Science of the Total Environment 500–501 (2014) 113–119

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Occurrence of phthalate esters in river sediments in areas with different land use patterns

Jun Wang [a,b], Luji Bo [a,c], Lina Li [a,c], Dejian Wang [a], Gangcai Chen [b], Peter Christie [a], Ying Teng [a,*]

[a] Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] Chongqing Research Academy of Environmental Sciences, Chongqing 401147, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Clarified the PAEs distribution in sediments of southern Jiangsu province, China.
- Confirmed the correlations between PAEs cocentration and sediments physicochemical.
- Evaluated the potential environmental risk of PAEs in sendiments.

ARTICLE INFO

Article history:
Received 23 May 2014
Received in revised form 19 August 2014
Accepted 26 August 2014
Available online xxxx

Editor: Adrian Covaci

Keywords:
Phthalate esters
River sediments
Southern Jiangsu
Risk assessment

ABSTRACT

Phthalate esters (PAEs) are widely used as plasticizers in both industrial and commercial products and have aroused considerable concern over their widespread distribution and potentially hazardous impacts on the environment. The present study investigated the distribution (concentrations at different sites) of PAEs in typical riverine sediments in southern Jiangsu Province and its relationship with the physical and chemical properties of the sediments. PAEs were detected in all 34 sediment samples analyzed, and the total concentrations of the six priority control PAEs in sediments ranged from 2.3 to 80.1 mg kg^{-1} with a mean concentration of 13.2 ± 14.7 mg kg^{-1}. Land use significantly ($p < 0.05$) influenced the PAE concentrations in the river sediments. The average PAE concentrations in mixed industrial and commercial districts were 27.8 ± 18.2 mg kg^{-1}, three and eight times higher than those in suburban areas (8.8 ± 3.7 mg kg^{-1}) and an agricultural field (3.4 ± 0.9 mg kg^{-1}), respectively. The concentrations of PAEs showed significant linear positive correlations with sediment organic matter and phosphorus but no significant correlation with sediment pH. Di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP) were the dominant PAE compounds present in all examined sediment samples. These PAEs have relatively high ecotoxicology, but the potential risk of their transfer to the food chain needs further study.

1. Introduction

Phthalate esters (PAEs) are chemical agents employed to increase the plasticity of industrial polymers, and their most important application is in the manufacturing of polyvinyl chloride (PVC). They are used ubiquitously in many commercial products, such as rubber, cellulose, styrene and a wide range of consumer products (Staples et al., 1997; Gómez-Hens and Aguilar-Caballos, 2003; Ventrice et al., 2013). However, PAEs are not chemically bound to the matrix of plastic products and exist in a freely mobile and leachable phase; consequently, they can leach, migrate or evaporate into the environment from domestic and industrial effluents, sewage sludge and storm water runoff, as well as from the manufacturing, use and indiscriminate disposal of phthalate-containing products (Staples et al., 1997; Wang et al., 2013). With their large-scale production and widespread application, approximately 5 million tons of PAEs is produced globally each year, resulting in extensive potential exposure to humans and other biota (Bauer and Herrmann, 1997; Mckee et al., 2004; Magdouli et al., 2013; Zhang et al., 2013; Meng et al., 2014). Studies on rodents have shown that di-n-butyl phthalate (DnBP), di(2-ethylhexyl) phthalate (DEHP), butylbenzyl phthalate (BBP) and their metabolites are oestrogenic and thus exhibit adverse reproductive effects (Fukuwatari et al., 2002; Scholz, 2004). Some PAEs and their metabolites have been identified in human urine and amniotic fluid samples, and recent studies indicate that they are suspected endocrine disrupting chemicals exhibiting carcinogenic properties (McKee et al., 2004). Perinatal exposure to some phthalates and their metabolites might result in human Leydig cell development and incomplete virilization in infant boys (Main et al., 2006). PAEs have become one of the most widespread classes of organic

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.scitotenv.2014.08.092

contaminants, and their distribution and potential human health risks have become the focus of much attention. The most commonly detected PAEs are dimethyl phthalate (DMP), diethyl phthalate (DEP), DnBP, BBP, DEHP and di-n-octyl phthalate (DnOP), and these have endocrine disruption impacts and carcinogenic, teratogenic and mutagenic effects, resulting in their classification as priority environmental pollutants by the United States Environmental Protection Agency (USEPA, 2013).

