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Enantiomeric composition of polycyclic musks in sediments from the Pearl River and Suzhou Creek

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Abstract Due to differences in stereostructure, enantiomeric compositions and enantiomeric ratios (ERs) of chiral compounds can be used to discriminate environmental processes such as abiotic and biotic degradation/transformation. In this study, the ERs of two chiral polycyclic musks, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), were investigated in the sediments of Zhujiang River and Dongjiang River in the Pearl River Delta (PRD), as well as in those of Suzhou Creek in Shanghai City. The results indicated that ER_{cis} of HHCB varied significantly, ranging from 1.09 to 1.53 and 1.40 to 1.48 in the PRD and Suzhou Creek samples, respectively, whereas ER_{trans} of HHCB exhibited limited variation, ranging from 0.98 to 1.10 and 0.98 to 1.05 for Pearl River and Suzhou Creek samples, respectively. In addition, ERs of AHTN varied substantially from 1.10 to 1.34 and 1.17 to 1.28 in the PRD and Suzhou Creek, respectively. These results suggest that HHCB in the sediment in the study area underwent biotic degradation and the preferential biotransformation isomer was (4*R*,7*S*)-HHCB, while AHTN simultaneously underwent a certain degree of biotic degradation/transformation.

Keywords Polycyclic musks · HHCB · AHTN · Enantiomeric composition · Biotic transformation · Sediment

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Introduction

Polycyclic musks containing 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) as the main components are widely used fragrance materials in cosmetics and household products, such as perfume, body lotion, shampoo, and detergent. After application, these compounds are generally discharged into domestic sewage systems or directly into receiving water. During the wastewater treatment procedure, about 30–95 % of polycyclic musks are removed depending on the treatment technology and operation parameters of the respective wastewater treatment plants (WWTPs), after which they are released via effluents into the aquatic environment at nanogram per liter levels, leading to elevated concentrations in receiving water (Bester 2005; Reiner et al. 2007; Zeng et al. 2007; Reif et al. 2008; Moldovan et al. 2009; Zhou et al. 2009; Sumner et al. 2010). Currently, polycyclic musks are frequently detected in various environmental media including water, sediment, sludge, biota, and human breast milk (Wan et al. 2007; Lignell et al. 2008; Shek et al. 2008; Hutter et al. 2009; Moldovan et al. 2009; Schiavone et al. 2009).

Due to their continuous discharge and potential toxicity (Schreurs et al. 2004; Lapworth et al. 2012), environmental polycyclic musks have been investigated for their persistence, degradation, and potential ecological risk to aquatic life (Carballa et al. 2007). However, there have been some

conflicting results. For example, some researchers found that HHCB and AHTN were preferentially adsorbed by soil or sludge without microbial degradation taking place for weeks to months (Litz et al. 2007; Chen et al. 2009), while Martin et al. (2007) reported that HHCB and AHTN could be transformed into polar metabolites via soil- and sediment-containing microcosms. Ternes et al. (2007) also observed that HHCB and AHTN were sorbed or transformed in the top soil layer following irrigation of arable land with treated wastewater. Therefore, it is necessary to further clarify which process (sorption, abiotic or biotic transformation) controls the fate of polycyclic musks in the aquatic environment.

AHTN and HHCB are chiral chemicals (see Fig. 1), sold and added into cosmetic and household products as racemic mixtures (Vetter and Bester 2006). As we know, the enantiomers of chiral chemicals have identical physicochemical properties, and abiotic processes such as sorption and abiotic transformation are generally identical for both enantiomers. However, biotic processes involving enzymes and biological receptors may differ among stereoisomers. Thus, enantiomeric ratios (ERs) of chiral chemicals can be used to discriminate environmental processes such as abiotic and biotic degradation/transformation (Wong 2006). Furthermore, ERs also could provide insight into the source, process, and ultra-fate of chiral chemicals, as well as precise data for risk assessment (Hühnerfuss et al. 2004). For HHCB and AHTN, previous studies indicated that enantiomer selective degradation in WWTPs or selective bioaccumulation into aquatic organisms was observed (Franke et al. 1999; Berset et al. 2004; Bester 2005); however, limited information is available regarding their selective degradation or transformation in riverine environments.

