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Occurrence, spatial distribution, and fate of polycyclic musks in sediments from the catchment of Chaohu Lake, China

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Abstract Twenty-nine surface sediments from Chaohu Lake in China and from its six main tributaries were sampled to investigate the concentrations of two important polycyclic musks (PCMs), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran (galaxolide, HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (tonalide, AHTN), as well as the concentration of 4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran-1-one (galaxolidon, HHCB-lactone), which is the main degradation product of HHCB. Except for the high concentrations of AHTN and HHCB measured in the Nanfei River (879 ng/g dw and 5,513 ng/g dw, respectively), the levels of AHTN and HHCB in the river sediments were 7.08–44.9 ng/g dw and 20.6–268 ng/g dw, respectively, which are slightly lower than those documented in various areas worldwide. The concentrations of AHTN and HHCB in the sediments of Chaohu Lake were one or two orders of magnitude lower than those in the tributary rivers and showed a clear regional distribution. The concentrations of HHCB-lactone were comparable to those of HHCB and presented a significant positive correlation with the concentrations of HHCB, suggesting that the HHCB-lactone originated directly from the degradation of HHCB in wastewater treatment plants (WWTPs) or in the natural environment. The diagnostic ratios of HHCB/AHTN and HHCB-lactone/HHCB and the enantiomeric fractions (EFs) of these PCMs showed that the direct origins of the target PCMs in the study area were municipal and industrial wastewaters discharged from adjacent cities or point sources and that the HHCB-lactone in sediment originated from the natural degradation of HHCB in the rivers and the lake. The results of the risk assessment showed that the PCMs in the watershed sediments were unlikely to pose a threat to aquatic species. However, the effluents of industrial and municipal wastewaters that are discharged into the Nanfei River should be investigated in future research.

Keywords Occurrence · Spatial distribution · Source · AHTN · HHCB · HHCB-lactone

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Introduction

Polycyclic musks (PCMs) constitute a group of important organic pollutants that are persistent in aquatic environments. These pollutants are causing increasing concern worldwide owing to their potential bioaccumulation and toxicity to aquatic species and humans (Lange et al., 2015; Pedrouzo et al., 2009; Sun et al., 2014; Vallecillos et al., 2017; Wang et al., 2018). In general, PCMs are used as fragrance components and fixatives in various household goods and personal care products, such as detergents, perfumes, cosmetics, and shampoos (Liu & Wong, 2013; Zhang et al., 2015, 2020). Unlike pharmaceuticals, these substances are not metabolically altered by the human body. They are removed incompletely by wastewater treatment plants (WWTPs) and enter the aquatic environment through effluent or by their direct discharge into surface water systems (Villa et al., 2012). The existence of these contaminants in aquatic environments has been accepted as an emerging ecological threat (Richardson & Ternes, 2005).

As the two most commonly detected PCMs in aquatic environments, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran (galaxolide,HHCB)and7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (tonalide, AHTN) are currently manufactured and used in large quantities of approximately 5,000–10,000 tons per year and are frequently detected in water, sediments, and aquatic organisms (European Union 2008a, b; Martin et al., 2007). The concentrations of HHCB and AHTN were 0.04–1.8 μg/L and < 0.005–0.36 μg/L, respectively, in surface waters in Germany (Clara et al., 2011; Regnery & Püttmann, 2010; Reinstorf et al., 2008), and concentrations of 0.004–0.026 μg/L and 0.005–0.023 μg/L were detected in wastewater discharged into the Hudson River in the USA (Reiner & Kannan, 2011). However, HHCB and AHTN are prone to adsorb onto suspended particles in water and are ultimately deposited in sediments because of their hydrophobic behaviour and high octanol–water partition coefficients (log $K_{OW} \geq 5$) (Necibi et al., 2016; Zeng et al., 2008). Therefore, sediment sample analysis is required to estimate the effects of anthropogenic activities on aquatic environments. In suspended sediment obtained from Italy's Molgora River, the median concentrations of HHCB and AHTN detected were 1349 ng/g dw and 927 ng/g dw, respectively (Villa et al., 2012). Comparable concentrations were detected in the Po River in Italy, at 16–159 ng/g dw and not detectable (ND)–400 ng/g dw (Luigi et al., 2015), and in the Hudson River, in the USA, at 72.8–388 ng/g dw and 113–544 ng/g dw, respectively (Reiner & Kannan, 2011). Owing to the increasing awareness of PCMs as organic contaminants, HHCB and AHTN have been used as markers of xenobiotic pollution originating from domestic wastewater (Buerge et al., 2003; Strauch et al., 2008; Zeng et al., 2008). Additionally, because HHCB-lactone is produced from the biotic oxidation process of HHCB in WWTPs, HHCB-lactone concentrations are frequently monitored in wastewater and river water (Vallecillos et al., 2017). The ratios of HHCB/AHTN and HHCB-lactone/HHCB and the enantiomeric fractions (EFs) of these PCMs have been adopted as powerful diagnostic indicators for assessing the relative contributions of various pollution sources and processes (Lange et al., 2015; Vallecillos et al., 2017; Zhang et al., 2020).

