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Occurrence and distribution of synthetic musks and organic UV filters from riverine and coastal sediments in the Pearl River estuary of China

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ABSTRACT

This study reports the occurrence and distribution of synthetic musks (SMs) and organic UV filters (UVFs) in sediment samples collected in 8 riverine runoffs from the Pearl River and Pearl River estuary (PRE). Here, 6 of the 8 target compounds were detected in all sediment samples with concentrations ranging from 0.35 ng g⁻¹ to 456 ng g⁻¹. Higher concentrations of SMs and UVFs were evident in the eastern outlets compared to the western outlets suggesting greater input of these contaminants from the Pearl River Delta (PRD) region. Amongst the SMs, tonalide (AHTN) and galaxolide (HHCB) are the 2 predominant polycyclic musks found in all sediment samples with a high correlation between them suggesting that the sources and exposure pathway of HHCB and AHTN are similar. In general, all the compounds showed a decreasing trend toward the seaward side of the PRE toward the South

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China Sea (SCS) confirming that it was the most important source of riverine runoff. Notably, high levels of SMs and UVFs were detected in two fishing harbors in the PRE area. In comparison to UVFs, the SM compounds showed a significant correlation with total organic carbon (TOC) content in the sediments.

Keywords: Synthetic musks; UV filters; Sediment; Riverine runoff; Pearl River estuary; Ecological risks

1. Introduction

Synthetic musks (SMs) and organic UV filters (UVFs) are new types of emerging pollutants in the environment that have raised significant concerns in recent years due to their potential threat to the ecological environment and human health (Fromme et al., 2001; Ramos et al., 2015). SMs are widely used by perfume industries as fragrance additives in a variety of consumer products (e.g., perfumes, lotions, sunscreens, shampoos, and laundry detergents) (Reiner and Kannan, 2011; Roosens et al., 2007; Zhang et al., 2008). UVFs are included in various pharmaceutical and personal care products (PPCPs) including body washes, sunscreens, and cosmetic products mainly to protect the skin against ultraviolet radiation (Nakata et al., 2012; Ramos et al., 2015). They are also included in plastics and furniture primarily for photo-protective purposes.

After application, both SMs and UVFs are generally discharged into sewage treatment plants (STP) or directly into the aquatic environment. However, a number of studies have shown that these compounds are incompletely removed during the
treatment at the STPs and do not biodegrade in the environment (Chase et al., 2012; Clara et al., 2011; Tsui et al., 2014a). Consequently, these compounds ultimately enter the aquatic environment and accumulate in various environmental matrices. During the past decade, several studies have documented the presence of SMs and UVFs in rivers, lakes, groundwater, estuaries, and coastal oceans with concentrations up to μg g⁻¹ levels (Bu et al., 2013; Guo et al., 2013; Kameda et al., 2011; Langford et al., 2015; Nakata et al., 2007; Ramos et al., 2015; Tsui et al., 2014b). In addition, due to their relatively low solubility and high octanol-water partition coefficient (K_{ow}), SMs and UVFs are easily absorbed by particulate matter and eventually accumulate in river sediment (Amine et al., 2012; Ramos et al., 2015; Subedi et al., 2014). These compounds can also be bio-accumulated in organisms at different trophic levels (Fent et al., 2010; Gago-Ferrero et al., 2015; Nakata et al., 2007). Oceans and coastal zones, act as reservoirs for many contaminants that originate from various sources. Riverine and marine sediments represent the final repository of SMs and UVFs compounds due to their sportive nature and may play a key role as potential sources of these contaminants. The Pearl River Delta (PRD) is one of the most developed and urbanized areas in China, connecting the Pearl River estuary (PRE) to the South China Sea (SCS) via 8 major riverine runoff outlets (Fig.1). It was estimated that about 1.73 ×10^{10} t per year of wastewater are discharged from the PRD into the PRE and the SCS. However, hardly any data are available regarding the occurrence and distribution of SMs and UVFs in sediments of the Pearl River and coastal environment (Chen et al., 2012; Zeng et al., 2008). In order to understand and
assess the impact of increased anthropogenic activities on the coastal environments of the PRD region, the present study investigated the occurrence and spatial distribution of 4 commonly consumed SMs, as well as 3 different UV-F compounds in river and marine sediment samples collected in the Pearl River and the coast of PRE.