In our previous studies, we investigated the concentration and distribution of six polycyclic musks in sediments

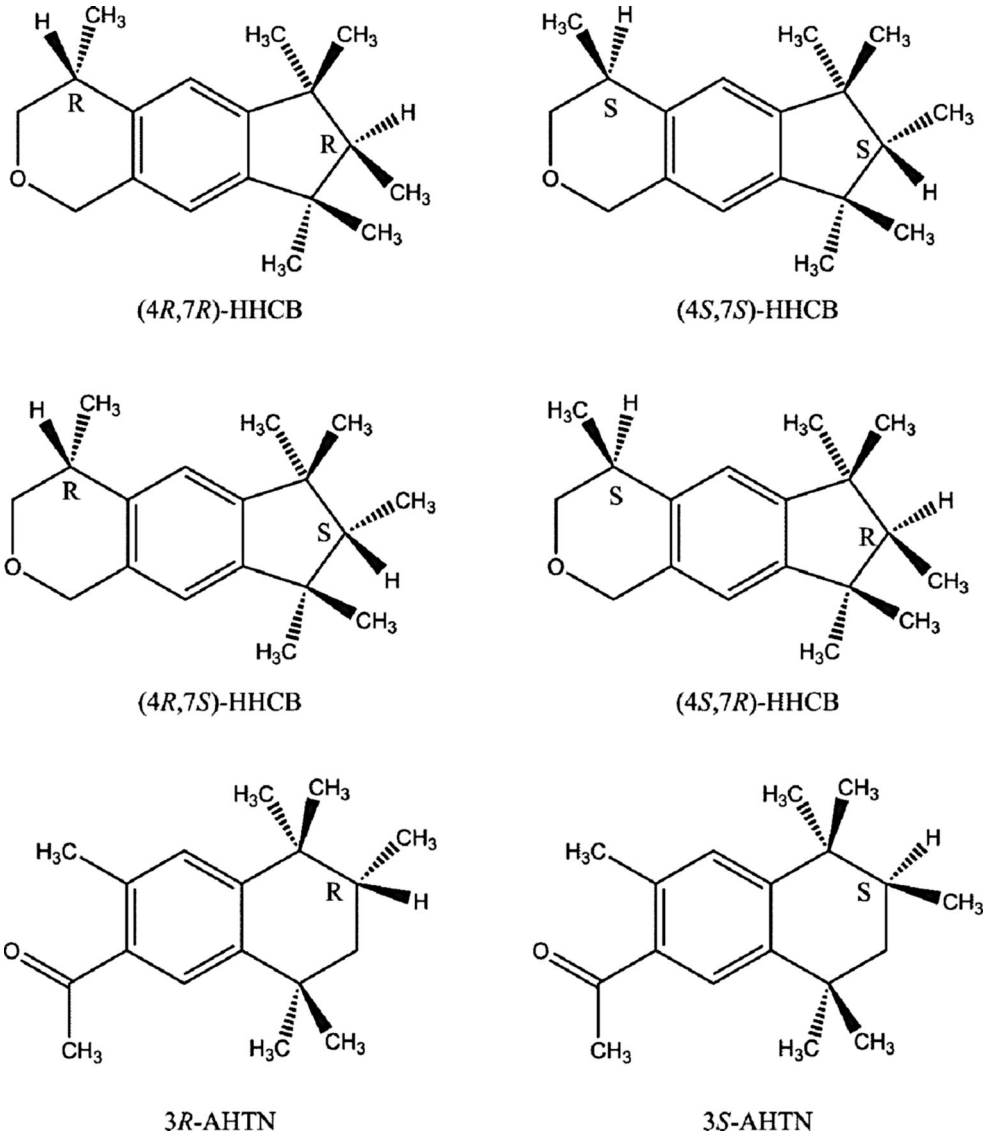

Fig. 1 Stereoisomers of HHCB and AHTN

collected from the Pearl River Delta (PRD) (Zeng et al. 2008a) and Suzhou Creek in Shanghai (Zeng et al. 2008b) and found that HHCB and AHTN were the main components of polycyclic musks in the studied area. The present study was conducted to measure the enantiomeric composition of HHCB and AHTN, as well as the ratios of isomers in the aforementioned samples to provide useful information regarding their source and degradation during transportation along rivers.

