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

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9

10 **ABSTRACT**

11 This study reports the occurrence and distribution of synthetic musks (SMs) and
12 organic UV filters (UVFs) in sediment samples collected in 8 riverine runoffs from
13 the Pearl River and Pearl River estuary (PRE). Here, 6 of the 8 target compounds
14 were detected in all sediment samples with concentrations ranging from 0.35 ng g⁻¹ to
15 456 ng g⁻¹. Higher concentrations of SMs and UVFs were evident in the eastern
16 outlets compared to the western outlets suggesting greater input of these contaminants
17 from the Pearl River Delta (PRD) region. Amongst the SMs, tonalide (AHTN) and
18 galaxolide (HHCB) are the 2 predominant polycyclic musks found in all sediment
19 samples with a high correlation between them suggesting that the sources and
20 exposure pathway of HHCB and AHTN are similar. In general, all the compounds
21 showed a decreasing trend toward the seaward side of the PRE toward the South

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

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

28

29 **1. Introduction**

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

41 After application, both SMs and UVFs are generally discharged into sewage
42 treatment plants (STP) or directly into the aquatic environment. However, a number
43 of studies have shown that these compounds are incompletely removed during the

44 treatment at the STPs and do not biodegrade in the environment (Chase et al., 2012;
45 Clara et al., 2011; Tsui et al., 2014a). Consequently, these compounds ultimately enter
46 the aquatic environment and accumulate in various environmental matrices. During
47 the past decade, several studies have documented the presence of SMs and UVFs in
48 rivers, lakes, groundwater, estuaries, and coastal oceans with concentrations up to μg
49 g^{-1} levels (Bu et al., 2013; Guo et al., 2013; Kameda et al., 2011; Langford et al., 2015;
50 Nakata et al., 2007; Ramos et al., 2015; Tsui et al., 2014b). In addition, due to their
51 relatively low solubility and high octanol-water partition coefficient (K_{ow}), SMs and
52 UVFs are easily absorbed by particulate matter and eventually accumulate in river
53 sediment (Amine et al., 2012; Ramos et al., 2015; Subedi et al., 2014). These
54 compounds can also be bio-accumulated in organisms at different trophic levels (Fent
55 et al., 2010; Gago-Ferrero et al., 2015; Nakata et al., 2007).

56 Oceans and coastal zones, act as reservoirs for many contaminants that originate
57 from various sources. Riverine and marine sediments represent the final repository of
58 SMs and UVFs compounds due to their sportive nature and may play a key role as
59 potential sources of these contaminants. The Pearl River Delta (PRD) is one of the
60 most developed and urbanized areas in China, connecting the Pearl River estuary
61 (PRE) to the South China Sea (SCS) via 8 major riverine runoff outlets (Fig.1). It was
62 estimated that about 1.73×10^{10} t per year of wastewater are discharged from the PRD
63 into the PRE and the SCS. However, hardly any data are available regarding the
64 occurrence and distribution of SMs and UVFs in sediments of the Pearl River and
65 coastal environment (Chen et al., 2012; Zeng et al., 2008). In order to understand and

66 assess the impact of increased anthropogenic activities on the coastal environments of
67 the PRD region, the present study investigated the occurrence and spatial distribution
68 of 4 commonly consumed SMs, as well as 3 different UV-F compounds in river and
69 marine sediment samples collected in the Pearl River and the coast of PRE.

70

71 **2. Methods and materials**

72 *2.1 Reagents and materials*

73 In this study, 5 SMs [including tonalide (AHTN), galaxolide (HHCB), celestolide
74 (ADBI), phantolide (AHMI), musk ketone (MK)], and 3 UVFs [including
75 4-methylbenzylidene camphor (4-MBC), octocrylene (OC) and
76 octyl-p-methoxycinnamate (OMC)] were selected. Standards ($\geq 98\%$) were purchased
77 from Sigma-Aldrich, Germany. All organic solvents used were of analytical grade and
78 redistilled using glass system. Laboratory glassware was baked at 250°C for 12 h and
79 then rinsed with acetone and n-hexane. Neutral silica gel (80-100 mesh) and
80 anhydrous sodium sulfate were cleaned with dichloromethane (DCM) using MX-
81 Soxhlet extractor for 24 h and then baked at 450°C for 12 h. Silica gel was
82 deactivated with 10% (w:w) of precleaned deionized water (extracted with DCM).

