeric matrices by the weight of up to 10–60%, PAEs easily penetrate into the ecosystem during manufacturing, storage, usage and after disposal (Bauer and Herrmann, 1997; Heudorf et al., 2007) and have been the most abundant and ubiquitous compounds in various environmental matrices such as air, water, sediment, soil, and human tissue (Staples et al., 1997).

The environmental quality of big city is a growing concern as the human population continues to dramatically increase. Beijing (39°48'N and 116°28'E), the capital of China, is a growing metropolis by leaps and bounds with a population of more than 20 million. Rapid urbanization resulted in aggravating environmental problem in the urban ecosystems. A few scattered data showed that PAEs have caused serious pollution to the environment of Beijing with a range of 0.12–10.10 μg L⁻¹ in the ground water (Wei et al., 1986), 3820.10–13425.50 ng m⁻³ in the atmosphere (Shao et al., 2009) and 25.39–77.77 mg kg⁻¹ in municipal sludge (Du et al., 2004). Despite of the high levels of seven common PAEs (0.72–8.33 mg kg⁻¹) were observed in urban soil in Beijing (Li et al., 2006), only few reports on PAEs are currently available in the suburban soils in Beijing (Hu et al., 2003; Ma et al., 2003).

The traditional suburban Beijing, out of the 4th Ring Road, is undergoing great changes and the transitional zones where commercial and agricultural land application interlocked have been formed. The organic pollutants in the soil would result in the indirect/direct exposure to human and loss of them from soil by evaporation or migration is continuously a possible source of atmosphere and groundwater pollution. For the safety of public health, a systematic scheme covering approximately 1100 km² was carried out by Chinese government in 2000 to investigate the fate of organic pollutants including PAEs in suburban

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soils. This study is one part of the tremendous project and will provide information needed to facilitate the implementation of mitigation measures for these toxic chemicals.

In the present study, composite surface soils on a large scale were collected for the first time to identify the concentrations, compositions and distributions of PAEs in suburban Beijing. Deep soils in the corresponding areas were characterized as well to check the possible vertical transportation of PAEs. The potential eco-toxicological effect of the hot phthalate esters is assessed. Geochemical distribution of PAEs is mapped based on geographic information system (GIS) to identify the hotspots. Furthermore, a modeling prediction based on soil volatilization fluxes is conducted to tell the contribution of PAEs in soils to those in the atmosphere.

2. Materials and methods

2.1. Chemicals and materials

The mixed standards were supplied by Supelco (West Chester, PA, USA), including 13 PAEs of dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DBP), bis(4-methyl-2-pentyl) phthalate (BMPP), di-*n*-amyl phthalate (DAP), di-*n*-hexyl phthalate (DHP), butylbenzyl phthalate (BBP), di(hexyl-2-ethyl-hexyl) phthalate (HEHP), dicyclohexyl phthalate (DCHP), di-(2-ethylhexyl) phthalate (DEHP), di-*n*-nonyl phthalate (DNP) and di-*n*-octyl phthalate (DOP) was supplied by Aldrich (WIS, USA). All solvents were of analytical purity (Beijing Chemical Factory, China) and were redistilled in an all-glass system before use. Florisil (60–100 mesh; Supelco) was activated at 130 °C for 16 h. Anhydrous sodium sulfate (analytical purity, Beijing Chemical Factory, China) was first washed with hexane, and then heated at 600 °C for 12 h prior to use.

Since phthalate esters are widespread in the environment, great care must be taken to minimize contamination during the experiment. Plastic tubing and containers were abstained. The glassware was prepared successively in the following order: washed with acetone and hot water, soaked overnight in $K_2Cr_2O_4/H_2SO_4$ solution, washed with tap water and distilled water in turn, dried in oven and then rinsed with acetone and hexane just prior to use.

2.2. Sampling

Beijing is located at the northwestern border of the Great North China Plain, and features a typical temperate continental monsoon climate. The city area is 16,807 km², with 748 km² classified as urban area. The 4th Ring Road was the traditional division line between urban and suburban city. The investigation area was out of the 4th Ring Road with 5 km to the east, 14 km to the south, 7 km to the west and 6 km to the north.

