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Occurrence, distribution and ecological risks of organophosphate esters and synthetic musks in sediments from the Hun River

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ABSTRACT

The Hun River is an important main tributary of the Liao River system. It is located in northeast China, and provides water resources for agriculture and industry. A man made reservoir (Dahuofang Reservoir, DHF) has been constructed mid-stream in the Hun River, supplying drinking water to surrounding cities. Pollution from organic contaminants is of great concern. In the present study, 40 sediment samples were collected and analyzed for the occurrence and distribution of two groups of emerging organic pollutants; namely, organophosphate esters (OPs) and synthetic musks (SMs). In all samples taken from upstream of the Hun River (UHR), downstream of the Hun River (DHR), and from DHF, the following concentrations were recorded: 0.141–4.39, 1.21–245, and 0.117–0.726 μg/kg galaxolide (HHCB), and 0.098–3.82, 2.79–213, 0.430–0.956 μg/kg tonalide (AHTN), respectively. For OPs, seven target analytes were detected in most of the sediment samples, with chlorinated OPs Tris-(2-chloroethyl) phosphate and Tris(2-chloro-isopropyl) phosphate being the dominant components, at levels varied in the range of LOD-0.810, ND-49.6, and 0.532–3.18 μg/kg, and LOD-0.786, ND-60.1, and 0.352–1.32 μg/kg from UHR, DHR and DHF, respectively. The elevated levels of these target compounds were detected in DHR, including its two main tributaries, Xi River and Pu River, which drain through cities with industrial development and dense populations. Our results indicate that domestic and industrial wastewater contributed to OPs and SMs sediment pollution, posing low to medium ecological risks to sediment dwelling organisms.

1. Introduction

Liaohe River Basin (LRB), composing of Liao River and Daliaohe River system, is located in northeast of China and represents one of seven river basins in China. Hun River, one of the main tributaries of the Daliaohe River system, runs through several cities, including Fushun and Shenyang, and it receives water from the Pu River and Xi River, which are two of the seven main tributaries flowing into the Hun River. The Dahuofang Reservoir (DHF), the largest man-made lake in Liaoning Province, is situated mid-stream in the Hun River; it acts as the primary source of drinking water for surrounding cities, such as Fushun, Shenyang, Liaoyang and Anshan (Liu et al., 2015a, 2015b). There are major oil, chemical, metallurgical, pharmaceutical and machinery industries in the LRB and wastewater discharge from these industrial sectors causes severe pollution, including heavy metals and traditional persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organic chlorine pesticides (OCPs) (Liu et al., 2015a, 2015b; Gong et al., 2016; He et al., 2016; Zhu et al., 2017). Until recently, limited data was available on emerging organic pollutants, such as organophosphate esters (OPs) and synthetic musks (SMs).

The OPs are widely used flame retardants and/or plasticizers in various consumer products, such as electronic and electrical equipment, textiles, furniture, decorative materials, and building materials due to their excellent flame retardancy and flexibility. Market share has grown because of the ban/restriction on polybrominated diphenyl ethers (PBDEs) in recent years, resulting in their ubiquitous and increasing presence in the environment (Wei et al., 2015; Kim et al., 2017; Wang et al., 2017). Depending on the different substituent group, three subgroups of OPs occur, chlorinated OPs, alkyl OPs, and aryl OPs, which

Abbreviations: LRB, Liaohe River Basin; DHF, Dahuofang Reservoir; UHR, upstream of the Hun River; DHR, downstream of the Hun River; Ops, organophosphate esters; SMs, synthetic musks