83

84 *2.2 Samples collection*

85 The Pearl River is the largest and most complex water system in the South
86 China. It has a catchment area of more than 450,000 km², with an annual mean
87 runoff volume of 326 billion m³. The river water finally enters the SCS via 8

88 major outlets that include Humen (HM), Jiaomen (JM), Hongqilimen (HQ),
89 Hengmen (HE) on the eastern side, and Modaomen (MD), Jitimen (JT),
90 Hutiaomen (HT), and Yamen (YM) on the western side (Fig.1). Detailed
91 information of the 8 outlets has been previously described (Xu et al., 2013).
92 Surface sediment samples (≤ 10 cm) from the 8 outlets were collected in 2010 using a
93 stainless steel grab. A total of 16 sediment samples in the PRE and 6 sediment
94 samples from 2 fishing harbors (Shenzhen and Zhuhai) were also collected during the
95 same period. Detailed information on sampling locations is shown in Fig.1. All the
96 samples were placed into polytetrafluoroethylene bags and immediately stored at
97 -20 °C.

98

99 *2.3 Samples preparation and extraction*

100 The collected sediment samples were freeze-dried at -20 °C and ground into
101 powder using an agate pestle and mortar. Briefly, the sediment samples (10.0 g) were
102 extracted with DCM for 16 h at a flow rate of 5 ml min^{-1} using MX-Soxhlet extractor.
103 Before extraction, $10 \mu\text{l}$ of $500 \text{ pg } \mu\text{l}^{-1}$ surrogate standards was added to monitor the
104 recovery and approximately 1.0 gram of activated copper granules was added to
105 remove elemental sulfur. Extracts were evaporated down to 1–2 mL using hexane as
106 keeper and further cleaned on a silica column (2.5 g, 10 % water deactivated) topped
107 with 3 g anhydrous granulated sodium sulfate. The extract was then purified by
108 eluting with 15 mL hexane (fraction 1) followed by 20 mL DCM/acetone (1:1, V/V)
109 (fraction 2). Fraction 2 was concentrated down to 200 μL by roti-evaporation and

110 nitrogen blower. Then, 10 micro liters of 50 pg $^{13}\text{C}_6$ -PCB 208 (Cambridge Isotope
111 Laboratories) was added as injection standard.

112

113 *2.4 Compounds analysis*

114 The samples were analyzed with an Agilent 6890N gas chromatography coupled to
115 an Agilent 5973 mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA,
116 USA), operating in electron impact and selective ion monitoring modes (SIM). An
117 HP-5MS capillary column (J&W Scientific. 30 m×250 μm i.d., 0.25 μm film
118 thickness) was employed. The transfer line and the ion source temperature were
119 maintained at 280 $^{\circ}\text{C}$ and 230 $^{\circ}\text{C}$, respectively. The temperature of the oven was
120 initiated at 60 $^{\circ}\text{C}$ for 1.0 min, increased to 180 $^{\circ}\text{C}$ at a rate of 30 $^{\circ}\text{C min}^{-1}$, and
121 ramped at 2 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C}$ and held for 10 min. The flow rate of the carrier gas
122 helium was kept constant at 1.3 mL min^{-1} . The extracts (1.0 μL) were injected onto
123 GC-MS in pulsed splitless mode with an inlet temperature program as following:
124 60 $^{\circ}\text{C}$ for 0.1 min, increased to 280 $^{\circ}\text{C}$ at a rate of 300 $^{\circ}\text{C min}^{-1}$ and held for 10 min.
125 Quantitation was performed using the internal calibration method based on a 9-point
126 calibration curve.

127

128 *2.5 Quality control and quality assurance*

129 Extraction efficiency was checked with 5 sediment samples that were twice
130 extraction, which showed that the proportion of target compounds in the first
131 extraction ranged from 70 \pm 12% to 99 \pm 1% for SMs and 95 \pm 3% to 99 \pm 0.4% for

132 UVFs. Matrix spiked recoveries ranged from 70% to 90%. Instrumental detection
133 limits using the present methods were calculated by signal to noise ratio of 3 and
134 ranged from 1 to 4 pg. The method detection limits (MDLs) were derived from the
135 procedural blanks and quantified as mean field blanks plus three times the standard
136 deviation (3σ) of field blanks. Four procedural blanks were extracted together with
137 the samples. The procedural blanks were 0.02-0.06 ng g⁻¹ for SMs, and 0.01-0.17 ng
138 g⁻¹ for UVFs, which account < 1% of those in the sediment samples. The results
139 reported in this work were not corrected with a procedural blank.