Materials and methods

Chemicals, reagents, and sample information

Two polycyclic musks, AHTN and HHCB, were purchased from LGC Promochem (Wesel, Germany). The internal standard hexamethylbenzene (HMB) was acquired from Ehrenstofer-Schäfer-Bgm-Schlosser (Augsburg, Germany). Analytical grade dichloromethane (DCM) and *n*-hexane were purchased from Damao Chemical Reagent Factory (Tianjin, China) and redistilled using a glass system before use. Two commercial HHCB (HHCB-A and HHCB-B) samples and one AHTN sample were kindly provided by a retailer in Guangzhou (China).

The sediment samples investigated in the present study include those from the PRD (Zhujiang River and Dongjiang River) and Suzhou Creek in Shanghai. The Pearl River, which is the second largest river in China, is located in South China and consists of a large number of plumes, with the Zhujiang, Dongjiang, and Xijiang rivers as its main tributaries. Among these, the Zhujiang River drains through the densely populated metropolis Guangzhou, while the Dongjiang River runs across a newly developing city, Dongguan, and the Xijiang River runs through an extensive agricultural region that is not heavily populated. The concentrations and distribution of six polycyclic musks in 20 sediment samples collected in the PRD were discussed previously. Due to the direct/indirect discharge of domestic and industrial wastewater, higher levels of HHCB and AHTN (∑HA) were detected in Zhujiang (51.2–163.4 μg kg^{-1}) and Dongjiang (7.1–59.9 μg kg^{-1}) than in Xijiang (5.8–7.0 μg kg^{-1}) (Zeng et al. 2008a).

Suzhou Creek is an important tributary of the Huangpu River that runs through the densely populated and highly urbanized Shanghai City. This creek has received a large amount of untreated domestic wastewater from along the river for more than 100 years. Nine sediment samples from the upstream to the downstream portion of this river were collected and analyzed for the levels and distribution of six polycyclic musks, and the results revealed increasing levels of HHCB (56.9–552.1 μg kg^{-1}) and AHTN (25.8–117.3 μg kg^{-1}) from the upper reach to the lower reach, which was likely due to the continuous wastewater discharge (Zeng et al. 2008b).

Further information about the sediment collection, extraction and separation, determination, and quantification analysis of the polycyclic musks measured in the Pearl River Delta is available elsewhere (Zeng et al. 2008a). The occurrence and distributions of polycyclic musks in Suzhou Creek were published in Chinese with an English abstract (Zeng et al. 2008b). Herein, a brief description is provided as follows: A total of nine sediment samples were collected from Suzhou Creek draining through Shanghai City. A top 5 cm layer was scooped using a precleaned Van Veen stainless steel grab into solvent-rinsed aluminum containers and was kept at −20 °C until analysis. Regarding the extraction, separation, and determination, please refer to Zeng et al. (2008a). The detailed recoveries of HHCB and AHTN are available in the supplementary data (Table S1).

In the present study, the enantiomeric compositions of HHCB and AHTN as well as the ERs in the sediment from Zhujiang River, Dongjiang River, and Suzhou Creek were discussed. Xijiang River was excluded because it contained lower concentrations of polycyclic musks in the sediment. The results were then used to investigate the potential biological transformation and/or degradation in the sediment of these rivers.