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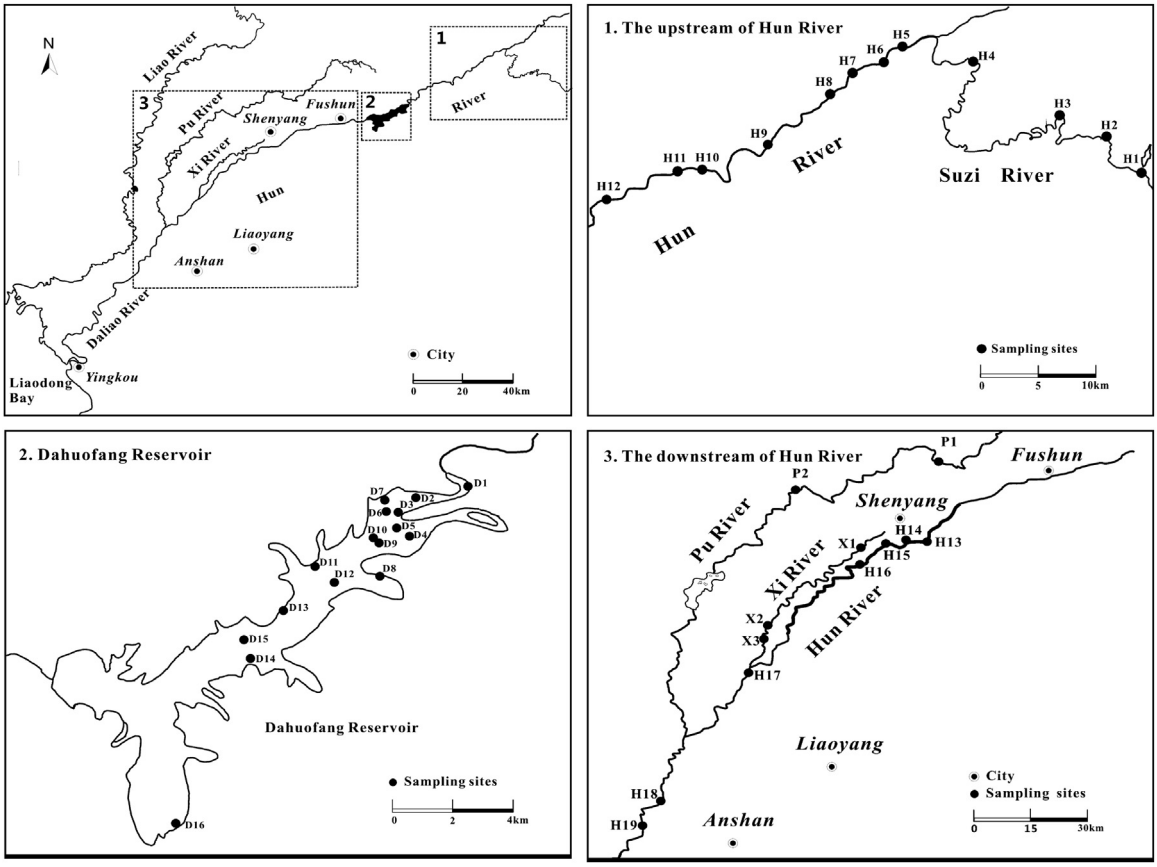

Fig. 1. Illustration of sampling location in the Hun River and Dahuofang Reservoir.

exhibit different physicochemical properties, such as water solubility and Log *K*ow; these properties can affect their distribution and ultimate fate in the environment (Wei et al., 2015). It has been reported that OPs, especially chlorinated OPs, are more toxic and much more persistent than PBDEs (Hou et al., 2016; Greaves and Letcher, 2017).

The SMs, a group of artificial fragrance chemicals, are widely used in daily household products and cosmetics. There are three groups of SMs in use: macrocyclic musks, polycyclic musks and nitro musks. Among polycyclic musks there are two dominant components, galaxolide (HHCB) and tonalide (AHTN) (Wilkinson et al., 2017; Zeng et al., 2018). Many studies have shown that these artificial fragrances materials exhibit a diverse range of effects on freshwater organisms and humans, and they are recognized as 'emerging pollutants'. Recently, Patel (2017) reviewed the published data on their toxicities and described synthetic fragrance chemicals as "wolves in sheep's clothing".

Generally, OPs and SMs are discharged into receiving water via treated/untreated wastewater, and they have been identified as the most prevalent and most hazardous chemicals in effluents from wastewater treatment plants (WWTPs) (Díaz-Garduno et al., 2017; Krzeminski et al., 2017; Wang et al., 2018). In addition, due to their continuous discharge these compounds are frequently detected at elevated levels in aquatic environments affected by domestic and/or industrial wastewater (Lange et al., 2015; Kim et al., 2017; Wang and Kelly, 2017). In recent years, an increasing number of researchers have paid attention to their occurrence, distribution and ultra-fate, as well as their toxicity.