Chaohu Lake, the fifth largest lake in China, has a surface area of 780 km^2 and is situated north of the Yangtze River in central Anhui Province, East China. As an important freshwater supply for the surrounding region, Chaohu Lake is affected by frequent eutrophication events and severe contamination owing to the discharges of industrial and municipal wastewaters into the lake watershed. Several previous studies have investigated the contamination characteristics of various anthropogenic toxic organic pollutants that are present in the lake's surface sediments, such as polycyclic aromatic hydrocarbons, linear alkylbenzenes, organophosphates, and synthetic pyrethroid insecticides; these pollutants threaten the aquatic ecosystem and the health of local residents (Li et al., 2014; Wang et al., 2012a, 2012b). However, only one study has investigated the recent appearance of synthetic musks in sediments (Lyu et al., 2020), even though only 45% of municipal sewage and industrial wastewater discharged into the whole Chaohu catchment is treated (Song et al., 2008). Moreover, the presence of HHCB-lactone in sediments has not been reported thus far. The continuous discharge of PCMs into the catchment area necessitates an analysis of their contaminant status and ultimate fate. Accordingly, the objectives of this study are to survey the occurrence and spatial distribution of AHTN, HHCB, and

HHCB-lactone in the surface sediments of Chaohu Lake and its main tributary rivers. In addition, the HHCB/AHTN and HHCB-lactone/HHCB ratios and their EFs are used to trace the direct sources of these substances, identify their potential transformation processes, and estimate the influence of increased anthropogenic activity on aquatic environments.

Materials and methods

Study area and sample collection

Chaohu Lake is a shallow lake with an average water depth of ~ 3 m, and its northwestern and northeastern shores are surrounded by two large cities (Hefei city and Chaohu city, respectively). Approximately 80% of the total annual inflow into the lake is contributed from six tributary rivers: the Nanfei, Shiwuli, Pai, Fengle, Hangbu, and Zhegao Rivers. The majority of pollutants in the lake originate from the Nanfei and Shiwuli Rivers, which receive municipal and industrial wastewater from Hefei city and discharge it into the western part of the lake (Li et al., 2014). During the sampling campaign in July 2011, twenty-nine surface sediments were obtained from Chaohu Lake and the six rivers mentioned above (Fig. 1). Of these samples, 12 were collected from the lake bed from west to east, and the remaining 17 were obtained from the riverbeds of the six rivers. The sediment samples were obtained with a manual stainless steel grabber, brought to the laboratory, freeze-dried, and sieved through a 100 mesh sieve. Finally, the samples were stored in a freezer at − 20 °C for analysis.

Sample preparation and instrumental analysis

The pretreatment process for sediment samples followed the procedure described by Gao et al. (2019) with minor modifications and is provided in the Supplementary Information. A 7890A-7000A gas chromatograph-triple quadrupole mass spectrometer (Agilent Technologies, USA) equipped with a DB-XLB capillary column (30 m × 0.25 mm i.d., film thickness 0.25 µm, J&W Scientific, USA) was used to identify and quantify AHTN, HHCB, and HHCB-lactone. The temperature program was as follows: the initial temperature was held at 100 °C for 2 min, ramped to 150 °C at 8 °C/min, then 210 °C at 5 °C/min, and 300 °C at 15 °C/min, and finally held for 20 min. Automatic splitless injection was used, with an injection volume of 1 µL. The injection port temperature was set at 230 °C, with helium at a 1.0 mL/min flow rate. The mass spectrometer was operated in selective ion monitoring mode with a mass scanning range of 35–600 amu. The transfer line, ion source, and quadrupole rods were maintained at temperatures of 210 °C, 230 °C, and 150 °C, respectively. Multiple reaction monitoring mode was used for quantification.