Enantioselective GC-MS

Identification and quantification of HHCB isomers and AHTN isomers were carried out using a Shimadzu 2010 gas chromatograph (Shimadzu Corporation, Tokyo, Japan) equipped with a quadrupole mass spectrometer in EI mode. For analysis, a Cyclosil chiral chromatography column (30 m length, 0.25 mm I.D.×0.2 μm film thickness) coated with a film of 50 % heptakis-(2,3-di-*O*-methyl-6-*O*-butyldimethylsilyl)-β-cyclodextrin in DB-1701 custom made by J&W Scientific (Agilent Technologies, Folsom, CA, USA) according to Franke et al. (1999) was used. During the analysis, the initial temperature was 110 °C, which was held for 1 min, after which it was raised to 140 °C at 5 °C/min, where it was held for 120 min, and then further increased to 190 °C at 0.7 °C/min and 230 °C at 5 °C/min, where it was held for 10 min. During the analysis, high purity He (99.999 %, provided by Guangzhou West City Industrial and Equipment Co., Guangzhou, China) was used as carrier gas at 1.1 mL/min, the injection was conducted at 180 °C using splitless mode, and the transfer line was set at 210 °C due to the temperature limit of the column being 230 °C. Quantification ion (*m*/*z*) and verification ion (*m*/*z*) for the analytes were 243 and 258, respectively. Under the specific chromatography conditions, the enantiomers of AHTN and enantiomers and diastereomers of HHCB were separated. Also, the elution order was confirmed according to those reported from references (Franke

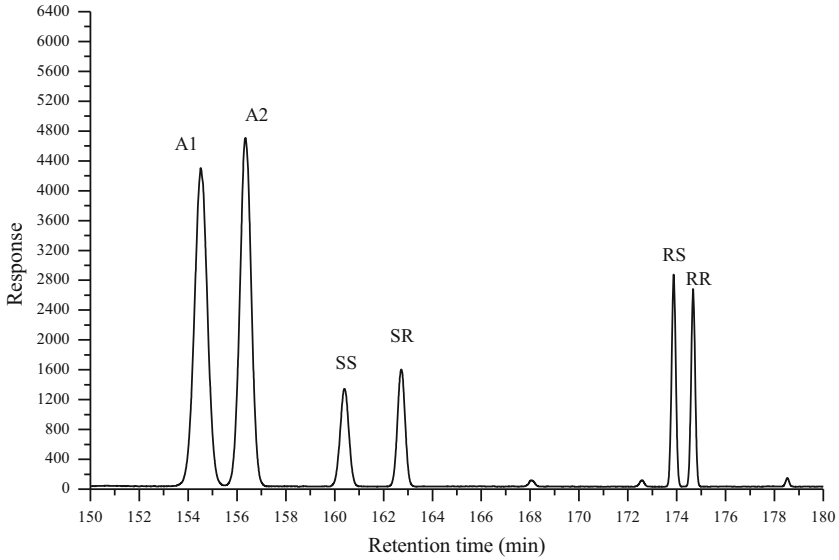

Fig. 2 Enantiomeric separation of HHCB and AHTN. *SS*: (4*S*,7*S*-HHCB), *SR*: (4*S*,7*R*-HHCB), *RS*: (4*R*,7*S*-HHCB), *RR*: (4*R*,7*R*-HHCB)

et al. 1999; Berset et al. 2004). The elution order was as follows: (4*S*,7*S*)-HHCB, (4*S*,7*R*)-HHCB, (4*R*,7*S*)-HHCB, and (4*R*,7*R*)-HHCB. Two isomers of AHTN were assigned as A_1 and A_2 according to the elution order of the standard (Fig. 2).

Quality control and quality assurance

Due to the effect of coating materials on the chiral chromatography column, the permitted column temperature of 250 °C as recommended by the manufacturer was observed; therefore, the temperature program was finished at 230 °C in our enantiomeric analysis. Consequently, partial interference with high molecular weight and low volatility might not be eluted and retained in the chiral column, resulting in decreasing column efficiency. In order to avoid ER variation originating from the decrease of column efficiency during analysis, a standard solution of HHCB and AHTN was analyzed as a quality control sample in every six sediment samples, and every sample was analyzed twice. And the ERs of HHCB