Little is known about the occurrence and levels of these emerging pollutants in the Hun River and Dahuofang Reservoir. The present study aimed to 1) study the occurrence and distribution of OPs and SMs in the Hun River, and try to locate their main emission sources, and 2) make a preliminary assessment of their potential ecological risk based on measured concentrations.

2. Materials and methods

2.1. Chemical standards and reagents

Seven organophosphate ester flame retardants/plasticizers and nine synthetic musks were chosen as target analytes. The OPs standards were purchased from Sigma-Aldrich (St. Louis, MO, USA), including Tributyl phosphate (TNBP, 99%), Tris(2-butoxyethyl) phosphate (TBEOP, 94%), Triphenyl phosphate (TPHP, 99%), Tris(methylphenyl) phosphate (TMPP, 90%), Tris(2-chloroethyl) phosphate (TCEP, 99.5%), Tris(2-chloroisopropyl) phosphate (TCIPP) and Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP, 97%). The synthetic musks were purchased from LGC Promochem GmbH (Mercatorstrasse, Wesel, Germany), including 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl- 4H-inden-4-one (Cashmeran, DPMI, 90%), 4-acetyl-1,1-dimethyl-6-tert-butylindan (Celestolide, ADBI, 98%), 6-acetyl-1,1,2,3,3,5-hexamethylindan (Phantolide, AHMI, 94.5%), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan (Traseolide, ATII, 90%), AHTN (98%), HHCB(75%), 4-tert-butyl-2,6-dimethyl-3,5-dinitroacetophenone (MK, 98.27%), 1-(tert-butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene (MA, 99%) and 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX, 98%). Their detailed information were listed in Table S1. Four deuterated compounds were obtained from C/D/N Isotopes Inc. (Quebec, Canada) and used as surrogate standards, including d27-TNBP (98%), d15-TPHP (98%), d12-TCEP (98%), and d15-MX (97.5%). The internal standard hexamethylbenzene (HMB, 99.5%) was obtained from the laboratories of Ehrenstofer-Schäfer Bgm-Schlosser (Augsburg, Germany).

All solvents used in the present study were of chromatographic grade. Dichloromethane and *n*-hexane were purchased from Merck Co. (Darmstadt, Germany), and ethyl acetate (EtOAc) was purchased from

CNW Technologies GmbH (Düsseldorf, Germany). Silica gel (70–230 mesh) was obtained from Merck Co. (Darmstadt, Germany) and activated at 180 °C for 12 h; neutral alumina (100–200 mesh) was Soxhlet-extracted with methanol and dichloromethane for 48 h, respectively. The activated silica gel and neutral alumina were deactivated with 3% (w/w) redistilled water and kept in *n*-hexane before use. Anhydrous sodium sulfate was baked at 450 °C for 4 h prior to use.

2.2. Sample collection

As indicated in Fig. 1, 40 sampling sites were selected and a total of 40 surface sediment (0–5 cm) samples were collected in July 2010, using a stainless-steel grab into an aluminum container, including 12 from upstream of Hun River (UHR, H1–12), 12 from downstream of Hun River (DHR, H13–19) and its attached tributaries Pu River (P1–2) and Xi River (X1–3), and 16 from Dahuofang Reservoir (DHF, D1–16). All sediment samples were freeze dried, then ground and homogenized after removal of organic debris and pebbles. After sieving through an 80-mesh sieve, all samples were stored in pre-cleaned amber bottles at − 20 °C until analysis.

2.3. Sample preparation

A method that was established previously in our laboratory was adopted for extraction and cleanup (He, 2014). Herein, a brief description was given as follow. Approximately 10 g of sediment samples were spiked with 50 ng surrogate standards (d27-TNBP, d15-TPHP, d12-TCEP and d15-MX), and then Soxhlet-extracted with 200 mL dichloromethane for 72 h. Activated copper was used to remove elemental sulfur potentially present in the sediment samples. The extracts were concentrated and solvent-exchanged into *n*-hexane, and then concentrated to approximately 1 mL with a rotary evaporator. The final extracts were loaded onto a combined column of neutral alumina/silica gel (1:2). The fraction containing SMs was eluted by a mixture of *n*-hexane and dichloromethane, and the fraction containing OPs was eluted using EtOAc. The fractions containing OPs and SMs were concentrated to about 1 mL, solvent-exchanged into *n*-hexane, and further concentrated to 200 μL under a gentle N2 stream. An aliquot of 100 ng internal standard (HMB) was added before instrumental analysis.