The enantiomeric analysis of target PCMs was performed on a 25 m × 0.25 mm × 0.25 µm Hydrodex-β-6TBDM chiral column (Macherey–Nagel, Düren, Germany). The detailed oven program and the calculation of the EFs were as described by Gao et al. (2019).

Ecological risk assessment

The ecological risk caused by PCMs was evaluated according to related approaches recommended by the European Chemicals Bureau (2003). Owing to a lack of available toxicity data, the ecological risk of the target PCMs was estimated by the risk quotient (RQ), which was calculated by dividing the measured environmental concentration (MEC) of each pollutant by the predicted no-effect concentration (PNEC). The evaluation process employed in this study was described by Zhang et al. (2020) and Lyu et al. (2020). The ecological risks were classified into three categories of risk to aquatic organisms: $RQ < 0.1$, extremely low expected risk; $0.1 \leq RQ < 1$, probable moderate risk; and $RQ \geq 1$, high risk.

Quality assurance and control

Blanks, spiked blanks, and spiked matrix samples were tested in parallel with each batch of samples as quality control for the analytical methods. None of the analytes were detected in any of the blanks, or they were present below the detection limit. The recoveries of AHTN, HHCB, and HHCB-lactone were 85.2 ± 3.5%, 84.7 ± 3.2%, and 88.6 ± 2.7% and 87.3 ± 1.2%, 84.3 ± 2.6%, and 90.6 ± 1.4% for the spiked blanks and spiked matrix samples, respectively. None of the reported concentrations were corrected using recovery rates. To control the EF