140

141 **3. Results and discussion**

142 *3.1 Concentration and distribution of SMs and UVFs in the riverine outlets*

143 The total concentration of SMs in surface sediment samples from the 8 outlets
144 ranged from 11.4 to 54.6 ng g⁻¹ with an average of 33.5 ng g⁻¹ (Table 1). Among the 5
145 SMs, the 2 polycyclic musks, HHCB and AHTN, were the predominant compounds
146 with concentrations ranging from 4.54 to 31.5 ng g⁻¹. Correspondingly, ADBI and
147 AHMI were below the MDLs in all the samples. Although MK was observed in all
148 the surface sediment samples, its exposure level was slightly higher than MDL. This
149 is not unusual as nitro musk compounds were known to be gradually replaced by
150 polycyclic musks due to their toxicological effects since the 1990s ([Nakata et al.,](#)
151 [2007](#); [Sommer, 2004](#)). The elevated levels and detection frequencies of HHCB and
152 AHTN depended primarily on the high consumption of polycyclic musks and their
153 relative persistence in the natural environment. The worldwide production of

154 polycyclic musks was up by 5600 t in 1996 (Reiner and Kannan, 2006). HHCB and
155 AHTN occupy 90–95% of the total production. The consumption pattern of SMs in
156 China was similar to most other countries. In addition, the higher lipophilic and
157 hydrophobic properties of AHTN and HHCB compared to MK also contributed to
158 their exposure in different environments.

159 Out of the 3 UVFs, OMC and OC showed 100% detection frequencies in the 8
160 outlets with maximum concentrations of $<105 \text{ ng g}^{-1}$ (Table 1). In terms of
161 composition profile, OMC was the most ubiquitous compound accounting for almost
162 70% of the total UV filters probably due to the high usage in various personal care
163 products as well as in cosmetics, indicating its ubiquitous occurrence in the marine
164 environment (Kameda et al., 2011; Tsui et al., 2014b). In general, the mean
165 concentration of OMC was 2 times higher than OC. 4-MBC showed low detection
166 frequencies (50%) in sediment as well as low occurrence with the highest
167 concentration reaching up to 3.1 ng g^{-1} that was likely due to the relatively lower
168 application rates in products (Ramos et al., 2015). The use of 4-MBC had been
169 forbidden in cosmetics as an ingredient in Japan and many other countries (Tsui et al.,
170 2015).

171 With regard to spatial variation, both the SMs and UVFs in the Eastern outlets were
172 generally higher than those in the western outlets; this was consistent with the other
173 observations on antibiotics and persistent organic pollutants (Wang et al., 2007; Xu et
174 al., 2013). It was clear that both the SMs and UVFs in the Pearl River system were
175 derived primarily from a large amount of municipal sewage and industrial wastewater

176 discharged from the cities in the river basin. This was expected as the eastern outlets
177 and their upper reaches are all located in the PRD region, one of the most densely
178 populated and highly polluted areas in China. HM and JM outlets showed relatively
179 higher contaminations. This was probably due to the fact that watercourses draining
180 into the HM outlet run through several large urban areas, including Guangzhou and
181 Dongguan. JM outlet runs through the large city of Zhongshan and several large-scale
182 agricultural farms.

183

184 *3.2 Concentration and distribution of SMs and UVFs in the PRE and fishing harbors*

185 HHCB, AHTN, OMC, and OC were the 4 dominant compounds found in
186 sediments from the PRE with 100% detection frequencies, which was consistent with
187 those in the 8 outlets suggesting that riverine runoff acts as a key source of SMs and
188 UVFs (Table 1). The concentration range of HHCB and AHTN was 4.55-27.1 ng g⁻¹
189 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
190 of the UVFs, OMC was generally 2 times higher than OC in the sediments. The mean
191 concentrations of OMC and OC were 30.2 ng g⁻¹ and 16.0 ng g⁻¹, respectively. The
192 high exposure of HHCB and OMC in the PRE was consistent with most previous
193 studies from riverine or coastal environments which indicated their global ubiquitous
194 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
196 selected fishing harbors in the PRE. On the whole, all the selected compounds were
197

