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Legacy and alternative plasticizers in surface sediment of black-odorous urban rivers across China: Occurrence, spatial distribution, and ecological risk assessment

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ABSTRACT

In this study, surface sediment samples from 173 black-odorous urban rivers in 74 cities of China were investigated regarding the occurrence, spatial distribution, and ecological risk of legacy phthalates (LPs) and alternative plasticizers (APs). The total concentrations of Σ_7LPs and Σ_6APs ranged from 0.0035 to 522 μg/g dw (median: 33 μg/g dw; mean: 60 μg/g dw) and from 0.0015 to 16 μg/g dw (median: 16 μg/g dw; mean: 2.2 μg/g dw), respectively. Di(2-ethylhexyl) phthalate (DEHP), di-*n*-butyl phthalate (DnBP), and di-*iso*-butyl phthalate (DiBP) were the dominant LPs, and di-*iso*-decyl phthalate and di-*iso*-nonylcyclohexane-1,2-dicarboxylate were the dominant APs. The concentrations and compositions of the LPs and APs varied among different sites and regions, implying location-specific use or production of LPs and APs. The pollutant concentrations in southern and central China were higher than those in northern China. Among the seven regions, Northwest China had the lowest concentrations of LPs and APs. This could be related to industry development level, municipal facilities, and population density. Total organic carbon (TOC) was significantly and positively correlated with the pollutant concentrations, implying that TOC could be an important influencing factor for the distribution of LPs and APs in sediments. The risk quotients of DiBP and DnBP in almost all sediment samples were above 1, indicating the high ecological risks to aquatic organisms. Nevertheless, DEHP, di-methyl phthalate, di-ethyl phthalate, and di-*n*-octyl phthalate showed low or moderate ecological risks for most sampling sites.

1. Introduction

Legacy phthalates (LPs) are the most commonly used plasticizers around the world. They are usually used to enhance the flexibility of materials such as polyvinyl chloride (PVC) products in flooring, cables, and wall decoration materials, and small amounts of LPs are also used in non-PVC products, such as paints, cosmetics, and glues (Bi et al., 2018; Christia et al., 2019a; Larsson et al., 2017; Wittassek et al., 2011). From 2007 to 2017, the annual global production of LPs increased from 2.7 million tons to almost 6 million tons (Bauer and Herrmann, 1997; Xie et al., 2007). In China, LPs are widely used in daily necessities, medical equipment, food packaging, industrial pipes, interior decoration, and agricultural plastic films, etc. (Gao et al., 2018). Since LPs are not chemically bonded but only physically added to polymeric materials, they can easily migrate from the products and into the environment during manufacture, use, and disposal processes (Cadogan et al., 1993). Nowadays, LPs are extensively and ubiquitously present in the environment, including in water, sediment, air, dust, soil, and biota (Christia

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et al., 2019a; Liu et al., 2019; Net et al., 2014; Wang et al., 2014, Zhao et al., 2020). Considering some LPs have endocrine-disrupting and other adverse health effects (Net et al., 2015a), six phthalates (including di-methyl phthalate (DMP), di-ethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), and butyl-benzyl phthalate (BBzP)) have been listed as priority pollutants by the US Environmental Protection Agency (Gao et al., 2018). Similarly, DMP, DnBP, and DNOP have been listed as priority pollutants by the China Environmental Monitoring Terminal; DnBP and DNOP have also been considered as the key monitoring pollutants in the recent implementation (Chen et al., 2019).

Due to strict restrictions on the use of traditional phthalates, alternative plasticizers (APs) which act as substitutes, are increasingly used in various industrial products (Bui et al., 2016; Calafat et al., 2015). Di-*iso*-decyl phthalate (DIDP), di-*iso*-nonyl phthalate (DINP), and di (2-propyl heptyl) phthalate (DPHP) are often used as replacements for DEHP due to their lower toxicity (Net et al., 2015a). Di-*iso*-nonylcyclohexane-1,2-dicarboxylate (DINCH) is the most commonly used non-phthalate AP (Bui et al., 2016). It was introduced to the European market in 2002 and is widely used in PVC materials (Fromme et al., 2016). Other representative non-phthalate APs, including di-ethylhexyl terephthalate (DEHT), di-ethylhexyl adipate (DEHA), and acetyl tributyl citrate (ATBC), are commonly used in food packaging materials, toys, childcare products, PVC flooring, and cosmetics (Bui et al., 2016; Nagorka et al., 2011; Van Vliet et al., 2011). Although these APs are considered to be less toxic or non-toxic substitutes for LPs (Bui et al., 2016), animal experimental data has shown that some of these chemicals could still cause weight loss and provided evidence of liver toxicity (Fromme et al., 2016).