2. Methods and materials

2.1 Reagents and materials

In this study, 5 SMs [including tonalide (AHTN), galaxolide (HHCB), celestolide (ADBI), phantolide (AHMI), musk ketone (MK)], and 3 UVFs [including 4-methylbenzylidene camphor (4-MBC), octocrylene (OC) and octyl-p-methoxycinnamate (OMC)] were selected. Standards (≥98%) were purchased from Sigma-Aldrich, Germany. All organic solvents used were of analytical grade and redistilled using glass system. Laboratory glassware was baked at 250°C for 12 h and then rinsed with acetone and n-hexane. Neutral silica gel (80-100 mesh) and anhydrous sodium sulfate were cleaned with dichloromethane (DCM) using MX-Soxhlet extractor for 24 h and then baked at 450°C for 12 h. Silica gel was deactivated with 10% (w:w) of precleaned deionized water (extracted with DCM).

2.2 Samples collection

The Pearl River is the largest and most complex water system in the South China. It has a catchment area of more than 450,000 km², with an annual mean runoff volume of 326 billion m³. The river water finally enters the SCS via 8
major outlets that include Humen (HM), Jiaomen (JM), Hongqilimen (HQ), Hengmen (HE) on the eastern side, and Modaomen (MD), Jitimen (JT), Hutiaomen (HT), and Yamen (YM) on the western side (Fig.1). Detailed information of the 8 outlets has been previously described (Xu et al., 2013). Surface sediment samples (≤10 cm) from the 8 outlets were collected in 2010 using a stainless steel grab. A total of 16 sediment samples in the PRE and 6 sediment samples from 2 fishing harbors (Shenzhen and Zhuhai) were also collected during the same period. Detailed information on sampling locations is shown in Fig.1. All the samples were placed into polytetrafluoroethylene bags and immediately stored at -20 °C.

2.3 Samples preparation and extraction

The collected sediment samples were freeze-dried at -20 °C and ground into powder using an agate pestle and mortar. Briefly, the sediment samples (10.0 g) were extracted with DCM for 16 h at a flow rate of 5 ml min⁻¹ using MX-Soxhlet extractor. Before extraction, 10 µl of 500 pg µl⁻¹ surrogate standards was added to monitor the recovery and approximately 1.0 gram of activated copper granules was added to remove elemental sulfur. Extracts were evaporated down to 1–2 mL using hexane as keeper and further cleaned on a silica column (2.5 g, 10 % water deactivated) topped with 3 g anhydrous granulated sodium sulfate. The extract was then purified by eluting with 15 mL hexane (fraction 1) followed by 20 mL DCM/acetone (1:1, V/V) (fraction 2). Fraction 2 was concentrated down to 200 µL by roti-evaporation and
nitrogen blower. Then, 10 micro litters of 50 pg $^{13}$C$_6$-PCB 208 (Cambridge Isotope
Laboratories) was added as injection standard.

2.4 Compounds analysis

The samples were analyzed with an Agilent 6890N gas chromatography coupled to
an Agilent 5973 mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA,
USA), operating in electron impact and selective ion monitoring modes (SIM). An
HP-5MS capillary column (J&W Scientific, 30 m×250 μm i.d., 0.25 μm film
thickness) was employed. The transfer line and the ion source temperature were
maintained at 280 °C and 230°C, respectively. The temperature of the oven was
initiated at 60 °C for 1.0 min, increased to 180 °C at a rate of 30 °C min$^{-1}$, and
ramped at 2 °C min$^{-1}$ to 300 °C and held for 10 min. The flow rate of the carrier gas
helium was kept constant at 1.3 mL min$^{-1}$. The extracts (1.0 μL) were injected onto
GC-MS in pulsed splitless mode with an inlet temperature program as following:
60 °C for 0.1 min, increased to 280 °C at a rate of 300°C min$^{-1}$ and held for 10 min.
Quantitation was performed using the internal calibration method based on a 9-point
calibration curve.

2.5 Quality control and quality assurance

Extraction efficiency was checked with 5 sediment samples that were twice
extraction, which showed that the proportion of target compounds in the first
extraction ranged from 70 ± 12% to 99 ± 1% for SMs and 95 ± 3% to 99 ± 0.4% for
UVFs. Matrix spiked recoveries ranged from 70% to 90%. Instrumental detection limits using the present methods were calculated by signal to noise ratio of 3 and ranged from 1 to 4 pg. The method detection limits (MDLs) were derived from the procedural blanks and quantified as mean field blanks plus three times the standard deviation (3σ) of field blanks. Four procedural blanks were extracted together with the samples. The procedural blanks were 0.02-0.06 ng g\(^{-1}\) for SMs, and 0.01-0.17 ng g\(^{-1}\) for UVFs, which account < 1% of those in the sediment samples. The results reported in this work were not corrected with a procedural blank.