198 detected from the 2 harbors with SMs ranging in concentration from 0.2 to 273 ng g⁻¹.
199 Meanwhile, HHCB and AHTN were the 2 dominant compounds amongst the SM that
200 were similar to those in the riverine outlets and PRE. Except for highest OC levels
201 (551 ng g⁻¹) detected in the sediment samples, higher OMC levels of 456 ng g⁻¹ from
202 the UVF group were also found from the 2 harbors. Notably, the fishing harbor is a
203 special water area in coastal environments with a high density of human activities that
204 receives various contaminants from terrestrial discharge as well as fishing ships. In
205 addition, most harbors are built in semi-close coastal regions that are likely to
206 decrease the seawater exchange ability. As a result, these contaminants can
207 dramatically increase in harbors' sediment. The high levels of SMs and UVFs from
208 the fishing harbors in the PRD region were consistent with other contaminants
209 documented in previous studies such as heavy metals and pesticides ([Chen et al., 2012](#);
210 [Lin et al., 2009](#); [Xu et al., 2012](#)).

211 The geochemical maps of SMs and UVFs in the PRE surface sediments are
212 presented in Fig. 2. Both SMs and UVFs generally showed a seaward decreasing
213 trend from the PRE towards SCS, strongly confirming that riverine runoff is the most
214 important source of these contaminants. However, OMC and OC exhibited different
215 spatial patterns. Regarding the contaminants originating from the river, they generally
216 displayed a northwest to southeast pattern of diffusion in the PRE due to the
217 hydrodynamic conditions in the PRE ([Li et al., 2000](#); [Shi et al., 2010](#); [Zhou et al.,](#)
218 [2004](#)). However, several hotspots for OMC and OC appeared on the eastern side of
219 the upper PRE. These hotspots may reflect a high anthropogenic input, probably due

220 to the sewage discharge from the large cities along the eastern bank of the PRE, such
221 as Shenzhen and Hong Kong.

222

223 *3.3 Global comparison of SMs and UVFs in freshwater and coastal environments*

224 During the past 2 decades, the occurrence of SMs and UVFs in water samples has
225 been well documented. Nonetheless, there are very few studies regarding the
226 contamination of sediments, particularly in marine environments (Lee et al., 2014;
227 Zeng et al., 2008). Table 2 summarizes the global exposures of SMs and UVFs in
228 sediments from both freshwater and coastal environments. Based on these limited data,
229 HHCb and AHTN levels from the riverine outlets detected in this study were similar
230 to those measured in the Haihe River, Songhua River, China (Hu et al., 2011a; Lu et
231 al., 2013). However, these values were significantly lower than those detected in
232 Hudson River, USA and Lippe River, Germany (Dsikowitzky et al., 2002; Reiner and
233 Kannan, 2011). Sedimentary concentrations of UVFs recorded in the present study are
234 also far lower than those in Ebro River, Spain, and some rivers and lakes in Japan
235 (Gago-Ferrero et al., 2011; Kameda et al., 2011), which indicates that the
236 consumption of UVFs is remarkably different among countries. Specifically, the
237 highest concentration of OC detected in Ebro River was 2400 ng g⁻¹ (Gago-Ferrero et
238 al., 2011). On the other hand, OMC and OC found in other rivers or lakes, such as
239 Rhine River, Germany are comparable with or slightly lower than those detected in
240 the outlets of the Pearl River (Baron et al., 2013; Kaiser et al., 2012; Langford et al.,
241 2015; Rodil and Moeder, 2008). With regard to the coastal environments, SMs and

242 UVFs are generally both lower than those found in the rivers (Langford et al., 2015;
243 Lee et al., 2014; Zeng et al., 2008). However, it is noteworthy that the harbors as well
244 as some small fishing harbors had high levels of contaminants and probably acted as a
245 point source of SMs and UVFs in coastal environments (Subedi et al., 2014; Tsui et
246 al., 2015).