With economic development and increasing urbanization, China's environmental problems have become increasingly prominent. Due to a lack of mature sewage treatment technologies and systematic wastewater discharge plans, as well as people's low environmental awareness, untreated domestic sewage and industrial wastewater were directly discharged into urban rivers, resulting in rapid accumulation of pollutants, extinction of aquatic organisms, and even blackening and odor generation (Wang et al., 2016; Zhang et al., 2017). According to the *National Urban River Pollution Guidelines*, as of 2017, there were 2100 black-odorous urban rivers in 295 cities of China (MOHURD, 2018). Nowadays, black-odorous rivers have become one of the environmental bottlenecks that threaten the health of Chinese citizens and restrict the development of the national economy. After a long period of physical, chemical, biological, and other interactions, pollutants entering the water are continuously deposited in sediment. Polluted sediments are closely related to the pollution of black-odorous water. To some extent, they can thus serve as an appropriate matrix to reflect the consumption and usage patterns of chemicals related to household and industrial activities.

China is one of the main producers of phthalates. Many studies have investigated the current status of phthalate pollution in different environmental media in China (Gao et al., 2018; Liu et al., 2019; Wang et al., 2014; Zhao et al., 2020). However, to date, comprehensive and systematical data on LPs and APs in sediments from black-odorous urban rivers in China remain sparse. In the present study, we collected surface sediment samples from 173 nationwide black-odorous urban rivers in 74 cities of China, to (a) document the occurrences of LPs and APs; (b) investigate the spatial distribution of LPs and APs in seven regions of China; (c) explore the potential factors affecting the distribution of LPs and APs; and (d) assess the ecological risk of these contaminants to three sensitive aquatic organisms in black-odorous urban rivers.

2. Materials and methods

2.1. Sample collection

From 28th June to October 15, 2018, surface sediment samples (top layer, <30 cm) were collected from 173 black-odorous urban rivers in 74 cities across China using a Van Veen grab sampler. These polluted rivers were selected according to the number and pollution level of black-odorous urban river recorded in the national-wide black-odorous urban river information system (MOHURD, 2018). The sampling cities are shown in Fig. 1, and detailed sample information is provided in Tables S1 and S2 of the Supporting Information (SI) (Lu et al., 2021). All collected sediment samples were immediately transported to the laboratory under cool conditions and stored in a refrigerator. Then, they were freeze-dried, pulverized, homogenized using an 80-mesh stainless steel sieve, wrapped in aluminum foil, and stored at −20 °C until chemical analysis.

2.2. Standards and reagents

In total, seven LPs, including DMP, DEP, Di-*iso*-butyl phthalate (DiBP), DnBP, BBzP, DNOP, and DEHP, and six APs (DIDP, DINCH, DEHT, DIBA, DEHA, and ATBC) were analyzed in this study and their standard solutions were obtained from AccuStandard (New Haven, CT, USA). Three internal standards (ISs) (including labeled DEHP-d4, DnBP-d4, and dibenzyl phthalate (DBzP-d4)) and triamyl phosphate (TAP), which was used as recovery standard, were also purchased from AccuStandard (New Haven, CT, USA). All solvents, including dichloromethane (DCM), methanol (MeOH), acetonitrile (ACN), toluene, acetone (ACE), ethyl acetate (EtAc), and *n*-hexane (Hex), were chromatography grade and were purchased from Merck (Germany).

2.3. Sample preparation and instrumental analysis

Sample pretreatment for LP and AP analysis of the sediments was performed mainly according to the method previously established by Christia et al. (2019b). In short, about 150 mg of freeze-dried sediment sample was extracted twice with 5 mL of ACN/toluene (*v/v*, 9/1) using a sonicator. Before extraction, these sediments were spiked with IS mixtures (500 ng). Clean-up was achieved by solid-phase extraction using a Florisil® ENVI cartridge (500 mg, 3 mL), which was conditioned with ACE, EtAc, and Hex. After loading the extract, the SPE cartridge was washed with a DCM and Hex mixture (*v/v*, 1/4), and then eluted with EtAc. Finally, the eluate was evaporated and replaced with 100 μL of MeOH, and spiked with 20 ng of TAP for liquid chromatographic analysis (LC-MS/MS). Meanwhile, 20 μL of the final mixture was added to 80 μL of EtAc for gas chromatographic analysis (GC-MS).

Target compounds, including DMP, DEP, DiBP, DnBP, BBzP, DIDP, and DINCH, were analyzed using an Agilent LC-MS/MS equipped with an electrospray ionization source (Christia et al., 2019b; Liu et al., 2020). The remaining analytes (DEHT, DIBA, DEHA, DEHP, DNOP, and ATBC) were measured using a Shimadzu GC-MS in electron ionization mode (Christia et al., 2019b; Liu et al., 2020). Additionally, after removing the inorganics, the total organic carbon (TOC) content was obtained using an elemental analyzer (Vario EL, Elementar, GmbH, Germany).

