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Distribution and ecotoxicological state of phthalate esters in the sea-surface microlayer, seawater and sediment of the Bohai Sea and the Yellow Sea☆

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ABSTRACT

The spatial distribution, chemical composition and ecological risk of 16 phthalate esters (PAEs) were investigated in the sea-surface microlayer (SML), seawater and sediment samples of the Bohai Sea (BS) and the Yellow Sea (YS). The concentration levels of the ΣPAEs spanned a range of 449–13441 ng L^{-1} in the SML, 453–5108 ng L^{-1} in seawater, and 1.24–15.8 mg kg^{-1} in the sediment samples, respectively, with diisobutyl phthalate (DiBP), di-n-butyl phthalate (DBP) and di-ethylhexyl phthalate (DEHP) as the dominant PAEs in both the water and sediment samples. The concentrations of ΣPAEs in the BS were higher than those in the YS. The vertical distribution of ΣPAEs in the water column showed that the concentrations were higher in the surface waters, but decreased slightly with depth, and started to increase at the bottom. Additionally, PAEs were significantly enriched in the SML, with an average enrichment factor of 1.46. The ecological risk of the PAEs was evaluated by the risk quotient (RQ) method, which indicated that DEHP posed a high risk to aquatic organisms in the whole water-phase, while the RQ values of DBP and DiBP reached a high risk levels in sedimentary environment.

1. Introduction

Phthalate esters (PAEs), one of the most commonly used plasticizers, are widely utilized in production of plastic products to enhance elasticity, transparency and durability. Additionally, PAEs have been widely used in numerous chemical industries to improve the quality and functions of products (Li et al., 2017). For example, PAEs with lower molecular weight, e.g., dimethyl phthalate (DMP) and diethyl phthalate (DEP), restrain volatilization of perfume fragrances (Net et al., 2015), whereas longer alkyl chain PAEs, such as, di-ethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP), are used to enhance the flexibility and handing of chemical and industrial materials (Paluselli et al., 2017). As reported by Information Handling Services (IHS) Chemistry, nearly 5.9 million tons of PAEs were used to produce plasticizers on a global scale in 2014. Additionally, IHS also showed that the amount of plasticizers used globally would increase to 10.3 million tons by 2019, when PAEs would account for 65% (IHS Markit).

Notably, PAEs are not chemically bound to the polymers but mixed with them, so it is entirely possible for PAEs to separate from the products during manufacture and operation and be discharged into the environment. PAEs are prevalent and have been detected in air, marine and continental environments (Xie et al., 2005; Liu et al., 2015; Wu et al., 2015; Wang et al., 2016; Chi et al., 2017; Paluselli et al., 2017; Zhang et al., 2018). In addition, PAEs are detected in terrestrial and marine organisms, such as marine turtles (Savoca et al., 2018), fish (Cheng et al., 2013; Adeogun et al., 2015), fresh algae and cyanobacteria (Babu and Wu, 2010), as well as humans (Net et al., 2015; Gao and Chi, 2015). Previous studies have shown that PAEs are prone to trigger carcinoma and dysplasia and negatively affect the reproductive system by decreasing sperm count (Su et al., 2012; Adeogun et al., 2015). Given the latent environmental and health risks, the United States Environmental Protection Agency listed six PAEs, i.e., DMP, DEP, di-n-butyl phthalate (DBP),

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butyl benzyl phthalate (BBP), DEHP and DnOP as priority pollutants. In 2017, the Committee for Risk Assessment and the Committee for Socio-Economic Analysis agreed upon a restriction proposal for four phthalates (DEHP, DnBP, diisobutyl phthalate [DiBP] and BBP) in products used by the general public. The recommendation was to ban PAEs in products that cause exposure through the skin or by inhalation, such as flooring, coated fabrics and paper, recreational gear and equipment, mattresses, footwear, office supplies and equipment, and other products molded or coated with plastic.

Previous studies have demonstrated that PAEs are ecotoxic and genotoxic (He et al., 2013; Chen et al., 2017; Al-Saleh et al., 2017; Li et al., 2017), for example, information from the IARC indicated that DEHP is an animal carcinogen and has the same effect on humans (IARC., 2000). Therefore, investigations of PAE concentrations and an eco-risk assessment are necessary for terrestrial and aquatic species and the entire ecosystem. Many toxicity experiments have been carried out to provide data for risk assessments. A predicted no-effect concentration (PNEC) is regarded as a concentration below which an unacceptable effect will most likely not occur (EC, 2003). A risk quotient (RQ) method was applied to evaluate the potential environmental risk of PAEs in the water and sedimentary phases. In the water-phase, values of $RQ > 1$, $0.01 < RQ < 1$ and $RQ < 0.01$ reflect high risk, medium risk and low or no risk to aquatic organisms, respectively, whereas PAEs have a high risk when $RQ > 10$ with $lgK_{OW} > 5$ and high risk when $RQ > 1$ with $3 < lgK_{OW} < 5$ in the sediment-phase (EC, 2003; Li et al., 2017). In addition, the predicted environmental concentration for environmental water and sediment samples (Net et al., 2015; Naito et al., 2006), the environmental quality standard for fresh and marine water (Butwell et al., 2001; Marchand et al., 2004), the environmental risk limit for soil (fresh weight) and sediment (dry weight) (Wezel et al., 2000), and the minor adverse effect concentration for marine sediment (Barrick et al., 1988, Net et al., 2015) were established as standard environmental risk assessment rules for PAEs.