The intensive sampling was carried out in 2000 and the sampling sites (Fig. 1) covered 1100 km². The studied area was divided into regular grids of 1 km² × 1 km² based on approximately equal longitude and latitude by GIS. For 47 surface soil samples (0–20 cm), multiple cores covering every 1 km² were collected with stainless steel drill to get one sub-sample firstly and then 16 vicinal sub-samples were mixed fully to obtain one composite surface sample. In each 16 km² area, multiple cores covering about 4 km² at the depth of 150–180 cm were sampled to get one deep layer soil. Each fully mixed sample was air-dried at room temperature in the fume hoods, well ground, passed through < 1 mm sieves and was stored in glass bottles at -4 °C until further processing.

The remaining water content in the soil was determined gravimetrically after drying individual composite sample at 105 °C for 12 h. All the results were reported as dried weight.

2.3. Sample extraction and cleanup

The detailed procedures of extraction, clean up and instrument analysis were according to the method described previously (Ma et al., 2003). Briefly, after DPP added as surrogate, soil was extracted by ultrasonic in acetone-petroleum ether followed and separated by centrifugation. The concentrated extract was transferred to a chromatograph column (30 cm × 10 mm i.d.) packed with 5 g of florisil, washed with 40 mL of hexane/diethyl ether (9/1, v/v) and followed by 40 mL of hexane/diethyl ether (2/3, v/v). The second fraction contained all the phthalate esters analyzed.

2.4. Instrumental analysis

Quantification of PAEs was performed on a 6890 N gas chromatograph (GC, Agilent J&W Co., USA) coupled to a flame ionization detector (FID) with a fused silica capillary (30 m × 0.25 mm i.d.) coated with a 0.25 μm thick film of DB-5 column (5% phenylmethylpolysiloxane, Agilent J&W Co., USA). The injector and detector temperature were 280 °C and 300 °C, respectively. The oven temperature program was as follows: initial temperature of 50 °C was held for 2 min, increased at a rate of 4 °C min⁻¹ to 280 °C, then held for 10 min. 1 μL of sample was injected in splitless mode and the carrier gas was N₂ with a flow of 1.2 mL min⁻¹.

The confirmation of the compounds was carried out on a Hewlett Packard 6890 GC-5973 MSD system with the same kind of column as in the GC, operating in electron impact (EI) and selective ion monitoring mode (SIM). The selected ion was 149, which was commonly observed in many phthalates (except for DMP: m/z 163, 194). The electron impact energy was 70 eV and the carrier gas was helium (99.999%) at a flow rate of 1 mL min⁻¹. The identification was based on the retention time and mass spectrum with appropriate individual standards.

To assure the quality of proposed analytical method, the method blank, spiked blank, matrix and every ten samples were successively analyzed in each analytical batch. The average recoveries of PAEs were in the range of 75–130% with the relative standard deviations of 3–13% (n = 5). No background subtraction was made to correct the results. The limits of detection (LODs), as three times response of signal-to-noise in matrix blanks (n = 5), ranged from 0.002 mg kg⁻¹ for DMP to 0.022 mg kg⁻¹ for DEHP.

2.5. Data analysis

Correlation analysis was performed with SPSS 13.0 for Windows (SPSS Inc., Chicago, IL). Surfer (Version 8.0, Golden software, CO, USA) was used to draw the spatial distribution maps.

3. Results and discussion

3.1. Levels and assessment

Phthalate esters were ubiquitous pollutants in soils and the total concentrations of 13 PAEs (\sum_{13} PAEs) in the surface soils ranged from 0.02 to 2.90 mg kg⁻¹ with a median of 0.38 mg kg⁻¹. The concentrations of 6 PAEs (\sum_{EPA} PAEs: DMP, DEP, DBP, BBP, DEHP and DOP) listed by USEPA were in a range of 0.02 to 1.36 mg kg⁻¹ in the surface soils which were much lower than those in the urban soils (0.51–7.96 mg kg⁻¹) collected in 2003 in Beijing (Li et al., 2006). In the deep soils, \sum_{13} PAEs ranged from not detected to 1.51 mg kg⁻¹ with a lower median of 0.12 mg kg⁻¹, except for one sample with the highest value of 3.63 mg kg⁻¹ in this study.

No comparable deep soils data are available until now. As summarized in Table 1, the concentrations of DEHP and DBP in surface soils were compared with other data to provide insights on the regional and temporal patterns. The levels of DBP and DEHP in soils in suburban Beijing were much lower than those in the urban soils collected in 2003

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