2.4. Quality assurance and quality control

To avoid background pollution, no personal care products (i.e., perfume, hand cream) were used during the entire experimental procedure. Furthermore, the experimental equipment used was either made of glass or Teflon. The reliabilities and repeatability of the LP and AP quantification methods were satisfactory for the native analytes in the triplicate spiked samples. The recoveries of the native analytes in the blank-spiked and matrix-spiked samples varied from 69% to 126% (Table S3), and the relative standard deviation (RSD) was below 15%. The intra-day and inter-day RSD in the studied samples were less than 10% and 15%, respectively. Twelve procedural blank samples were conducted during the sample treatment process. All target analytes were detected in the procedural blanks (Table S4), with average levels of 0.68–547 ng/mL. The final concentrations were subsequently blank-

Fig. 1. Map of 74 sampling cities across China in the present study. Note: This chart only shows mainland China where data is available.

subtracted. The limits of quantification (LOQs) were set as the mean blank values plus 3*SD, and the calculated LOQs for LPs and APs were between 8.1 ng/g for BBzP and 515 ng/g for DnBP, between 2.0 ng/g for DEHT and 42 ng/g for DIDP (Table S4). The recoveries of the three ISs in all samples were 105 ± 15% for DnBP-d4, 99 ± 11% for DBzP-d4, and 92 ± 14% for DEHP-d4.

2.5. Statistical analysis and ecological risk assessment

All statistical analyses were carried out using IMB SPSS Statics 19.0 (SPSS Inc., Chicago, Illinois, USA) and Origin 8.5 software. An independent samples *t*-test was performed to compare the differences in concentrations and compositions of the LPs and APs in the sediment samples between two groups. One-way analysis of variance (ANOVA) was performed to conduct comparisons of the pollutant concentrations among seven different areas across China. Pearson correlation analysis was used to investigate the relationships between the LPs and APs, between pollutant concentrations and TOC, and between pollutant concentrations and the values of the three-year-average Gross Domestic Product (GDP) or industrial output of each city. Statistical significances were defined as $p < 0.05$.

The potential ecological risk of the pollutants in the present study were assessed by following the proposed risk quotient (RQ) method from the Technical Guidance Document (EC, 2003), and were calculated as the ratios of the measured contamination concentration to the predicted no effect concentration for the sediment phase ($PNEC_{sediment}$) (Li et al., 2017). The calculation method for $PNEC_{sediment}$ followed that of previous studies (EC, 2003; Li et al., 2017), and the toxicity data and relevant information are provided in Table S5. Algae, crustaceans, and fish were selected as model aquatic species for the risk assessment. Three ecological risk levels were divided according to common assessment criteria (EC, 2003; Li et al., 2017): low risk with RQ < 0.1, moderate risk with 0.1 <RQ < 1.0, and high risk with RQ > 1.0 and RQ > 10 for substances with log K_{OW} values of 3–5 and >5, respectively.

3. Results and discussion

3.1. Concentrations and compositions

All LPs and APs were detected in >85% of the 173 surface sediment samples analyzed in the present study. The concentrations of the LPs and APs in the sediment samples of seven different regions and of each analyzed city across China are listed in Table 1 and Tables S6–S7, respectively. The compositional patterns of the LPs and APs are shown in Fig. 2 and Figure S1.

3.1.1. LPs

The concentrations of Σ_7LPs in the analyzed sediment samples ranged between 0.0035 and 522 μg/g dw, with a median and mean of 33 μg/g dw and 60 μg/g dw, respectively. The concentrations in the present study were much higher than those previously reported in marine sediments from China, including the East China Sea (1.6–7.4 μg/g dw) (Zhao et al., 2020), Bohai and Yellow Sea of northern China (1.24–15.8 μg/g dw) (Zhang et al., 2018), and Yellow Sea of southern China (0.31–6.2 μg/g dw) (Li et al., 2014), as well as other areas worldwide, such as the coastal areas of Kuwait (2.15–15.72 μg/g dw) (Saeed et al., 2017) and Canada-False Creek Harbor (0.004–2.1 μg/g dw) (Mackintosh et al., 2006). They also exceeded the phthalate levels of river sediments from the Pearl River Delta, South China (0.57–47 μg/g dw) (Li et al., 2016a), Pu River, Northeast China (3.7–47 μg/g dw) (Li et al., 2016b), Qiantang River, East China (0.59–6.7 μg/g dw) (Sun et al., 2013), and Nigeria-Ogun River (0.33–2.9 μg/g dw) (Adeniyi et al.,

Table 1
Concentrations (median and range, μg/g dw) of LPs and APs in sediments of black-odorous urban rivers in China.