Identification and determination of target compounds were performed using a Shimadzu GC-MS-QP 2010 (Shimadzu, Kyoto, Japan) in electron impact (EI) ionization mode with helium as the carrier gas at a flow rate of 1 mL/min. For GC separation, a TG-5MS column (30 m × 0.25 mm I.D × 0.25 μm film) (Thermo Fisher Scientific, Waltham, MA, USA) and a DB-5MS column (30 m × 0.25 mm I.D × 0.25 μm film) (J & W Scientific Co. Ltd., Folsom, CA, USA) were used for OPs and SMs, respectively. The detailed analytical parameters have been reported previously (He, 2014).

2.4. Quality assurance and quality control

Procedural blanks (solvent, $n = 4$), spiked blanks (spiked standards into solvent, $n = 4$), spiked matrix (standards spiked into pre-extracted sediment, $n = 4$), and duplicate samples ($n = 4$) were analyzed in each batch of samples. The surrogate recoveries were 83.0 ± 4.8%, 118.2 ± 9.7%, 82.7 ± 6.4%, and 86.6 ± 8.9% for D_{27}-TNBP, D12-TCEP, D15-TPHP, and D15-MX, respectively. Procedural blanks contained no detectable amount of the target analytes.

3. Results and discussion

3.1. Levels and distribution of OPs in sediment samples

The results indicated that the seven target OPs were ubiquitously found in the studied areas. Their levels and distribution in different river section and DHF are summarized in Table 1, and detailed information about their occurrence and distribution in each sampling location are given in Table S2.

As can be seen from these data, the seven target OPs were present at low levels in most of the UHR samples. In detail, TBP, TPHP, TMPP and two chlorinated OPs (TCEP and TCIPP) were detected in all the sediment samples collected in this section of the Hun River. In half of the samples TNBP was found above LOD, and in 4 and 5 of the samples TCEP and TCIPP were found at levels above LOD, respectively. In H11, TPHP (0.958 μg/kg) and TMMP (1.09 μg/kg) were found higher than LOD. TBEOP was detected in 7 out of the 12 samples, and 0.941 μg/kg TBEOP was found in H12. TDCIPP was found at LOD in 10 sediments and at 0.746 μg/kg in H11.

DHR runs through Fushun City and Shenyang City and flows into Bohai Bay. Seven sediments were collected (H13–19, Fig. 1) and analyzed. The results indicated (Tables 1 and S2) that varying levels of OPs (3.49–45.7 μg/kg) occurred in these sediment samples showing obvious input of OPs. The highest levels in the reach were found in sampling site H15 (ΣOPs 45.7 μg/kg), followed by H16 (ΣOPs 42.9 μg/kg), which were located in the section of the Hun River that drains through Shenyang City, where it receives large amounts of domestic sewage and industrial wastewater (Li et al., 2015). Xi River is one of the important tributaries that conveys industrial wastewater originating from Tiexi Economic Development Area and domestic sewage along the river (Liu et al., 2015a), so the high levels of OPs found in X1(ΣOPs 117 μg/kg), and X3 (ΣOPs 86.9 μg/kg) were expected. Lower levels of sedimentary OPs in the second sampling site X2 (ΣOPs 42.9 μg/kg) may be attributable to dilution effects and possible degradation or transformation in the river after input into X1. Pu River is also an important inland river in Shenyang City transporting industrial wastewater from industrial parks located in Puhe New City, as well as domestic wastewater along the river (Li et al., 2015), so it was not unexpected that a high concentration of OPs (ΣOPs 154 μg/kg) was detected in P1 adjacent to the industrial park.