PAEs have been detected in various environmental media worldwide including air (Xie et al., 2005; Teil et al., 2006), water (Vitali et al., 1997; Adeniyi et al., 2011; He et al., 2013), soils (Wang et al., 2013), wastes (Bauer and Herrmann, 1997; Cai et al., 2007; Aparicio et al., 2009) and sediments (Liu et al., 2010; Sun et al., 2013). Sediments are important sources and sinks for PAE distribution and bioaccumulation in water and have been used extensively as environmental indicators for evaluating PAE pollution levels (Vitali et al., 1997; Huang et al., 2008). PAEs have been detected in river sediments in North Rhine-Westphalia, Rheinland-Pfalz, Brandenburg and Berlin in Germany (Fromme et al., 2002), the Rieti district in Italy (Vitali et al., 1997), the estuaries in the Bay of Biscay in Spain (Bartolomé et al., 2005) and the Gomti River in India (Srivastava et al., 2010), as well as in aquatic surface sediments in the Netherlands (Vethaak et al., 2005; Klamer et al., 2005), estuarine sediments in New Zealand (Stewart et al., 2014) and tidal salt marsh sediments in the United States (Hwang et al., 2006).

The production and consumption levels of PAEs in China are the highest in the world with a 2011 consumption of approximately 2.2 million tons, most of which was used in PVC production (Wang et al., 2013). Several studies have focused on the concentrations and distribution of PAEs in lakes and large rivers, but studies on suburban river networks are limited (Yuan et al., 2002; Xu et al., 2007; Sun et al., 2013; Zheng et al., 2014). Zeng et al. (2008) reported that the Σ_{16}PAEs concentrations in urban lake sediments ranged from 2.3 to 74.9 mg kg^{-1} dry weight (dw) with a mean concentration of 20.8 mg kg^{-1} in Guangzhou, South China. The PAE concentrations in sediments of the Yellow River were 30.5 to 85.2 mg kg^{-1}, which are much higher than those reported for other river sediments around the world (Sha et al., 2007). PAEs in Qiantang River sediments were detected in all examined samples, and the total concentrations of 16 congeners ranged from 0.6 to 6.7 mg kg^{-1} dw with a geometric mean value of 2.0 mg kg^{-1} dw (Sun et al., 2013). The highest DEHP concentration in the Houjing River in south Taiwan was 20.2 mg kg^{-1} with a mean of 3.8 ± 6.4 mg kg^{-1} dw (Lin et al., 2009). Previous studies show that PAEs had no effect on the survival or growth of invertebrate benthos (*Chironomus tentans* and *Hyalella azteca*) exposed to sediments (Call et al., 2001), but they can accumulate during gastrointestinal digestion and are bioavailable in fish muscle (Adeniyi et al., 2011). PAEs can affect human health through the consumption of some species of fish; the potential risks of PAEs in sediments need to be taken into account because humans will be inevitably exposed to PAEs through the ingestion of contaminated surface water and consumption of aquatic organisms (He et al., 2013; Zhang et al., 2013). However, there is no published information on the distribution of PAEs in the sediments of suburban river networks in the southern Jiangsu Province.