Compound	DF	East China	South China	Central China	North China	Northwest China	Southwest China	Northeast China
N		40	21	30	21	19	24	18
LPs								
DMP	96%	0.40 (ND–110)	0.49 (ND–2.8)	0.12 (ND–1.3)	0.26 (ND–3.8)	0.013 (ND–0.59)	0.22 (0.013–2.0)	0.19 (ND–2.3)
DEP	92%	0.34 (ND–4.1)	0.27 (ND–2.1)	0.13 (ND–1.8)	0.16 (ND–1.1)	0.0094 (ND–0.47)	0.23 (0.0077–1.9)	0.059 (ND–1.3)
DiBP	97%	13 (0.44–177)	9.1 (ND–40)	5.2 (0.16–70)	4.4 (ND–40)	1.1 (ND–26)	10 (0.64–104)	2.3 (ND–63)
DnBP	89%	10 (ND–382)	11 (ND–246)	5.8 (ND–58)	11 (ND–56)	4.6 (ND–98)	9.8 (ND–129)	4.4 (ND–54)
BBzP	87%	0.0051 (ND–0.057)	0.0029 (ND–0.058)	0.0021 (ND–0.036)	0.0069 (0.0013–0.086)	0.0035 (ND–0.019)	0.0013 (ND–0.019)	0.0070 (ND–0.028)
DNOP	97%	0.56 (0.0042–79)	0.26 (ND–1.1)	0.36 (ND–1.5)	0.30 (0.0050–0.99)	0.12 (ND–1.0)	0.39 (0.0061–3.4)	0.077 (ND–2.9)
DEHP	100%	11 (0.97–242)	11 (0.41–295)	12 (0.33–278)	9.2 (0.14–45)	3.4 (0.0035–140)	11 (0.74–337)	6.5 (0.098–28)
∑7LPs		40 (1.6–431)	36 (1.6–522)	38 (4.5–291)	42 (2.0–86)	12 (0.0035–256)	37 (5.1–454)	23 (0.49–95)
APs								
DIDP	100%	1.0 (0.14–3.1)	0.64 (0.060–8.1)	0.87 (0.056–2.7)	0.91 (0.017–2.3)	0.22 (0.0015–1.1)	0.79 (0.13–2.4)	0.68 (0.012–1.9)
DINCH	98%	0.56 (0.070–12)	0.57 (0.028–5.8)	0.70 (0.0078–2.0)	0.48 (0.0098–3.1)	0.18 (ND–0.72)	0.53 (0.064–2.0)	0.58 (0.00050–1.8)
DETH	95%	0.016 (ND–0.56)	0.0068 (ND–0.66)	0.0069 (ND–0.79)	0.037 (ND–0.34)	0.0072 (ND–0.69)	0.0058 (0.00053–0.22)	0.025 (ND–0.15)
DIBA	89%	0.037 (ND–2.1)	0.027 (ND–2.1)	0.013 (ND–0.57)	0.0016 (ND–0.20)	0.0061 (ND–2.0)	0.010 (0.00013–0.12)	0.0017 (ND–0.23)
DEHA	95%	0.19 (ND–3.8)	0.15 (0.00016–1.6)	0.095 (0.00034–1.9)	0.12 (ND–1.3)	0.017 (ND–0.65)	0.15 (0.00029–1.4)	0.014 (ND–0.84)
ATBC	97%	0.039 (0.00045–4.3)	0.057 (0.00094–0.20)	0.039 (ND–0.29)	0.027 (0.00050–0.27)	0.012 (ND–0.30)	0.041 (0.00049–0.61)	0.015 (ND–0.14)
∑6APs		2.1 (0.24–16)	1.8 (0.095–14)	1.9 (0.071–5.8)	1.8 (0.032–6.5)	0.78 (0.0015–3.6)	1.7 (0.20–5.1)	1.3 (0.013–4.3)

N: the sample number; ND: undetected or below the LOQs; DF: detection frequency.