DHF, located mid-stream of the Hun River, receives water from several tributaries, with Hun River as its main influx. The reservoir provides drinking water to more than five million local inhabitants in nine cities; consequently, there is considerable concern about the occurrence, input and potential risks to human health from high-risk substances, including POPs, heavy metals and PPCPs (Liu et al., 2015a, 2015b; Sun et al., 2015). Comparable levels of OPs with similar distribution characterization were detected in 16 sediments collected in the reservoir, these measured levels were higher than those found upstream of the Hun River. Specifically, TBP (0.231–0.752 μg/kg), TBEOP (LOD-4.19 μg/kg), TCEP (0.532–3.18 μg/kg) and TCIPP (0.352–1.32 μg/kg) were found in all the sediments; meanwhile, trace levels of TDCIPP, TPHP and TMMP were found in most of the studied samples.

Based on these findings, we have found that lower levels of OPs with limited variance were found in sediments from the UHR and DHF, suggesting they are ubiquitous in the studied region without an obvious emission source. After receiving large amounts of domestic and industrial wastewater from Fushun and Shenyang, elevated levels of OPs were detected in sediments from downstream of the Hun River and its two main tributaries, the Xi and Pu Rivers.

Compared to published data (Table S3), levels of OPs in the upstream area of Hun River and DHF were comparable to those from Taihu Lake (Cao et al., 2012) and the Great Lake (Cao et al., 2017), as well as marine sediment from the Pearl River Estuary (with exception of TCIPP) (Pintado-Herrera et al., 2017), Pacific and Arctic areas (Ma et al., 2017), and they were much lower than those from regions influenced heavily by industrialization and urbanization, such as the Pearl River Delta (Tan et al., 2016), Chicago Sanitary and Ship Canal (Peverly et al., 2015), and Aire River, with the exception of TCIPP (Cristale et al., 2013). However, OPs levels from DHR and its attached tributaries (Xi River and Pu River) were similar to these polluted areas (Cristale et al., 2013; Peverly et al., 2015; Tan et al., 2016).

Table 1
Concentrations and distribution of OPs in sediments from Hun River and Dahuofang Reservoir (μg/kg).

	TBP	TBEOP	TCEP	TCIPP	TDCIPP	TPHP	TMPP	Σ7OPs
The upstream of Hun Rive (n = 12)	LOD-1.83	ND-0.941	LOD-0.810	LOD-0.786	ND-0.746	LOD-0.958	LOD-1.09	LOD-5.83
The downstream of Hun River (n = 7)	0.474–10.2	ND-16.6	ND-8.08	ND-14.4	LOD-23.0	ND-11.2	ND-9.63	3.49–45.7
Dahuofang Reservoir (n = 16)	0.231–0.752	LOD-4.19	0.532–3.18	0.352–1.32	ND-LOD	LOD-0.483	ND-LOD	1.15–7.01
Pu River (n = 2)	0.767–38.9	LOD	0.758–49.6	0.718–60.1	0.589–2.32	0.992–1.82	0.957–1.56	4.78–154
Xi River (n = 3)	0.257–18.7	1.43–21.2	2.01–34.5	0.437–8.66	0.595–28.1	0.771–72.8	2.55–7.95	14.1–117

ND: not detected; LOD: below the limit of detection.
TNBP: Tributyl phosphate; TBEOP: Tris-(2-butoxyethyl) phosphate; TPHP: Triphenyl phosphate; TMPP: Tris(methylphenyl) phosphate; TCEP: Tris-(2-chloroethyl) phosphate; TCIPP: Tris(2-chloroisopropyl) phosphate; TDCIPP: Tris(1,3-dichloro-2-propyl) phosphate.