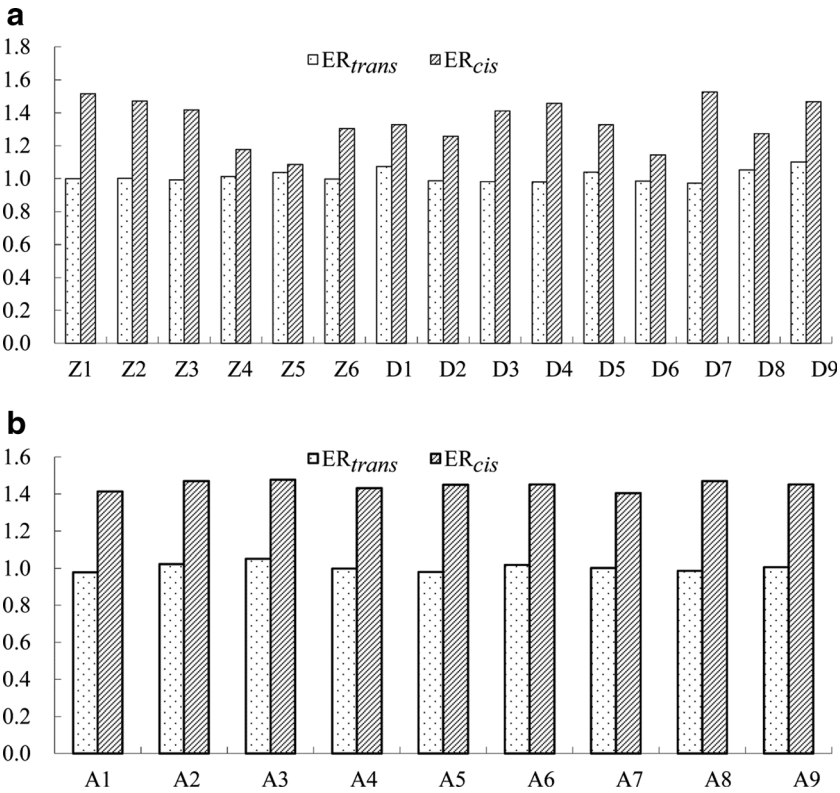

Fig. 3 Variations of ER_{trans} and ER_{cis} of HHCB in sediments from Zhujiang River and Dongjiang River (**a**) and from Suzhou Creek (**b**)

and AHTN during the sample extraction and cleanup were also determined using a standard spiked experiment. The results indicated that there were no ER variations in the whole sample pretreatment procedure.

Results and discussion

The enantiomeric ratios of commercial HHCB and AHTN

When using enantiomeric compositions (ERs) of chiral chemicals to discuss their environmental degradation or transformation, it is important to know the ERs of the commercial product. As shown in Fig. 1, chiral HHCB has two diastereomeric enantiomeric pairs. The ERs of (4*S*,7*R*)- vs (4*R*,7*S*)-HHCB were denoted as ER_{cis}, whereas the ERs of (4*S*,7*S*)- vs (4*R*,7*R*)-HHCB were denoted as ER_{trans}. AHTN has only one enantiomeric isomer pair, which was defined as ER_{AHTN}.

In this study, we first analyzed the ERs of two commercial HHCB products and one AHTN obtained from a Guangzhou market. The results indicated that the ER_{cis} values were about 1.00 and 1.02 for the two commercial products, respectively, whereas the ER_{trans} values were 0.99 and 1.01, respectively. Simultaneously, ER_{AHTN} was 1.00. These results were similar to those of previously reported studies. For example, Berset et al. (2004) found that ER_{trans} and ER_{cis} of HHCB and ER of AHTN were all close to 1.00.