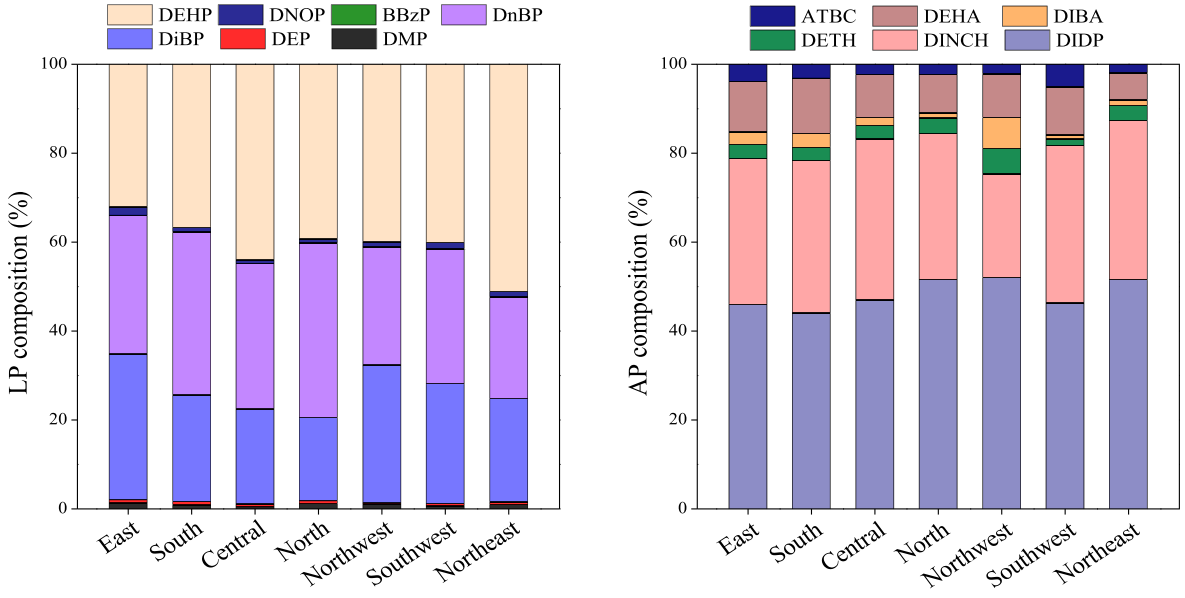

Fig. 2. Compositional profiles of LPs and APs in sediments from seven different regions of China.

2011). Additionally, the obtained LP levels are comparable with those observed in some urban sediments/soil from the Yangtze River, Wuhan (76–450 μg/g dw) (Wang et al., 2008a, 2008b), Guangzhou (1.7–322 μg/g dw) (Zeng et al., 2009), and Berlin (28–154 ng/g dw) (Fromme et al., 2002), which is not unexpected because the pollutants in the sediments from black-odorous urban rivers studied in the present study usually come from household or industrial output without any pretreatment.

Among the seven analyzed phthalates, DEHP exhibited the highest concentration (range: 0.0035–337 μg/g dw, median: 9.5 μg/g dw), followed by DnBP (range: ND–382 μg/g dw, 7.2 μg/g dw) and DiBP (range: ND–177 μg/g dw, 6.6 μg/g dw), accounting for 40%, 32%, and 26% of the total contamination, respectively. This is mainly due to the extensive use of these three phthalates in industrial and commercial applications. We note that DEHP is one of the most abundant phthalate plasticizers, accounting for 80% and one-third of the total phthalates produced in China and the European Union (EU), respectively (Huang et al., 2008; Meng et al., 2014). DnBP and DiBP are also among the most extensively used LPs globally, and their global and Chinese consumptions are growing rapidly (Wang et al., 1995; Fang et al., 2010). The

present finding is in accordance with commonly reported results that DEHP, DnBP, and DiBP are the dominant phthalate components in sediments in China (Li et al., 2016a, 2017; Yuan et al., 2002; Zhang et al., 2018; Zhao et al., 2020). Meanwhile, DEHP and DnBP were also found in abundance in sediments in Germany (Fromme et al., 2002), South Africa (Fatoki et al., 2010), and France–Belgium (Net et al., 2015b).

3.1.2. APs

The concentrations of Σ_6APs ranged between 0.0015 and 16 μg/g dw (median: 1.6 μg/g dw; mean: 2.2 μg/g dw) in the analyzed sediments from across China, which is an order of magnitude lower than those of the Σ_7LPs. DIDP, DINCH, and DEHA were the dominant APs in these sediments, with mean contributions of 48%, 33%, and 10% to the total levels, respectively. Their concentrations were 0.0015–8.1 μg/g dw, ND–12 μg/g dw, and ND–3.8 μg/g dw, respectively, with median values of 0.74 μg/g dw, 0.48 μg/g dw, and 0.12 μg/g dw, respectively. The concentrations of the other three APs were ND–4.3 μg/g dw for ATBC, ND–2.1 μg/g dw for DIBA, and ND–0.79 μg/g dw for DEHT.

In contrast to the LPs, reported data on APs in sediments are scarce (Lee et al., 2019; Kim et al., 2020). Kim et al. (2020) and Lee et al. (2019) were the first to report the occurrences of five APs in coastal sediments from semi-enclosed bays of Korea and in sludge samples from three types of wastewater treatment plants (WWTPs) in Korea, with concentrations of 0.0032–1.22 μg/g dw and ND–24 μg/g dw for DIDP, 0.00001–0.0536 μg/g dw and 0.15–770 μg/g dw for DEHT, 0.00029–0.0167 μg/g dw and ND–8.6 μg/g dw for DINCH, 0.00004–0.00231 μg/g dw and ND–19 μg/g dw for ATBC, and 0.0001–0.00497 μg/g dw and 0.01–5.1 μg/g dw for DEHA, respectively. It is clear that the levels of these APs obtained in the present study are much higher than those in the coastal sediments (Kim et al., 2020), but comparable to those of the sludge samples (Lee et al., 2019), with the exception of DEHT, which was two orders of magnitude greater in the sludge than in our sediments.