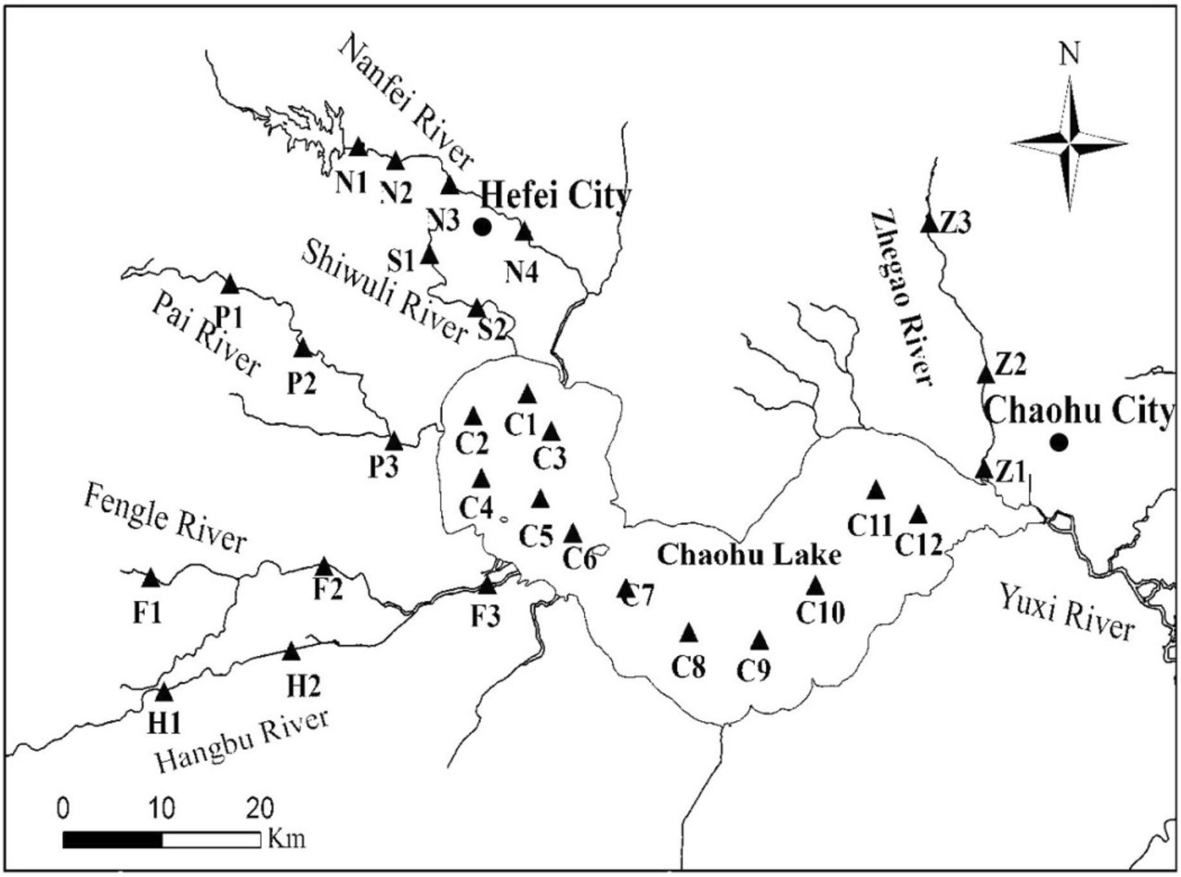

Fig. 1 Map of the sampling sites (N, Nanfei River; S, Shiwuli River; P, Pai River; F, Fengle River; H, Hangbu River; Z, Zhegao River)

variation derived from the decrease in column efficiency during the enantiomeric analysis, 100 ng/mL of a standard mixture was analysed after six consecutive sediment samples were processed. The results showed no EF variation throughout the instrumental sample analysis procedure.

Results and discussion

Concentrations and spatial distributions of PCMs

Table 1 lists the concentrations of the target PCMs found in the sediments of Chaohu Lake and its six tributary rivers. In general, HHCB, AHTN, and HHCB-lactone were detected in all of the tributary river sediments and in most of the surface sediments of the lake. In the river sediments, no clear increasing or decreasing trend in PCM concentration was observed from upstream to downstream, but higher concentrations were detected at locations near obvious emission sources. The highest PCM residue concentrations were found in sediments sampled from the Nanfei River, which had AHTN and HHCB concentrations of 26.5–879 ng/g dw and 80.6–5513 ng/g dw, respectively. This result was expected, because the Nanfei River runs through the capital city (Hefei city) of Anhui Province, from which it receives massive amounts of municipal and industrial wastewaters (Liu et al., 2012). A significant correlation ($p < 0.01$) was discovered between the concentrations of HHCB and AHTN, which indicated that the types of sewage effluent in the tributary rivers were roughly similar. However, the concentrations of the target PCMs in the sediments of the lake were significantly lower, by one or two orders of magnitude, at ND–7.50 ng/g dw

Table 1 Concentrations (ng/g dw) of AHTN, HHCB and HHCB-lactone in sediment samples from Chaohu Lake and its inflowing rivers

Sample		AHTN	HHCB	HHCB-lactone
River sediment	FL ($n=3$)	7.33–44.9	22.4–268	16.5–304
	SWL ($n=2$)	9.61–24.5	30.9–112	26.5–221
	HB ($n=2$)	7.08–16.0	20.6–107	21.9–83.7
	NF ($n=4$)	26.5–879	80.6–5513	205–3435
	ZG ($n=3$)	8.42–11.6	23.2–31.9	19.2–43.7
	P ($n=3$)	13.6–21.1	57.7–101	95.8–170
Lake sediment	C1	6.39	13.7	15.8
	C2	6.40	14.7	20.3
	C3	7.50	25.5	34.3
	C4	5.48	11.1	10.9
	C5	6.25	15.6	12.6
	C6	5.91	13.8	13.9
	C7	2.87	6.89	13.7
	C8	ND	ND	ND
	C9	5.85	13.2	11.0
	C10	3.93	5.29	8.14
	C11	ND	ND	ND
	C12	4.99	10.0	ND

ND means below the limit of detection

FL Fengle River, *SWL* Shiwuli River, *HB* Hangbu River, *NF* Nanfei River, *ZG* Zhegao River, *P* Pai River

and ND–25.5 ng/g dw for AHTN and HHCB, respectively. Moreover, a notable regional distribution was observed, i.e., the sediments with higher PCM levels were all obtained from the western part of the lake, which is the location of the five main wastewater inflow channels of Chaohu Lake: the Nanfei, Shiwuli, Paihe, Fengle, and Hangbu Rivers (Li et al., 2014; Liu et al., 2012). This result suggests that the PCMs in Chaohu Lake sediments are strongly associated with the extensive discharge of municipal sewage into rivers. Recent studies have also indicated that the influx of pollutants from industrial sources, municipal sewage, and non-point source pollution in the western part of Chaohu Lake is much greater than that in the eastern part (Wang et al., 2012b; Yu et al., 2011).