The sea-surface microlayer (SML) is defined as the top of the ocean surface with a total thickness of 1–1000 μm (Kozarac et al., 2003; Wurl and Obbard, 2004). This interface acts as a sink and a source of contaminants, such as the persistent organic pollutants, organotin compounds and heavy metals (Wurl and Obbard, 2004). Additionally, the SML also serves as a fundamental microhabitat for a huge diversity of microorganisms, fish eggs and larvae. A variety of chemical and microbiological substances are enriched in the SML compared with subsurface water. Previous studies have shown that organic contaminants, particularly hydrophobic organic pollutants, such as organic chloride pollutants and other pesticides (Hardy et al., 1987), polycyclic aromatic hydrocarbons (Kucklick and Bidleman, 1994), DEHP (Chi et al., 2003) and polychlorinated biphenyls (Abd-Allah., 1999) are more easily enriched in the SML. SML pollutant concentrations are generally higher in the coastal zone where they occur via direct inputs. Furthermore, pollutants can also enter the SML by wet or dry deposition (Guitart et al., 2007; Cunliffe et al., 2013; Net et al., 2015).

The land areas surrounding the Bohai Sea (BS) and the Yellow Sea (YS) are some of the most highly urbanized and industrialized zones in China and Korea. Additionally, hundreds of rivers, in both China and the Korean Peninsula, discharge industrial wastewater and municipal sewage into these regions (Xu et al., 2016). As a result, these domestic and industrial wastewater and rivers carry nutrients (He et al., 2017), heavy metals (Xiao et al., 2017), organic matter (Zhao et al., 2017), and persistent organic pollutants (Chiesa et al., 2016) into the BS and the YS, which greatly influence the coastal marine ecosystem. The BS and the YS are also affected by marine litter and microplastics (Yu et al., 2016), which may deliver PAEs to the marine environment during crushing or degradation (Andrady, 2011). Although numerous studies have reported PAEs in water environments (Sun et al., 2013; Liu et al., 2014; Adeogun et al., 2015; Paluselli et al., 2017), no data are available about the PAEs levels in the seawater and sediment of the BS and the YS. Furthermore, no investigations on the concentration distribution, composition, or ecological and health risks of PAEs in these seas have been reported. Therefore, the main purpose of this study was to examine, for the first time, the concentration levels, distribution, composition and pollution levels of PAEs in the SML, seawater and sediment of the BS and the YS.

2. Experimental section

2.1. Study areas

The BS is located between latitudes 37°07′–41°00′ N and longitudes 117°35′–121°10′ E and is composed of Liaodong Bay, Bohai Bay, Laizhou Bay, shallow sea basin of the central region and Bohai Strait, with a total surface area of 7.728×10^4 km^2 and a mean depth of 18 m. The YS, which has an average depth of 44 m and an area of 38×10^4 km^2, is surrounded by China, North Korea and South Korea and connect to the BS through the Bohai Strait. Both the BS and the YS are semi-enclosed epicontinental seas of China. Agricultural, industrial and domestic activities produce large amounts of sewage and wastewater, which seriously deteriorate the water quality of the BS and the YS (Lu et al., 2013; Shen et al., 2013; Wang et al., 2015). In addition, the YS is a marginal sea in the western Pacific Ocean and is influenced by lots of ocean currents, e.g., the Kuroshio Current, Changjiang Diluted Water, Taiwan Warm Current and the Yellow Sea Coastal Current.

2.2. Materials and reagents

The 16 PAE standards used in this study were DMP, DEP, DnBP, DiBP, dipentyl phthalate (DPP), dimethylglycol phthalate (DMEP), bis (4-methyl-2-pentyl) phthalate (BMPP), bis (2-ethoxyethyl) phthalate (DEEP), BBP, di-n-hexyl phthalate (DnHP), bis (2-n-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), diphenyl phthalate (DPhP), DEHP, DnOP, and diisononyl phthalate (DiNP) at 1000 μg mL^{-1} each, as well as benzyl benzoate (BBZ) as an internal standard. All standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). High-performance liquid chromatography grade n-hexane, dichloromethane, and ethyl acetate were obtained from Merck Co. (Darmstadt, Germany). A CNWBOND Si solid phase extraction (CS–SPE) device (1 mg, 6 mL) was purchased from ANPEL Laboratory Technologies (Shanghai, China). Tinfoil-covered glass fiber membranes (Whatman, London, UK) were heated at 400 °C in a muffle furnace for 4 h and stored in a sealed desiccator prior to use. All glassware was stored in concentrated sulfuric acid for 24 h, and then cleaned with ultrapure water, combusted at 450 °C for 4 h, and rinsed with acetone and n-hexane prior to use.

2.3. Sample collection

The cruise was conducted onboard the R/V *Dong Fang Hong 2* from 7 November to 26 November 2014. The 61 sampling stations (Table 1) were carefully selected and meticulously constructed across the BS to the YS (Fig. 1). The distance between adjacent sites and some special areas, such as the Yellow River Estuary and the Bohai Economic Rim, were considered based on Parts 3 and 5 of Specifications for Marine Monitoring in China (GB 17378, 2007). Ultimately, 110 water samples, which included 46 surface water samples, 29 samples at different water depths and 35 SML samples as well as 38 sediment samples were collected.

The water samples (both surface and different depth samples)