The ERs of HHCB in sediments and potential biodegradation

The ER_{trans} of HHCB was calculated based on the measured enantiomeric compositions. Figure 3 shows the profile of ER_{trans} of HHCB in the PRD (Fig. 3a) and in Suzhou Creek from Shanghai (Fig. 3b). As shown in Fig. 3a, the ER_{trans} of HHCB in sediments from Zhujiang River ranged from 0.99 to 1.04 (1.01±0.02), with a relative standard deviation (RSD) of 1.65 %. The ER_{trans} of HHCB measured in Dongjiang River ranged from 0.98 to 1.10 (1.02±0.05) with a RSD of 4.71 %. All ER_{trans} values of HHCB in the sediments in the PRD were close to 1. A similar trend was observed in Suzhou Creek. Specifically, the ER_{trans} of HHCB in Suzhou Creek ranged from 0.98 to 1.05 (1.00±0.02) with a RSD of 2.46 %. When the ER_{trans} of sedimentary HHCB was compared with those of commercial products, there was no significant difference ($P>0.1$). As proposed by Berset et al., an ER close to that of commercial racemic (ER≈1) indicates a low transformation potential for a system, whereas an ER that differs from 1 may indicate enantioselective transformation (Berset et al. 2004). These findings imply that limited enantioselective transformation exists between (4*S*,7*S*)-HHCB and (4*R*,7*R*)-HHCB in the riverine systems evaluated in this study.

Conversely, the ER_{cis} of sediments from Zhujiang River (1.09–1.52), Dongjiang River (1.14–1.53), and Suzhou Creek (1.40–1.48) obviously deviated from the ER (≈1) of commercial products. Furthermore, the ER_{cis} values were somewhat different in these sediment samples. For example, ER_{cis} in Zhujiang River changed significantly from 1.09 to 1.52 with an average value of 1.33±0.17 and 12.84 % RSD, especially that of HHCB in samples (Z1–Z3), located in the upper channel of Zhujiang in Guangzhou, changed from 1.42 to 1.52, while it changed from 1.09 to 1.33 in samples (Z4–Z6) collected from the lower channel of Zhujiang (the Shiziyang River), which was far from Guangzhou and heavily affected by the less contaminated water from the northern watershed of the Dongjiang River and inflow of strong tidal flushes from the PRD estuary (Zeng et al. 2008a). The ER_{cis} of HHCB

Table 1 Concentrations of HHCB and AHTN as well as ERs of HHCB and AHTN measured in sediments from Pearl River and Suzhou Creek

Samples	Concentrations[a]		ERs[b]		
	HHCB	AHTN	ER_{trans}	ER_{cis}	ER_{AHTN}
D1	6.9	6.3	1.07	1.33	1.10
D2	12.9	6.7	0.99	1.26	1.13
D3	11.7	6.2	0.98	1.41	1.20
D4	48.6	11.2	0.98	1.46	1.22
D5	5.7	5.7	1.04	1.33	1.19
D6	13.1	8.8	0.99	1.14	1.12
D7	5.1	4.4	0.97	1.53	1.25
D8	3.6	3.5	1.05	1.27	1.27
D9	9.8	9.2	1.10	1.47	1.21
Z1	121	42.5	1.00	1.52	1.26
Z2	33.5	17.7	1.00	1.47	1.30
Z3	58.5	25.7	0.99	1.42	1.22
Z4	4.5	4.5	1.01	1.18	1.34
Z5	3.3	3.6	1.04	1.09	1.27
Z6	3.5	3.8	1.00	1.30	1.29
A1	436.0	92.9	0.98	1.41	1.21
A2	338.3	75.7	1.02	1.47	1.17
A3	552.1	117.3	1.05	1.48	1.22
A4	221.5	55.3	1.00	1.43	1.24
A5	282.8	69.7	0.98	1.45	1.26
A6	68.8	28.8	1.02	1.45	1.28
A7	56.9	25.8	0.92	1.41	1.27
A8	149.1	41.9	0.99	1.47	1.28
A9	78.7	30.3	1.01	1.45	1.26

[a] Concentrations of HHCB and AHTN in sediments from Pearl River and Suzhou Creek were reported in our previous studies (Zeng et al. 2008a, b), which were measured by GC-MS using DB-5MS (Agilent Technologies, 30 m length, 0.25 mm I.D., 0.25 μm film thickness)

[b] ERs were measured and calculated in the present study, and a Cyclosil chiral chromatography column (30 m×length, 0.25 mm I.D., 0.2 μm film thickness) was used

ranged from 1.14 to 1.53 (mean value 1.36±0.12) with a RSD of 8.97 % in sediments from the Dongjiang River. A lower ER_{cis} (1.14) was observed at sample site D6, which is located upstream of the Dongjiang River, while the highest ER_{cis} (1.53) was detected at site D7, in the city of Dongguan. However, the ER_{cis} value ranged from 1.41 to 1.48 (mean= 1.45±0.03) with a RSD of 1.76 % in Suzhou Creek. No significant difference was observed among the samples with increasing concentrations of HHCB along the river (Table 1).