3.2. Spatial distribution

The spatial distributions of LPs and APs in the analyzed sediments are presented in Fig. 3 and Figure S2. Overall, among the seven regions of China, the lowest concentrations of LPs and APs were observed in Northwest China, which is attributed to its relatively backward industrial development and low population density. Compared with the northern areas of China (including Northwest China, Northeast China, and North China), the southern and central areas (including East China, South China, Central China, and Southwest China) had higher concentrations of LPs and APs in sediments from black-odorous urban rivers. To the best of our knowledge, the major manufacturers of phthalates in China are located in the eastern and southern regions, such as the provinces of Shandong, Guangdong, and Jiangsu (Zhang et al., 2015), which may be an important reason for the present finding. Gao et al. (2018) also pointed out that the presence of phthalates in surface water was more widespread in southern cities than in northern cities of China, which is consistent with our results.

The total concentrations of Σ_7LPs and Σ_6APs in the sediments analyzed from across China varied widely among the different sampling sites. The highest concentrations of Σ_7LPs (387 μg/g dw) and Σ_6APs (14 μg/g dw) were found at site FJ1 (Zhangzhou City, East China) and GD3 (Shenzhen City, South China), respectively, while the lowest concentrations were found at site GS3 (Dunhuang City, Northwest China). Noteworthy is also that in Northwest China, with generally low contaminant levels, the site ShanX1 (Weinan City) showed especially high concentrations of Σ_7LPs, which could be due to specific industrial input of phthalates at this location. Among the four prosperous tier-one cities of China, only Shenzhen City (site GD3) exhibited relatively high concentrations of LPs and APs, whereas the other three cities, including Beijing (BJ), Shanghai (SH), and Guangzhou (GD5), had low and moderate pollutant levels. In addition to the industrial states and population densities mentioned above, wastewater treatment technology may also

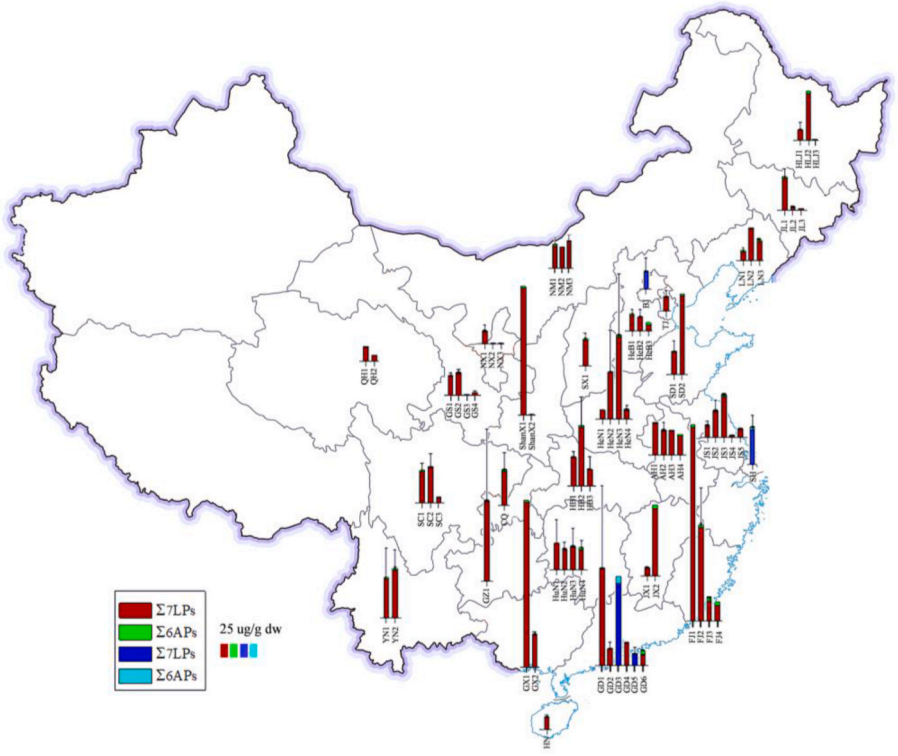

Fig. 3. $\sum_7$LPs and $\sum_6$APs in sediments of each city analyzed in mainland China. Error bars represent standard errors. Note: the dark-blue columns and light-blue columns represent $\sum_7$LPs and $\sum_6$APs in the four tier-one cities, respectively, i.e., Beijing (BJ), Shanghai (SH), Guangzhou (GD5), and Shenzhen (GD3). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Pearson correlation coefficients among the LPs and APs in all sediment samples.