3. Results and discussion

3.1 Concentration and distribution of SMs and UVFs in the riverine outlets

The total concentration of SMs in surface sediment samples from the 8 outlets ranged from 11.4 to 54.6 ng g\(^{-1}\) with an average of 33.5 ng g\(^{-1}\) (Table 1). Among the 5 SMs, the 2 polycyclic musks, HHCB and AHTN, were the predominant compounds with concentrations ranging from 4.54 to 31.5 ng g\(^{-1}\). Correspondingly, ADBI and AHMI were below the MDLs in all the samples. Although MK was observed in all the surface sediment samples, its exposure level was slightly higher than MDL. This is not unusual as nitro musk compounds were known to be gradually replaced by polycyclic musks due to their toxicological effects since the 1990s (Nakata et al., 2007; Sommer, 2004). The elevated levels and detection frequencies of HHCB and AHTN depended primarily on the high consumption of polycyclic musks and their relative persistence in the natural environment. The worldwide production of
polycyclic musks was up by 5600 t in 1996 (Reiner and Kannan, 2006). HHCB and AHTN occupy 90–95% of the total production. The consumption pattern of SMs in China was similar to most other countries. In addition, the higher lipophilic and hydrophobic properties of AHTN and HHCB compared to MK also contributed to their exposure in different environments.

Out of the 3 UVFs, OMC and OC showed 100% detection frequencies in the 8 outlets with maximum concentrations of <105 ng g\(^{-1}\) (Table 1). In terms of composition profile, OMC was the most ubiquitous compound accounting for almost 70% of the total UV filters probably due to the high usage in various personal care products as well as in cosmetics, indicating its ubiquitous occurrence in the marine environment (Kameda et al., 2011; Tsui et al., 2014b). In general, the mean concentration of OMC was 2 times higher than OC. 4-MBC showed low detection frequencies (50%) in sediment as well as low occurrence with the highest concentration reaching up to 3.1 ng g\(^{-1}\) that was likely due to the relatively lower application rates in products (Ramos et al., 2015). The use of 4-MBC had been forbidden in cosmetics as an ingredient in Japan and many other countries (Tsui et al., 2015).

With regard to spatial variation, both the SMs and UFVs in the Eastern outlets were generally higher than those in the western outlets; this was consistent with the other observations on antibiotics and persistent organic pollutants (Wang et al., 2007; Xu et al., 2013). It was clear that both the SMs and UFVs in the Pearl River system were derived primarily from a large amount of municipal sewage and industrial wastewater.
discharged from the cities in the river basin. This was expected as the eastern outlets
and their upper reaches are all located in the PRD region, one of the most densely
populated and highly polluted areas in China. HM and JM outlets showed relatively
higher contaminations. This was probably due to the fact that watercourses draining
into the HM outlet run through several large urban areas, including Guangzhou and
Dongguan. JM outlet runs through the large city of Zhongshan and several large-scale
agricultural farms.

3.2 Concentration and distribution of SMs and UVFs in the PRE and fishing harbors

HHCB, AHTN, OMC, and OC were the 4 dominant compounds found in
sediments from the PRE with 100% detection frequencies, which was consistent with
those in the 8 outlets suggesting that riverine runoff acts as a key source of SMs and
UVFs (Table 1). The concentration range of HHCB and AHTN was 4.55-27.1 ng g\(^{-1}\)
and 1.89-13.6 ng g\(^{-1}\) with a mean of 13.3 ng g\(^{-1}\) and 7.43 ng g\(^{-1}\), respectively. In terms
of the UVFs, OMC was generally 2 times higher than OC in the sediments. The mean
concentrations of OMC and OC were 30.2 ng g\(^{-1}\) and 16.0 ng g\(^{-1}\), respectively. The
high exposure of HHCB and OMC in the PRE was consistent with most previous
studies from riverine or coastal environments which indicated their global ubiquitous
occurrence over the past 20-year period (Fromme et al., 2001; Hu et al., 2011a; Lu et
al., 2013; Nakata et al., 2007; Ramos et al., 2015; Reiner and Kannan, 2011; Tsui et
al., 2015). It is noteworthy that higher levels of SMs and UVFs were found from the 2
selected fishing harbors in the PRE. On the whole, all the selected compounds were
detected from the 2 harbors with SMs ranging in concentration from 0.2 to 273 ng g\(^{-1}\). Meanwhile, HHCB and AHTN were the 2 dominant compounds amongst the SM that were similar to those in the riverine outlets and PRE. Except for highest OC levels (551 ng g\(^{-1}\)) detected in the sediment samples, higher OMC levels of 456 ng g\(^{-1}\) from the UVF group were also found from the 2 harbors. Notably, the fishing harbor is a special water area in coastal environments with a high density of human activities that receives various contaminants from terrestrial discharge as well as fishing ships. In addition, most harbors are built in semi-close coastal regions that are likely to decrease the seawater exchange ability. As a result, these contaminants can dramatically increase in harbors' sediment. The high levels of SMs and UVFs from the fishing harbors in the PRD region were consistent with other contaminants documented in previous studies such as heavy metals and pesticides (Chen et al., 2012; Lin et al., 2009; Xu et al., 2012).