247

248 *3.4 Correlation between compounds and TOC*

249 The ratios of HHCB and AHTN in sediments have been used as a tool to trace
250 fragrance composition in PPCPs (Dsikowitzky et al., 2002; Moldovan, 2006; Nakata
251 et al., 2007). In this study, the ratio of HHCB and AHTN in the sediments ranged
252 from 1.02 to 2.71 in the order of fishing harbor > riverine outlets > PRE (Fig. 3). This
253 level is similar to those in most sediment samples from other regions such as Lippe
254 River (<3.1), Germany (Dsikowitzky et al., 2002), Pearl River (0.72-4.33) and Haihe
255 River (0.75-4.80), China (Hu et al., 2011a; Zeng et al., 2008) and Hudson River, USA
256 (0.13-3.43) (Reiner and Kannan, 2011). A rather higher ratio of 16.7 was observed in
257 Ontario Lake, USA (Peck et al., 2006). These discrepancies in HHCB/AHTN ratio
258 probably result from variation in consumption patterns in different regions and
259 countries, effective removal in STPs, and environmental behavior of these compounds
260 (e.g., volatilization, degradation, and sorption). Generally, the mean ratios in sediment
261 are lower than those in water that could be mainly explained by the higher photolysis
262 rate in water and adsorption by sediments of AHTN (Buerge et al., 2003; Hu et al.,
263 2011b; Nakata et al., 2012; Xie et al., 2007). Figure 3 shows that the HHCB values

264 were highly correlated with the AHTN values in all samples suggesting that the
265 sources and exposure pathway of HHCB and AHTN are similar. Significant
266 correlation between HHCB and AHTN was also found in sediment and wastewater
267 samples from other regions (Clara et al., 2011; Ekpeghere et al., 2016). Regarding the
268 regression lines (Fig. 3), the samples from the fishing harbors had a higher slope (0.47)
269 than those in riverine outlets (0.42) and PRE (0.39).

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

280

281 *3.5 Environmental implications*

282 This study indicated that both SMs and UVFs were ubiquitous in sediments from
283 the riverine and coastal environments in the PRD region. In addition, previous studies
284 had found SMs and UVFs in the soluble phase at different levels in this region and
285 other coastal environments (Grabicova et al., 2013; Hu et al., 2011a; Nakata et al.,
286 2012; Sumner et al., 2010; Tsui et al., 2014b). Consequently, SMs and UVFs could

287 have certainly accumulated in aquatic organisms and algae (Grabicova et al., 2013;
288 Groz et al., 2014; Hu et al., 2011a, b; Nakata et al., 2009; Nakata et al., 2007; Nakata
289 et al., 2010; Reiner and Kannan, 2011; Tsui et al., 2015). Previous studies have
290 demonstrated that both SMs and UVFs could pose low to medium risk to aquatic
291 organisms and environments based on HQ (hazard quotients) method (Lee et al., 2014;
292 Sánchez Rodríguez et al., 2015). For UV compounds, previous studies have revealed
293 that organisms at lower trophic levels were more susceptible to 4-MBC and that OMC
294 could pose a higher risk to both cladocerans and algae (Gao et al., 2013; Sieratowicz
295 et al., 2011). A recent study showed that OC can affect the endocrine system in
296 zebrafish, such as hematopoiesis, blood flow, and blood vessel formation (Bluethgen
297 et al., 2014). Oestrogenic effects and larval inhibition have been reported for synthetic
298 musks (Dietrich and Hitzfeld, 2004; Gooding et al., 2006). Among SMs, MK
299 generally posed a higher ecological risk than other musks due to its well-known
300 toxicity effect, although MK's exposure in environments is lower than others musk
301 compounds (Lee et al., 2014; Tas et al., 1997). Notably, there is little information
302 available on the toxic effects of MKs on marine species at present due to the fact that
303 the most toxicity tests were conducted in freshwater systems using freshwater
304 organisms. In addition, there is insufficient information available for SMs and UVFs
305 in the marine benthic environment. In addition, SMs and UVFs were found in
306 diffident environments as a mixture of several compounds however, the joint or
307 synergic effects of these mixtures have yet to be quantified based on limited toxicity
308 data. Hence, more ecotoxicological information is needed in the future for evaluation

309 of the potential risks induced by these compounds in marine sediment.