As the main transformation product of HHCB, HHCB-lactone was found in comparable concentrations to those of HHCB in all tributary river and lake surface sediments. In particular, in the Nanfei River, the HHCB-lactone concentrations were in the range of 205 to 3435 ng/g dw. Pearson's correlation analysis revealed a significant positive correlation between the concentrations of HHCB-lactone and HHCB, with a correlation coefficient of 0.961 ($p=0.000$). Moreover, the spatial distribution of HHCB-lactone was not different from those of HHCB and AHTN. All of these results strongly suggest that the HHCB-lactone in the study area had the same primary source as its parent compound, HHCB, or was sourced directly from the degradation of HHCB in WWTPs or in natural environments.

Comparison with published data

Few studies thus far have focused on PCMs in sediments obtained from rivers or lakes. Moreover, no available research discusses the HHCB-lactone concentrations in sediments. This absence of information prevented us from comparing the HHCB-lactone level obtained in the present study with those in other regions. In the present study, AHTN and HHCB were detected in the sediments of Nanfei River at high levels, 879 ng/g dw and 5513 ng/g dw, respectively; these values are higher than those reported in the majority of sediments from various areas (Table 2) but lower than those found in sediment of Italy's Molgora River, which has the highest concentrations of AHTN and HHCB of all locations considered, at 4320 ng/g dw and 18,000 ng/g, respectively (Villa et al., 2012). The Molgora and Nanfei Rivers both carry large amounts of municipal sewage from adjacent cities (Liu et al., 2012; Villa et al., 2012). The concentrations of AHTN and HHCB in sediments from the other rivers of Chaohu Lake, including

Table 2 Levels of AHTN, HHCB, and HHCB-lactone in sediment from various areas

Location	Concentrations (ng/g dw)			References
	AHTN	HHCB	HHCB-lactone	
Nanfei River, China	26.5–879	80.6–5513	205–3435	This study
Fengle River, China	7.33–44.9	22.4–268	16.5–304	This study
Shiwuli River, China	9.61–24.5	30.9–112	26.5–221	This study
Pai River, China	13.6–21.1	57.7–101	95.8–170	This study
Hangbu River, China	7.08–16.0	20.6–107	21.9–83.7	This study
Zhegao River, China	8.42–11.6	23.2–31.9	19.2–43.7	This study
Chaohu Lake, China	ND–7.50	ND–25.5	ND–34.3	This study
North Canal River, China	1.21–731	4.10–818	ND	Zhang et al., 2020
Pearl River, China	4.31–439	0.44–547	ND	Zeng et al., 2018b
Shanghai River	ND–2.78	ND–61.7	ND	Wang et al., 2018
Liangtan River, China	ND–99.8	ND–268	ND	Sang et al., 2012
Hun River, China	0.10–213	0.14–245	ND	Zeng et al., 2018a
Songhua River, China	ND–5.70	ND–17.5	ND	Lu et al., 2015
Jiaozhou Bay, China	3.06–14.5	13.1–273	ND	Jiang et al., 2018
Dahuofang Reservoir, China	0.43–0.96	0.12–0.73	ND	Zeng et al., 2018a
Dianshan Lake, China	ND–0.31	0.30–2.50	ND	Gu et al., 2017
Taihu Lake, China	ND–0.35	0.18–1.21	ND	Che et al., 2011
Taihu Lake, China	0.12–1.29	0.08–1.17	ND	Zeng et al., 2016
Hudson River, USA	113–544	72.8–388	ND	Reiner & Kannan, 2011
Molgora River, Italy	ND–4320	ND–18000	ND	Villa et al., 2012
Po River, Italy	16.0–159	ND–400	ND	Luigi et al., 2015
Nakdong River, South Korea	ND–2.30	ND–6.30	ND	Lee et al., 2014
Erie and Ontario Lake, USA	0.96	3.20–16.0	ND	Peck et al., 2006
Bizerte Lagoon, Tunisia	0.30–1.70	1.09–2.80	ND	Necibi et al., 2016