3.2. Spatial distribution of OPs and their possible emission source

The source of the Hun River is in Qingyuan Country, where it drains through extensive agricultural areas in its upper reach. Sedimentary OPs were recorded at levels of 5.83 μg/kg in H11, which suggests possible input, and this agreed with the occurrence of PAHs found in our previous study (Liu et al., 2015a). In contrast, trace OPs (See Table S2) were found in the remaining 11 sediment samples taken in this area, which suggested non-point emission in this section of the river. These findings may be due to dry/wet deposition during long-range transportation (Li et al., 2017) as there were no obvious domestic/industrial wastewater discharges. The distribution characterization was similar to brominated flame retardants PBDEs and hexabromocyclododecane (HBCD) (Su et al., 2015). The Dahuofang Reservoir receives three tributaries (including Suzi River, Shehe River, and upstream of Hun River inflow) and it acts as a source of drinking water; similar concentrations of sedimentary OPs were detected in sediment samples showing no obvious emission. It can be concluded that dry/wet deposition (Li et al., 2017) makes an important contribution to OPs distribution in sediment combined with the input from the above mentioned tributaries. However, a different distribution pattern occurred downstream of the river as well as in the Xi River and Pu River. Based on their average concentrations and detected frequencies (DFs), it was identified that TBP, TCEP and TCIPP were the main pollutants in DHR. Downstream Hun River drains through several cities receiving a large amount of domestic/industrial wastewater (Liu et al., 2015b), and this may be the reason for the presence of OPs in sediment samples. The results agreed with published studies that have reported the correlation between the presence of halogenated flame retardants and industrialization/urbanization, especially the rapid development of the electrical industry and increasing consumer demand for electrical/electronic devices (Liu et al., 2014; Schreder and La Guardia, 2014). Due to replacement for PBDEs, it is reasonable that higher levels of OPs were found in the sediments and would be increased gradually. Xi River and Pu River are the two inland drains conveying domestic/industrial wastewater, and significant high OPs levels were found in X1, X3 and P1 disclosing their obvious discharge from industrial emission.

It was noted that OPs concentrations varied in the range of LOD-5.83, 3.49–154, 1.15–7.01 μg/kg from UHR, DHR (including Xi River and Pu River), and DHF, respectively, these concentrations were slightly lower than the corresponding levels of PBDEs, that were 3.96–51.1, 12.4–327, and 5.62–45.5, respectively (Su et al., 2015). The results may reflect the fact that PBDEs are still in use and are dominant flame retardant in market in our country with increasing demand consumption of OPs (Global and China Flame Retardant Industry Report, 2014–2016, http://www.chinamarketresearchreports.com/114859.html, accessed 15 December 2017).

3.3. Levels and distribution of SMs in sediments

As listed in Tables 2 and S4, it was found that the three nitro musks (including MA, MX and MK) and two polycyclic musks (DPMI and ATII) were not found in any of the sediment samples in the studied area. ADBI and AHMI were found at LOD in most of the samples; two polycyclic musks HHCB and AHTN were found in all the sediment samples, with concentrations varying significantly between 0.117 and 245 μg/kg and 0.0980–213 μg/kg, respectively. The highest level of SMs (ΣSMs 458 μg/kg, 245 μg/kg HHCB and 213 μg/kg AHTN, respectively) was measured in X1 which was located in the important wastewater drain from Tiexi Economic development Area, followed by P1 (ΣSMs 73.7 μg/kg, 49.5 μg/kg HHCB and 24.2 μg/kg AHTN, respectively) adjacent to the Puhe New City.

Relatively lower concentrations of HHCB (0.141–4.39 μg/kg) and AHTN (0.0980–3.82 μg/kg) were detected in the 12 sediment samples from UHR. H11 had the highest level of HHCB and AHTN, followed by H6, suggesting possible point-emission sources in the two sampling sites in this section. However, low levels of SMs with limited variance were detected in 16 sediments from the DHF: HHCB was found in the range of 0.117–0.726 μg/kg, and AHTN ranged from 0.430 μg/kg to 0.956 μg/kg. It was notable that sedimentary AHTN concentrations in DHF were slightly higher than those of HHCB. After outflowing from DHF the Hun River runs through an area heavily affected by anthropogenic activities, including urban agglomeration, such as Fushun, Shenyang, Liaoyang and Anshan. The highest level of SMs in downstream of the Hun River was observed in H16 (ΣSMs 75.4 μg/kg), which was located downstream of Shenyang. Notably, it was the only sampling site where we measured quantifiable ADBI at 0.643 μg/kg, suggesting a possible discharge near the sampling site.