310

311 **4. Conclusions**

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

322

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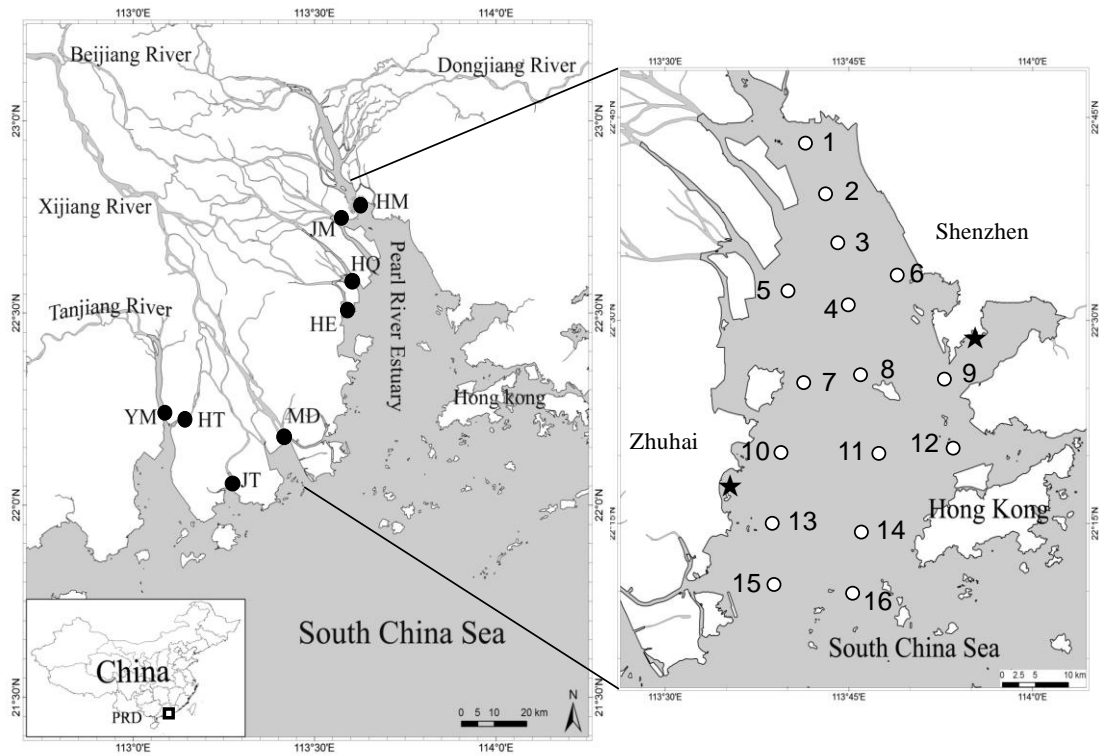
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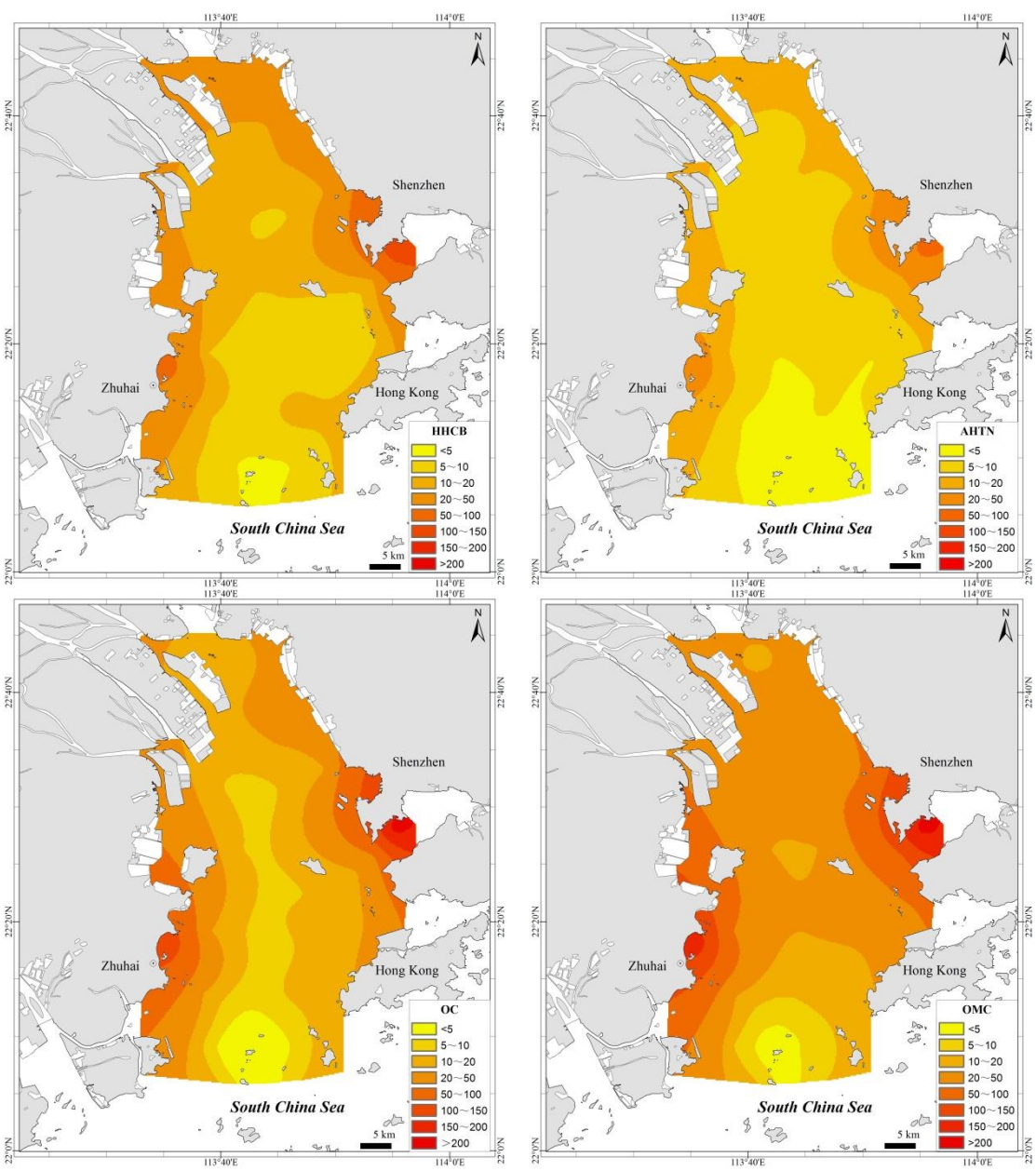
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 501 **Fig. 1** Maps of sampling sites in the eight major runoff outlets (●), Pearl River estuary (○) and
 502 fishing harbors (★)
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Fig. 2 Geochemical maps of SMs and UVFs in the PRE