Previous studies have found correlations between PAE concentrations in sediments and anthropogenic activities, urbanization and the level of industrialization of the surrounding areas (Zeng et al., 2008; Zheng et al., 2014). Southern Jiangsu is situated in the center of the Yangtze River Delta region and is one of the most industrialized and urbanized areas in China with rapid economic growth and the most highly developed inland waterway transportation system. Thus, the river network is integrated with the urban centers and is an important water resource for agricultural irrigation and industrial production. However, the rivers are also receptors of pollutants from agricultural and urban areas, and the sediments act as a sink in which many pollutants accumulate. The objectives of the present study were to investigate the PAE concentrations, congener profiles, distribution and environmental risks and to assess the influence of different land use types on the distribution of PAEs in the river sediments in the southern Jiangsu Province.

2. Materials and methods

2.1. Study area and sampling

A total of 34 sediment samples were collected from the rivers with three different land use patterns around Yangyuan Town (31°33 14.4 N, 120°39 40.32 E) at Changshu, southern Jiangsu Province, China in November 2012 (Fig. 1). Eleven sediment samples were collected at a depth of 2 to 3 m where both sides of the river are agricultural fields (AF). Twelve sediment samples were collected from the river where the depth of the water was approximately 4 to 5 m and both sides have rural residential areas (RR). Eleven sediment samples were collected from water depths of approximately 2 to 3 m in areas which have mixed industrial and commercial activity (CR). The sediment samples were collected from the mid-stream of the river using a stainless steel grab sampler, and each sample was scooped using a pre-cleaned stainless steel scoop into solvent-rinsed aluminium containers. An investigation indicated that the age of the top river sediments was approximately 20 years. Each sediment sample consisted of five sub-samples collected from each site and was cooled in an ice box during transport. The samples were refrigerated, transported directly to the laboratory and stored at −20 °C until further analysis. The sample treatment and analysis followed the procedures of Wang et al. (2013).

2.2. Materials and chemicals

A standard mixture of six PAEs consisting of DMP, DEP, DnBP, BBP, DEHP and DnOP, each at a concentration of 1.0 g mL^{-1}, and an isotope surrogate standard of di-n-butyl phthalate-d4 (DnBP-D4, 0.1 g mL^{-1}) were purchased from Dr Ehrenstorfer (Augsburg, Germany).

Neutral silica gel and alumina (100- to 200-mesh) and anhydrous sodium sulfate were activated at 400 ± 1 °C for 6 h. The acetone and n-hexane used were HPLC grade purchased from Tedia Company Inc., Fairfield, Ohio. Before use, all glassware was washed in a detergent solution in a laboratory ultrasonic washer (KQ-600DB, Kun Shan Ultrasonic Instruments Co., Ltd., Jiangsu Province, East China), air dried and immersed in sulphuric acid (guaranteed reagent) and washed with tap water and ultrapure water before oven-drying and rinsing with acetone and n-hexane. No plastic vessels were employed in the experimental procedures.

2.3. PAE extraction and clean-up

The freeze-dried sediment samples were ground and homogenized using a mortar and pestle and then sieved through a stainless steel sieve (60-mesh) and stored in brown glass bottles at −20 °C until extraction. Weighted sediment samples (3.0 g) were placed into glass centrifuge bottles, mixed with 20 mL acetone/hexane (1:1 v/v), left overnight and extracted ultrasonically for 30 min. The procedure was replicated twice, and each extract was subsequently filtered into a round bottom flask. Then, the filtrates were concentrated to 1–2 mL with a rotary evaporator, solvent exchanged with n-hexane and then cleaned on a 10-mm i.d. silica/alumina column packed (from bottom to top) with neutral silica gel (12 cm), neutral alumina (6 cm) and anhydrous sodium sulfate (1 cm). The column was conditioned with 15 mL n-hexane and then with 15 mL acetone/n-hexane (1:1 v/v), and the eluents were discarded. Then, the concentrated extract was transferred to the silica/alumina column and eluted with 40 mL acetone/n-hexane (1:4 v/v), and the resulting eluent was collected. The fraction containing the PAEs was concentrated to less than 1 mL; next, the isotope surrogate standard was added, and the fraction was adjusted to a constant volume of 1 mL and passed through a 0.25 μm