	DMP	DEP	DiBP	DnBP	BBzP	DEHP	DIDP	DINCH	DNOP	DEHT	DIBA	DEHA	ATBC
DMP	1												
DEP	0.215**	1											
DiBP	0.593**	0.549**	1										
DnBP	0.155*	0.336**	0.403**	1									
BBzP	0.338**	0.310**	0.288**	0.154*	1								
DEHP	0.012	0.267**	0.206**	0.301**	−0.065	1							
DIDP	0.225**	0.527**	0.378**	0.211**	0.407**	0.119	1						
DINCH	0.689**	0.540**	0.532**	0.175*	0.329**	0.125	0.665**	1					
DNOP	0.003	0.09	0.227**	0.089	0.087	0.02	0.043	−0.002	1				
DEHT	0.04	−0.098	0.107	−0.022	0.158*	−0.048	0.287**	0.229**	0.318**	1			
DIBA	−0.021	−0.016	−0.004	−0.022	0.094	−0.016	0.081	0.068	0.002	0.400**	1		
DEHA	0.045	0.346**	0.280**	0.244**	0.074	0.527**	0.206**	0.125	−0.002	−0.049	0.112	1	
ATBC	−0.004	0.158*	0.301**	0.128	0.094	0.042	0.102	0.046	0.975**	0.347**	0.031	0.031	1

*$p < 0.05$ (two-tailed); **$p < 0.01$ (two-tailed).

affect the pollution levels, considering the potential environmental risk associated with the discharge of contaminants from WWTPs (Gao et al., 2018). Shenzhen, the economic center of China, is located in the Pearl River Delta region of South China and hosts advanced manufacturing and modern service industry bases. According to a survey, there were no water plants with advanced treatment technology in the cities studied in the Pearl River Delta region, except for city GD5 (Li et al., 2019), which may also be an important reason for the high pollutant levels in city GD3.

The compositional patterns of LPs and APs in the analyzed surface sediments from black-odorous urban rivers varied slightly among different sampling sites across China (Figure S1), indicating that the use or production of these plasticizers in specific locations is somewhat different, although DEHP, DnBP, and DiBP were generally the dominant LPs, and DIDP, DINCH were the major APs. Notably, Northwest China exhibited a significantly lower proportion of DINCH ($p < 0.05$), but higher contributions of DEHT and DIBA than the other regions (each $p < 0.05$) (Fig. 2).

3.3. Correlation analysis

The results of the Pearson correlation analysis of the LP and AP concentration data in the analyzed sediments are shown in Table 2. The greatest correlation was observed between the levels of DNOP and ATBC ($r = 0.975$, $p < 0.01$). The lowest correlations were found between DNOP and DIBA and between DNOP and DEHA, which could be attributed to their trace levels in the sediment samples. Significant correlations were observed among five LP compounds with short branched chains, including DMP, DEP, DiBP, DnBP, and BBzP, implying that these chemicals could share similar sources and environmental behaviors. Additionally, significant correlations were found between the three major APs (DIDP, DINCH, and DEHA) and three LPs (DiBP, DnBP, and DEP), and between DEHA and DEHP in the present study. Moreover, the concentrations of Σ_7LPs were significantly correlated with those of Σ_6APs ($r = 0.466$, $p < 0.01$). These findings suggested that LPs and APs might be consumed at the same time in the industrial market (Lee et al., 2019).

Because TOC is a key component in the analyzed surface sediments, the relationships between the pollutant concentrations and TOC were also investigated in the present study. Significantly positive correlations were observed between Σ_7LPs and TOC, and between Σ_6APs and TOC in all sediments (Figure S3, $r = 0.54$ and 0.61, each $p < 0.01$). Except for the correlation between Σ_7LPs and TOC in Northeast China, significantly positive correlations between the contaminant concentrations and TOC were also found in the sediment samples from the seven different regions (Figure S3). These results suggest that TOC is the all-important factor influencing the distribution of LPs and APs in surface sediment from black-odorous urban rivers, although other factors, such as emission intensity and degradation, may also influence their distribution to a certain extent. Additionally, the relationships between the mean pollutant concentrations and GDP or industrial output of each city were explored. The levels of Σ_6APs were significantly and positively correlated with both GDP and industrial output ($r = 0.31$ and 0.39, each $p < 0.05$). However, no significant correlations were found for Σ_7LPs (Figure S4), which could be explained by the fact that the LPs are conventional plasticizer chemicals with a long and extensive history of use.