The geochemical maps of SMs and UVFs in the PRE surface sediments are presented in Fig. 2. Both SMs and UVFs generally showed a seaward decreasing trend from the PRE towards SCS, strongly confirming that riverine runoff is the most important source of these contaminants. However, OMC and OC exhibited different spatial patterns. Regarding the contaminants originating from the river, they generally displayed a northwest to southeast pattern of diffusion in the PRE due to the hydrodynamic conditions in the PRE (Li et al., 2000; Shi et al., 2010; Zhou et al., 2004). However, several hotspots for OMC and OC appeared on the eastern side of the upper PRE. These hotspots may reflect a high anthropogenic input, probably due
to the sewage discharge from the large cities along the eastern bank of the PRE, such as Shenzhen and Hong Kong.

3.3 Global comparison of SMs and UVFs in freshwater and coastal environments

During the past 2 decades, the occurrence of SMs and UVFs in water samples has been well documented. Nonetheless, there are very few studies regarding the contamination of sediments, particularly in marine environments (Lee et al., 2014; Zeng et al., 2008). Table 2 summarizes the global exposures of SMs and UVFs in sediments from both freshwater and coastal environments. Based on these limited data, HHCB and AHTN levels from the riverine outlets detected in this study were similar to those measured in the Haihe River, Songhua River, China (Hu et al., 2011a; Lu et al., 2013). However, these values were significantly lower than those detected in Hudson River, USA and Lippe River, Germany (Dsikowitzky et al., 2002; Reiner and Kannan, 2011). Sedimentary concentrations of UVFs recorded in the present study are also far lower than those in Ebro River, Spain, and some rivers and lakes in Japan (Gago-Ferrero et al., 2011; Kameda et al., 2011), which indicates that the consumption of UVFs is remarkably different among countries. Specifically, the highest concentration of OC detected in Ebro River was 2400 ng g⁻¹ (Gago-Ferrero et al., 2011). On the other hand, OMC and OC found in other rivers or lakes, such as Rhine River, Germany are comparable with or slightly lower than those detected in the outlets of the Pearl River (Baron et al., 2013; Kaiser et al., 2012; Langford et al., 2015; Rodil and Moeder, 2008). With regard to the coastal environments, SMs and
UVFs are generally both lower than those found in the rivers (Langford et al., 2015; Lee et al., 2014; Zeng et al., 2008). However, it is noteworthy that the harbors as well as some small fishing harbors had high levels of contaminants and probably acted as a point source of SMs and UVFs in coastal environments (Subedi et al., 2014; Tsui et al., 2015).

3.4 Correlation between compounds and TOC

The ratios of HHCB and AHTN in sediments have been used as a tool to trace fragrance composition in PPCPs (Dsikowitzky et al., 2002; Moldovan, 2006; Nakata et al., 2007). In this study, the ratio of HHCB and AHTN in the sediments ranged from 1.02 to 2.71 in the order of fishing harbor > riverine outlets > PRE (Fig. 3). This level is similar to those in most sediment samples from other regions such as Lippe River (<3.1), Germany (Dsikowitzky et al., 2002), Pearl River (0.72-4.33) and Haihe River (0.75-4.80), China (Hu et al., 2011a; Zeng et al., 2008) and Hudson River, USA (0.13-3.43) (Reiner and Kannan, 2011). A rather higher ratio of 16.7 was observed in Ontario Lake, USA (Peck et al., 2006). These discrepancies in HHCB/AHTN ratio probably result from variation in consumption patterns in different regions and countries, effective removal in STPs, and environmental behavior of these compounds (e.g., volatilization, degradation, and sorption). Generally, the mean ratios in sediment are lower than those in water that could be mainly explained by the higher photolysis rate in water and adsorption by sediments of AHTN (Buerge et al., 2003; Hu et al., 2011b; Nakata et al., 2012; Xie et al., 2007). Figure 3 shows that the HHCB values
were highly correlated with the AHTN values in all samples suggesting that the
sources and exposure pathway of HHCB and AHTN are similar. Significant
correlation between HHCB and AHTN was also found in sediment and wastewater
samples from other regions (Clara et al., 2011; Ekpeghere et al., 2016). Regarding the
regression lines (Fig. 3), the samples from the fishing harbors had a higher slope (0.47)
than those in riverine outlets (0.42) and PRE (0.39).