Overall, the concentration of ΣSMs varied in the range of 0.239–8.21 μg/kg, 0.614–1.68 μg/kg, and 5.16–458 μg/kg in UHR, DHF, and DHR (including Xi River and Pu River), respectively, with their corresponding average concentrations at 1.79 μg/kg, 1.05 μg/kg and 63.3 μg/kg. The concentration of ΣSMs were much lower from UHR and DHF compared to those from the lower reach.

In the past decades, extensive studies have focused on occurrence and distribution of SMs in the environment as well as their possible risk to ecological systems and human health. Partial results about sedimentary synthetic musks are listed in Table S5. Compared to the published data, levels of SMs in the sediment in UHR and DHF were comparative to those found in Taihu Lake (Che et al., 2011), Yellow River (Lou et al., 2016), and Haihe River (Hu et al., 2011) in China, and in Nakdong River and the coastal marine sediment in South Korea (other than two sampling sites receiving wastewater) (Lee et al., 2014), and much lower than those from several rivers in China, such as the Pearl River (Zeng et al., 2018), Pearl River Estuary (Huang et al., 2016; Pintado-Herrera et al., 2017), and Huangpu River (Wang et al., 2018), as well as from heavily polluted areas, such as the urban catchment from Singapore (Wang and Kelly, 2017), urban/suburban playa lakes (Chase et al., 2012) and Hudson River (Reiner and Kannan, 2011) in the USA. However, levels of SMs in the lower reach of the Hun River (including the two main tributaries) were similar to those heavily polluted areas described above (Chase et al., 2012; Huang et al., 2016; Pintado-Herrera et al., 2017; Wang and Kelly, 2017; Zeng et al., 2018; Wang et al., 2018).

Table 2
Concentrations and distribution of synthetic musks in sediment from Hun River and Dahuofang Reservoir (μg/kg).

	ADBI	AHMI	HHCB	AHTN	ΣSMs	HHCB/AHTN
The upstream of Hun Rive (n = 12)	LOD	LOD	0.141–4.39	0.098–3.82	0.239–8.21	1.01–1.98
The downstream of Hun River (n = 7)	ND-0.643	ND-LOD	1.21–32.9	2.79–41.9	5.16–75.4	0.243–1.33
Dahuofang Reservoir (n = 16)	LOD	ND-LOD	0.117–0.726	0.430–0.956	0.614–1.68	0.189–1.23
Pu River (n = 2)	LOD	ND-LOD	6.19–49.5	5.01–24.2	11.2–73.7	1.24–2.05
Xi River (n = 3)	LOD	ND-LOD	6.69–245	5.45–213	12.1–458	1.15–1.65

ND: not detected; LOD: below the limit of detection.
ADBI: 4-acetyl-1,1-dimethyl-6-tert-butylindan; AHMI: 6-acetyl-1,1,2,3,3,5-hexamethylindan.
HHCB: 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8- hexamethylcyclopenta (g)-2-benzopyran.
AHTN: 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene.

3.4. Spatial distribution of SMs and their possible emission source

The highest levels of SMs (ΣSMs 458 μg/kg, 245 μg/kg HHCB and 213 μg/kg AHTN) were measured in X1 which was located in the main wastewater drain from Tiexi Economic Development Area, followed by P1 (ΣSMs 73.7 μg/kg, 49.5 μg/kg HHCB and 24.2 μg/kg AHTN) which was located in the upper reach of the Pu River. These findings disclosed their possible emission sources in industrial and domestic wastewater from Tiexi Economic Development Area and Pu New City. The spatial distribution of SMs was similar to those of OPs and PAHs (Liu et al., 2015a), PBDEs and HBCDs (Su et al., 2015), as well as perfluoroalkyl acids (Gong et al., 2016). The results suggested the wastewater drains (Pu River and Xi River) carries variety of organic pollutants discharged into Hun River, combined with domestic sewage from million inhabitants in the city.

The distribution pattern of SMs was consistent with their use in the perfume industry (Zeng et al., 2018). Due to their obvious toxicities and potential for accumulation, nitro musks were banned as additives in cosmetics and restricted to application in household products. Meanwhile, macrocyclic musks were only used in perfume given their high costs, consequently polycyclic musks especially HHCB and AHTN are currently the dominant fragrance materials on the market (Homem et al., 2015).