These observed phenomena were partially similar to those of previous studies. Berset et al. (2004) also found that HHCB in sludge samples exhibited enantioselective transformation, with one sludge having ER_{trans} deviation and the other three sludges having ER_{cis} deviation. In our study, significantly different ER_{cis} deviations were observed in all sediment samples, suggesting that (4*R*,7*S*)-HHCB was more prone to biological degradation or transformation than its racemic isomer in the studied riverine system. These results are also supported by Bester (2005), who observed obvious microbial degradation in *cis*-HHCB isomers based on the ERs determined for HHCB-lactone.

Another interesting observation is that ER_{cis} in our study exhibited greater variation than previously reported. If the entire study area had no wastewater discharge or HHCB emission source, the different ER_{cis} values might reveal a certain degree of biological degradation or transformation related to the different microflora in the sediment. Several experiments have already verified that HHCB was biotransformed in the environment and that microbial species and natural redox mediators in particular environments were all important factors affecting its degradation/transformation efficiencies and metabolites (Balk and Ford 1999; Martin et al. 2007). Our sample areas were located across cities including Guangzhou and Dongguan, indicating that there might be new discharges and sources that diluted the ER_{cis} variation.

The variation of ER_{AHTN} and possible biodegradation

The ER_{AHTN} values measured in the Pearl River Delta (Zhujiang River and Dongjiang River) and Suzhou Creek are shown in panels a and b of Fig. 4, respectively. As shown in Fig. 4, the ER_{AHTN} values in sediment samples changed from 1.22 to 1.34 (1.28±0.04, 3.18 % RSD) in Zhujiang River and from 1.10 to 1.27 (1.18±0.06, 5.36 % RSD) in Dongjiang River. In addition, the values changed from 1.17 to 1.28 (1.24±0.04) with 2.99 % RSD in Suzhou Creek. These results indicated that all ER_{AHTN} values measured in the present study deviated from 1, which was measured in the commercial product, suggesting that enantioselective biological degradation/transformation exists in the studied riverine system (Berset et al. 2004; Valdersnes et al. 2006; Martin et al. 2007).