ND means not detected

the Fengle, Shiwuli, Pai, Hangbu, and Zhegao Rivers, were 7.08–44.9 ng/g dw and 20.6–268 ng/g dw, respectively (Table 2). These levels are slightly lower than the respective levels of AHTN and HHCB found in China's North Canal River, at 1.21–731 ng/g dw and 4.10–818 ng/g dw (Zhang et al., 2020), and Pearl River, at 4.31–439 ng/g dw and 0.03–547 ng/g dw (Zeng et al., 2018b), and in the upper region of the USA's Hudson River, at 113–544 ng/g dw and 72.8–388 ng/g dw (Reiner & Kannan, 2011). The levels are comparable to those of Italy's Po River, at 16.0–159 ng/g dw and ND–400 ng/g dw (Luigi et al., 2015), and China's Liangtan River, at ND–99.8 ng/g dw and ND–268 ng/g dw (Sang et al., 2012), and Hun River, at 0.10–213 ng/g dw and 0.14–245 ng/g dw (Zeng et al., 2018a). However, the concentrations were obviously higher than those in South Korea's Nakdong River, at ND–2.30 ng/g dw and ND–6.30 ng/g dw (Lee et al., 2014), and China's Shanghai River, at ND–2.78 ng/g dw and ND–61.7 ng/g dw (Wang et al., 2018), and Songhua River, at ND–5.70 ng/g dw and ND–17.5 ng/g dw (Lu et al., 2015).

Compared with those measured in various other areas, the levels of AHTN and HHCB in the sediments of Chaohu Lake were low and are similar to those in Lake Erie and Lake Ontario in the USA (Peck et al., 2006), Bizerte Lagoon in Tunisia (Necibi et al., 2016), and other lakes in China, such as Dianshan Lake (Gu et al., 2017), Taihu Lake (Che et al., 2011; Zeng et al., 2016), and Dahuofang Reservoir (Zeng et al., 2018a). However, the concentrations were one or two orders of magnitude lower than those in Jiaozhou Bay in China (Jiang et al., 2018).

Diagnostic ratios and EF analysis for source identification

The ratios of HHCB/AHTN and HHCB-lactone/HHCB as well as the results of EF analysis have been used to trace the direct sources of PCMs and to identify their potential transformation processes (Lange et al., 2015; Rusconi et al., 2017; Vallecillos et al., 2017; Zhang et al., 2020). In this study, the HHCB/AHTN ratios of the tributary river sediments were 2.7–8.2, with a mean value of 4.2. This result is in good agreement with the relative proportions of the production volumes for these compounds, i.e., an HHCB/AHTN ratio of approximately 3–4, and is also consistent with that in consumer products, at approximately 2–20 (Wang & Kelly, 2017; Zhang et al., 2020). Zeng et al. (2008) found HHCB/AHTN ratios of 3.4–7.6, with an average value of 5.3, in sewage sludge collected from WWTPs in Guangdong. Our results almost matched those of sewage sludge from WWTPs (Zeng et al., 2008), demonstrating a significant link with the current discharge of municipal sewage and industrial wastewater from adjacent cities. However, we found significantly lower ratios, 1.3–3.4, with a mean value of 2.3, in the sediments of Chaohu Lake. Similarly, lower HHCB/AHTN ratios have been calculated for sediments taken from the Songhua River in China (Lu et al., 2015) and from an aquatic environment in Germany (Kronimus et al., 2004), likely owing to the transformation of HHCB to HHCB-lactone in the sediment (Bester, 2005).

The HHCB-lactone/HHCB ratios calculated in the present study were 0.6–2.5 and 0.8–2.0 in the river and lake sediments, with mean values of 1.3 and 1.2, respectively. This wide range in the HHCB-lactone/HHCB ratio reflected variability in the sources of wastewater or instability in the WWTP processes that take place before the effluent is discharged into rivers and the lake. Lange et al. (2015) found that variability in the concentration of suspended solids in rivers also affects the HHCB-lactone/HHCB ratio because HHCB has a greater sorption tendency than the more polar HHCB-lactone. Considering that the transformation from HHCB to HHCB-lactone is a biotic oxidation process, it can also occur naturally in rivers and lakes. Therefore, the physicochemical and hydrological conditions in rivers and lakes can also influence the ratio of HHCB-lactone/HHCB (Rusconi et al., 2017). Obviously, further investigations should be performed to make the HHCB-lactone/HHCB ratio a powerful means for assessing the relative contributions of various sources and transformation processes to aquatic pollutant levels.