TOC content in all the sediment samples ranged from 0.25 to 2.2%. For the SM
compounds, significant correlations of HHCB (r=0.87) and AHTN (r=0.79) between
TOC were found in the samples from the riverine outlets and PRE that suggested a
common pollution source for these compounds (Fig. 4). It is interesting to note that
there was a lack of correlation between UVFs and organic carbon in all sediment
samples which was consistent with previous studies (Gago-Ferrero et al., 2011; Tsui
et al., 2015). This indicated that UV compounds are able to partition to other phases in
the aquatic environments (Tsui et al., 2015). Furthermore, the samples from the
fishing harbors exhibited rather weak correlation with TOC content for both SM and
UV compounds.

3.5 Environmental implications

This study indicated that both SMs and UVFs were ubiquitous in sediments from
the riverine and coastal environments in the PRD region. In addition, previous studies
had found SMs and UVFs in the soluble phase at different levels in this region and
other coastal environments (Grabicova et al., 2013; Hu et al., 2011a; Nakata et al.,
2012; Sumner et al., 2010; Tsui et al., 2014b). Consequently, SMs and UVFs could
have certainly accumulated in aquatic organisms and algae (Grabicova et al., 2013; Groz et al., 2014; Hu et al., 2011a, b; Nakata et al., 2009; Nakata et al., 2007; Nakata et al., 2010; Reiner and Kannan, 2011; Tsui et al., 2015). Previous studies have demonstrated that both SMs and UVFs could pose low to medium risk to aquatic organisms and environments based on HQ (hazard quotients) method (Lee et al., 2014; Sánchez Rodríguez et al., 2015). For UV compounds, previous studies have revealed that organisms at lower trophic levels were more susceptible to 4-MBC and that OMC could pose a higher risk to both cladocerans and algae (Gao et al., 2013; Sieratowicz et al., 2011). A recent study showed that OC can affect the endocrine system in zebrafish, such as hematopoiesis, blood flow, and blood vessel formation (Bluethgen et al., 2014). Oestrogenic effects and larval inhibition have been reported for synthetic musks (Dietrich and Hitzfeld, 2004; Gooding et al., 2006). Among SMs, MK generally posed a higher ecological risk than other musks due to its well-known toxicity effect, although MK’s exposure in environments is lower than others musk compounds (Lee et al., 2014; Tas et al., 1997). Notably, there is little information available on the toxic effects of MKs on marine species at present due to the fact that the most toxicity tests were conducted in freshwater systems using freshwater organisms. In addition, there is insufficient information available for SMs and UVFs in the marine benthic environment. In addition, SMs and UVFs were found in different environments as a mixture of several compounds however, the joint or synergic effects of these mixtures have yet to be quantified based on limited toxicity data. Hence, more ecotoxicological information is needed in the future for evaluation.
of the potential risks induced by these compounds in marine sediment.

4. Conclusions

SMs and UVFs concentrations are reported for riverine and coastal sediment samples collected from the Pearl River and PRE. HHCB, AHTN, OMC, and OC were the 4 predominant compounds among the SM and UVF group in accordance with previous studies. Results show a clear input pattern from the riverine outlets to the PRE and coastal environments for both SMs and UVFs. It was worth noting that high levels of SMs and UFVs were detected in 2 selected fishing harbors in the PRE area. Although it is well known that acute toxicological effects are highly unlikely at the level of SMs and UFVs detected in the present study, their ubiquitous exposure in the coastal environments in the PRD region certainly could lead to chronic exposure with unknown long-term consequences.

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Fig. 1 Maps of sampling sites in the eight major runoff outlets (●), Pearl River estuary (○) and fishing harbors (★)
Fig. 2 Geochemical maps of SMs and UVFs in the PRE
Fig. 3 Correlations between the concentrations of AHTN and HHCB
Fig. 4 Correlations between the selected compounds and TOC content

$R^2 = 0.76$ (HHCB)  
$R^2 = 0.62$ (AHTN)  
$R^2 = 0.22$ (OMC)  
$R^2 = 0.18$ (OC)