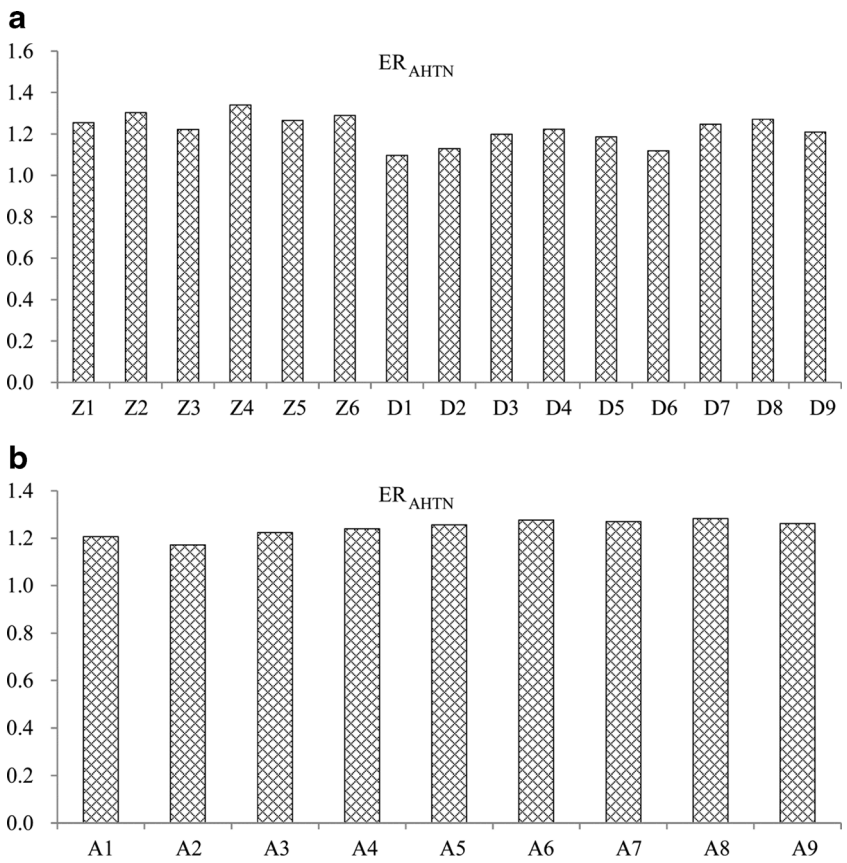

Fig. 4 Variations of ERs of AHTN in sediments from Zhujiang River and Dongjiang River (**a**) and from Suzhou Creek (**b**)

To date, different results of AHTN transformation in sediment and biota samples have been reported. For instance, several studies indicated that abiotic processes played a dominant role in the elimination of AHTN in the environment, with photodegradation exerting an important influence (Buerge et al. 2003; Bester 2005). Valdersnes et al. (2006) also detected several AHTN transformation products in human milk samples and fish samples, implying the probability of degradation/transformation of AHTN in organisms without involving enantioselective variation. However, Martin et al. (2007) found that AHTN was biologically degraded/transformed into different metabolites with different efficiencies depending on specific fungi inhabiting the upper layers of the sediments, which implied the biodegradability of AHTN in aquatic environments. In our study, we observed statistically enantioselective biotransformation of AHTN in sediments from both the PRD riverine system and Suzhou Creek. Another interesting phenomenon is that the ERs of AHTN were significantly larger than those of $HHCB_{trans}$. This might be explained by the different half-lives of AHTN and HHCB. Based on his field observations, Bester (2005) reported that the half-life (as in-river half-life) was 15 days for AHTN and 67 days for HHCB. As a result, AHTN has less opportunity for biotransformation when compared with HHCB in the river system. Although several studies reported the biotransformation of HHCB and AHTN in the sediment (Martin et al. 2007), in biota samples and human milk (Valdersnes et al. 2006), however, limited information is available about their enantioselective biotransformation/degradation. Therefore, further studies are needed to clarify the biodegradation mechanism, which is essential to ecological risk assessment of AHTN.

Conclusion

Generally, due to their interaction with enzymes or other naturally occurring chiral molecules, enantiomers of chiral pollutants exhibit different biological properties and undergo distinctive microbial degradation/transformation, resulting in variation of the enantiomer ratios; consequently, we can discriminate biotic and abiotic processes of chiral compounds based on changes in ERs. In the present study, significant changes of ER_{cis} of HHCB were measured in sediments from Zhujiang River, Dongjiang River, and Suzhou Creek, indicating an enantioselective degradation/transformation of HHCB with preferential degradation/biotransformation for (4*R*,7*S*)-HHCB over its enantiomer (4*S*,7*R*)-HHCB. Conversely, ER_{trans} measured in these rivers was approximately 1, implying that limited enantioselective transformation occurs during transportation in rivers. In the case of AHTN, deviation of ER_{AHTN} values considerably from 1 might suggest that biotic degradation/transformation occurred in sediments from the studied riverine system.

Numerous organic contaminants have been reported to be more persistent and/or more toxic than their parent compounds; thus, it is crucial to obtain integrated information regarding the environmental levels, degradation/transformation and bioaccumulation of certain compounds as well as their toxic data to enable risk assessment. In the present study, no transformation products of HHCB and AHTN were analyzed owing to the absence of relative standards. Accordingly, further studies promoting insight into the fate of these materials are warranted.

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