3.4. Ecological risk assessment

Due to the limited and available toxicity data, the RQ values of DMP, DEP, DnBP, and DEHP for the three sensitive aquatic organisms (algae, crustaceans, and fish) and the RQ values of DiBP and DNOP for fish in sediments were calculated in the present study, as shown in Fig. 4. Overall, the RQ values of these six LPs in sediments of black-odorous urban rivers for the three sensitive aquatic organisms followed the order: DiBP > DnBP > DEHP > DEP and DMP > DNOP, which is similar to the findings for sediments from the Yangtze River Delta, Jiulong River, East China Sea, and the Sub-Saharan Rivers (Chen et al., 2019; Li et al., 2017; Ogunwole et al., 2021; Zhang et al., 2018). Somewhat different from the present study, Liu et al. (2020) found that the potential ecological risk of DEHP was higher than those of DiBP and DnBP in surface sediments from the Haihe River, North China.

DiBP exhibited the highest RQ values for fish, with an average value of 288, followed by DnBP, with average values of 9, 7.2, and 19 for algae, crustaceans, and fish, respectively. The RQ values of DiBP and DnBP ($3 < \log K_{OW} < 5$) in the vast majority of sediment samples studied in the present study were above 1, suggesting a high risk of these two chemicals for aquatic organisms in China. The average RQs of DMP and DEP ($\log K_{OW} < 3$) were 0.78 and 0.15 for algae, 0.81 and 0.45 for

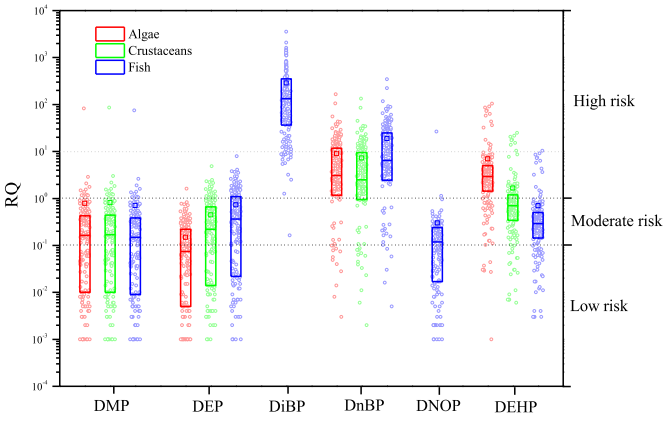

Fig. 4. Risk assessment of six LP compounds in all sediment samples. Box plots show the median (horizontal line in the box) and mean (square) values.

crustaceans, and 0.71 and 0.73 for fish, respectively. Additionally, for the other two LPs with log K_{OW} >5, the average RQs of DEHP for algae, crustaceans, and fish were 7, 1.7, and 0.7, respectively, and the average RQ of DNOP for fish was 0.3. In most sediment samples, the RQs of DMP and DEP were less than 1, and the RQs of DEHP and DNOP were below 10, which indicates that these contaminants pose low and moderate risks to aquatic organisms, respectively. Notably, the RQ values of the six LPs in the present study were generally 1–2 order of magnitude greater than previous results (Chen et al., 2019; Concha-Graña et al., 2021; Li et al., 2017; Liu et al., 2020; Zhang et al., 2018), indicating that more attention should be paid to the potential ecological risk of these LPs in black-odorous urban rivers.

4. Conclusion

The prevalence, spatial distribution, and ecological risk of LPs and their substitutes (APs) have been investigated systematically in surface sediments from black-odorous urban rivers across China for the first time. All analyzed LPs and APs were detected in the sediment samples, suggesting the widespread use and extensive existence of these chemicals. The total concentrations of the LPs were significantly correlated with those of the APs, indicating a possible simultaneous use of both. DEHP, DnBP, DiBP, DIDP, and DINCH were found to be the dominant LPs and APs in China. The pollutant concentrations and compositions varied among different sampling sites and different regions, implying location-specific use or production. Among the seven regions, Northwest China showed the lowest pollutant concentrations. Compared with the northern areas of China, the southern and central regions showed higher contaminant levels. This could be explained by the industry development level, municipal facilities, and population density. TOC was found to be an important influencing factor for the distribution of LPs and APs in sediment in all cases. Additionally, DiBP and DnBP posed high ecological risks to the investigated aquatic organisms, and DEHP, DMP, DEP, and DNOP showed low and moderate ecological risks at most sampling sites.

Credit author contribution statement

Yin-E Liu: Investigation, Writing - Original Draft Preparation, Formal analysis, Formal analysis, Methodlogy. Xiao-Jun Luo: Conceptualization, Writing - Review & Editing, Supervision, Funding acquisition. Chen-Chen Huang: Investigation. Yan-Hong Zeng: Investigation. Qihong Lu: Investigation. Shanquan Wang: Conceptualization, Investigation, Supervision. Bi-Xian Mai: Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131206.

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