As we known, SMs have been widely used as fragrances in various household and personal care products; subsequently they have been used as indicators for domestic sewage discharge as well as industrial wastewater from the related manufacturers (Wang and Kelly, 2017; Zeng et al., 2018). Furthermore , the ratio of HHCB/AHTN is an important parameter that has been commonly used to discriminate different patterns of application in different countries and to trace their transportation in a receiving river after discharge from a specific emission source (Huang et al., 2016; Lou et al., 2016; Zeng et al., 2018). In the present study, HHCB/AHTN ratios ranged from 0.189 to 2.05 in the studied area, most of which were similar to those found in Haihe River (Hu et al., 2011) and the Pearl River Delta (Zeng et al., 2008), and dissimilar to those from Singapore (Wang and Kelly, 2017); this phenomenon may be related to their different application in different countries. In 15 of the 16 sediments in DHF, the ratios of HHCB/AHTN were lower than 1 except in D12 (1.23), and slightly lower than those from Xi River and Pu River, which may be attributable to stronger sorption of AHTN to organic matter in the sediment, and easier degradation of HHCB in the reservoir. In other words, under the relative static hydrodynamic conditions in the reservoir, AHTN was preferentially distributed in the bottom sediment, while HHCB underwent further degradation in the reservoir (Wang and Kelly, 2017).

3.5. The potential ecological risk posed by OPs and SMs

In the present study, we assessed primarily the potential ecological risk posed by the main components of OPs and SMs, using risk quotient (RQ) which was expressed as followed:

$$RQ = MEC/PNEC \quad (1)$$

where, MEC was the measured environmental concentration, and PNEC was the predicted no effect concentration. According to EU risk assessment reports, PNEC values were 0.2 mg/kg for TCEP (European Commission, 2009), 2.92 mg/kg for TCIPP (European Commission, 2007), 10.9 mg/kg for HHCB (European Commission, 2008a), and 8.42 for AHTN (European Commission, 2008b). The potential risk was evaluated on the basis of commonly recommended criteria, as low risk ($0.01 \leq RQ < 0.1$), medium risk ($0.1 \leq RQ < 1.0$), and high risk ($RQ \geq 1.0$) (Fu et al., 2017).

Based on the calculated RQs, medium risk posed by TCEP was found in X1 (0.17) and P1 (0.25), and low risk was found in 9 sampling sites; meanwhile, RQs less than 0.01 were recorded in the rest of the sampling locations, suggesting limited ecological risk posed to sediment dwelling organisms. As for TCIPP, low risk was found in P1 (RQ = 0.021), with a TCIPP concentration of 60.1 μg/kg. Similarly, low risk was found in X1, with RQ for HHCB (245 μg/kg) and AHTN (213 μg/kg) being 0.022 and 0.025, respectively. However, taking into consideration the variety of organic pollutants in the river and reservoir, ecological risk posed by combined pollution should be paid much closer attention.

4. Conclusion

In the present study, 40 sediment samples were collected from the Hun River and Dahuofang Reservoir, as well as from two main tributaries downstream of the Hun River, and analyzed for the occurrence and distribution of emerging pollutants, OPs and SMs. The findings indicated that OPs were ubiquitously distributed in the studied region, with the concentration of Σ7OPs varying significantly in the range of LOD-117 μg/kg. Four polycyclic musks (ADBI, AHMI, HHCB, and AHTN) were frequently detected in sediment samples, with HHCB and AHTN being predominant compounds. The total concentration of SMs varied significantly from 0.239 to 458 μg/kg. The results indicated that industrial and domestic wastewater were the main emission sources in the river. Based on the measured concentrations, we calculated the ecological risk of the 2 chlorinated OPs (TCEP and TCIPP) and 2 polycyclic musks (HHCB and AHTN), and the results indicated that TCEP posed low to medium risk to organisms dwelling in sediment; similarly, low ecological risk was found for TCIPP in P1, and HHCB and AHTN posed limited risks to sediment-dwelling organisms. However, we should not neglect the possible risk from the synergistic interactions of a variety of organic pollutants and heavy metals widely detected in the studied region.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2018.05.034.

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