In the present study, EF analysis was also conducted to identify the potential sources and transformation processes occurring in the rivers and the lake. As illustrated in Table 3, the EFs of AHTN in sediment from the tributary rivers were 0.48–0.51, with a mean value of 0.49 ± 0.01. This indicated that no apparent enantioselective biotransformation occurred. In comparison, the EFs of AHTN in the sediment from Chaohu Lake showed more obvious deviations in EFs from 0.5, as they ranged from 0.46 to 0.49 with a mean value of 0.48 ± 0.01. Two factors appeared to be responsible for this difference: the continuous input of wastewater into the tributary rivers and the possible enantioselective degradation in the lake sediments. For HHCB, greater deviations from 0.5 were detected for both *trans*-HHCB enantiomers and *cis*-HHCB enantiomers, which had EFs of 0.37–0.55 and 0.43–0.54 and mean values of 0.47 ± 0.04 and 0.49 ± 0.02, respectively. It should be noted that all of the samples with HHCB concentrations lower than 40 ng/g dw had EF values smaller than 0.5 (Table S1), which indicated preferential degradation of the 4*S* HHCB enantiomers. This phenomenon has also been reported in sludge in WWTPs in Guangdong (Gao et al., 2019) and in fish tissue and zebra mussels obtained from a municipal sewage treatment plant in Germany (Hühnerfuss et al., 2004). Nevertheless, the EFs of samples with HHCB concentrations greater than 40 ng/g dw did not deviate from 0.5 or rise above 0.5. This trend was particularly notable at sampling sites N3 and N4 in the Nanfei River (Table S1), which receives large amounts of sewage and industrial wastewater discharge from the adjacent Hefei city. That is, the enantiomeric composition of HHCB was influenced more by the input of point sources near the sampling sites than by inputs from other sources. The EFs of *cis*-HHCB-lactone were 0.45–0.54, with a mean value of 0.48 ± 0.03, and no correlation was discovered between the EFs of *cis*-HHCB-lactone and *cis*-HHCB. However, the EFs of *trans*-HHCB-lactone were 0.45–0.59, with a mean value of 0.52 ± 0.03, indicating an expected enrichment of the 4*S* HHCB-lactone enantiomer compared with *trans*-HHCB. Furthermore, Spearman's correlation analysis presented a significant positive correlation between the EFs of *trans*-HHCB-lactone and *trans*-HHCB, with a correlation coefficient of 0.619

Table 3 Ratios of HHCB/AHTN and HHCB-lactone/HHCB and enantiomeric fractions (EFs) of AHTN, HHCB, and HHCB-lactone in sediment samples from Chaohu Lake and its inflowing rivers

Samples		HHCB/AHTN	HHCB-lactone/ HHCB	EFs				
				AHTN	*trans*-HHCB	*cis*-HHCB	*trans*-HHCB-lactone	*cis*-HHCB-lactone
River sediment	FL ($n=3$)	2.8–6.0	0.7–1.1	0.48–0.49	0.45–0.49	0.47–0.51	0.46–0.59	0.47–0.51
	SWL ($n=2$)	3.2–4.6	0.9–2.0	0.49–0.49	0.44–0.50	0.47–0.50	0.51–0.56	0.45–0.50
	HB ($n=2$)	2.9–6.7	0.8–1.1	0.48–0.49	0.47–0.50	0.49–0.50	0.52–0.54	0.45–0.47
	NF ($n=4$)	3.0–8.2	0.6–2.5	0.50–0.51	0.47–0.55	0.50–0.54	0.52–0.54	0.50–0.54
	ZG ($n=3$)	2.7–2.8	0.8–1.4	0.49–0.49	0.45–0.46	0.48–0.49	0.52–0.55	0.48–0.49
	P ($n=3$)	4.2–4.8	1.7–1.7	0.50–0.50	0.50–0.51	0.51–0.52	0.54–0.54	0.49–0.52
Lake sediment	C1	2.1	1.2	0.49	0.45	0.48	0.51	0.48
	C2	2.3	1.4	0.46	0.43	0.48	0.49	0.48
	C3	3.4	1.3	0.47	0.47	0.49	0.53	0.49
	C4	2.0	1.0	0.49	0.46	0.47	0.50	0.45
	C5	2.5	0.8	0.48	0.45	0.48	0.50	0.47
	C6	2.3	1.0	0.49	0.45	0.48	0.51	0.46
	C7	2.4	2.0	ND	0.44	ND	0.49	0.45
	C8	-	-	ND	ND	ND	ND	ND
	C9	2.3	0.8	0.49	0.45	0.48	0.51	0.46
	C10	1.3	1.5	0.47	0.37	0.43	0.45	0.45
	C11	-	-	ND	ND	ND	ND	ND
	C12	2.0	-	0.47	0.44	0.51	ND	ND

-, means not available; *ND* means the EFs is immeasurable because the concentrations of one or both enantiomers are below the limit of detection

FL Fengle River, *SWL* Shiwuli River, *HB* Hangbu River, *NF* Nanfei River, *ZG* Zhegao River, *P* Pai River

($p=0.000$). This result again demonstrated that the *trans*-HHCB-lactone in the sediments originated from the enantioselective degradation of HHCB in WWTPs or natural environments. However, the EFs of *trans*-HHCB-lactone did not differ notably between the sediments with higher levels of HHCB-lactone and point source inputs and those with lower levels of HHCB-lactone and no obvious point source inputs (Table S1). This difference between the EFs of HHCB-lactone and HHCB suggests that the *trans*-HHCB-lactone in the sediment originated from the natural degradation of HHCB in the rivers and the lake rather than from degradation in WWTPs. Given that various environmental factors such as riverine redox conditions, the composition of the microbial population, and diverse wastewater treatment technologies also affect the enantiomeric composition of PCMs, further investigations of PCM biotransformation mechanisms should be performed in future studies.

Evaluation of potential ecological risks

The potential ecological risks of AHTN and HHCB to aquatic environments and drinking water were evaluated and are summarized in Table S2. The RQ value of HHCB-lactone is not presented owing to the lack of important parameters and ecotoxicity data. As shown in Table S2, the RQ values of AHTN and HHCB were less than 0.1 for nearly 97% (28 of 29) and 90% (26 of 29) of the sampling sites, respectively, which suggests that the sediment PCMs likely pose minimal ecological risk to local aquatic species. However, at sampling sites N2, N3, and N4 in the Nanfei River, the RQ values of AHTN and HHCB were 0.055–0.180 and 0.117–0.558, respectively, indicating that they pose a moderate ecological risk to aquatic communities. This result indicates that the ecological risks posed by the emission of industrial and municipal wastewaters from Hefei city into the Nanfei River should be sufficiently emphasized.

It should be noted that our evaluation included some uncertainties associated with several limitations of this study. First, the sample size was insufficient. Second, the toxic effects were likely underestimated because the synergism from individual PCMs or other coexisting contaminants was not taken into account during the risk assessment (Wang et al., 2009; Zhang et al., 2020). Third, the toxicity data and exposure parameters were obtained from other studies rather than from experimental or observed values. Additionally, factors such as the bioaccumulation, absorptivity, and biodegradation of these chemicals in aquatic species also bring uncertainty into risk assessment (Guo et al., 2013). Therefore, more investigations are needed to fully understand the ecological risks of PCMs in the catchment of Chaohu Lake.

Conclusion

In the present study, AHTN, HHCB, and HHCB-lactone in the surface sediments of Chaohu Lake and six of its tributary rivers were determined to explore the occurrence and spatial distributions of these PCMs in the catchment of the lake. The PCM levels in the catchment were comparable to those reported in sediments from various areas worldwide. High PCM levels were detected in the sediment from the Nanfei River, which is close to Hefei city. The diagnostic results for the ratios of HHCB/AHTN and HHCB-lactone/HHCB indicated that the occurrences of AHTN, HHCB, and HHCB-lactone in the sediments were linked directly to the emission of municipal sewage and industrial wastewater from the adjacent city or to point input sources. Although various environmental factors and WWTP processes can affect source identification and transformation process identification for PCMs, the EF analysis in this study indicated that the HHCB-lactone in sediment originated from the natural degradation of HHCB in the rivers and the lake rather than from degradation in WWTPs. The ecological risk assessment indicated that the PCMs in the investigated sediments pose minimal risk to aquatic species. However, more investigations of the ecological risks of PCMs are needed because various factors in this study produced uncertainties.

Supplementary information

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