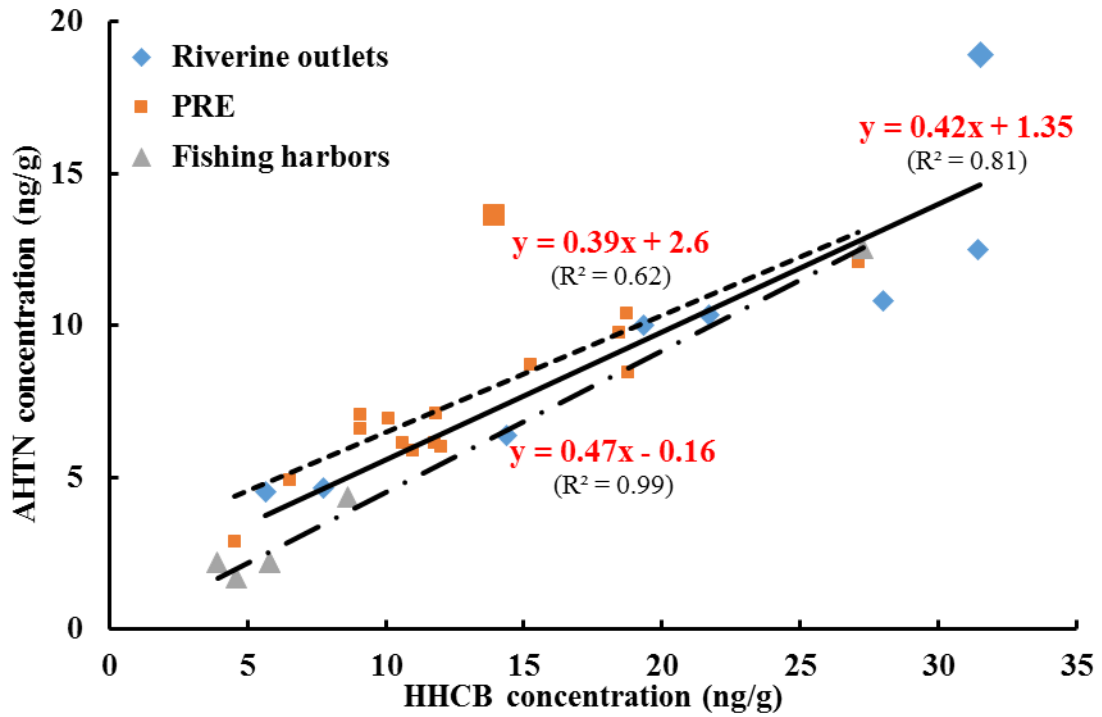


Fig.3 Correlations between the concentrations of AHTN and HHCB

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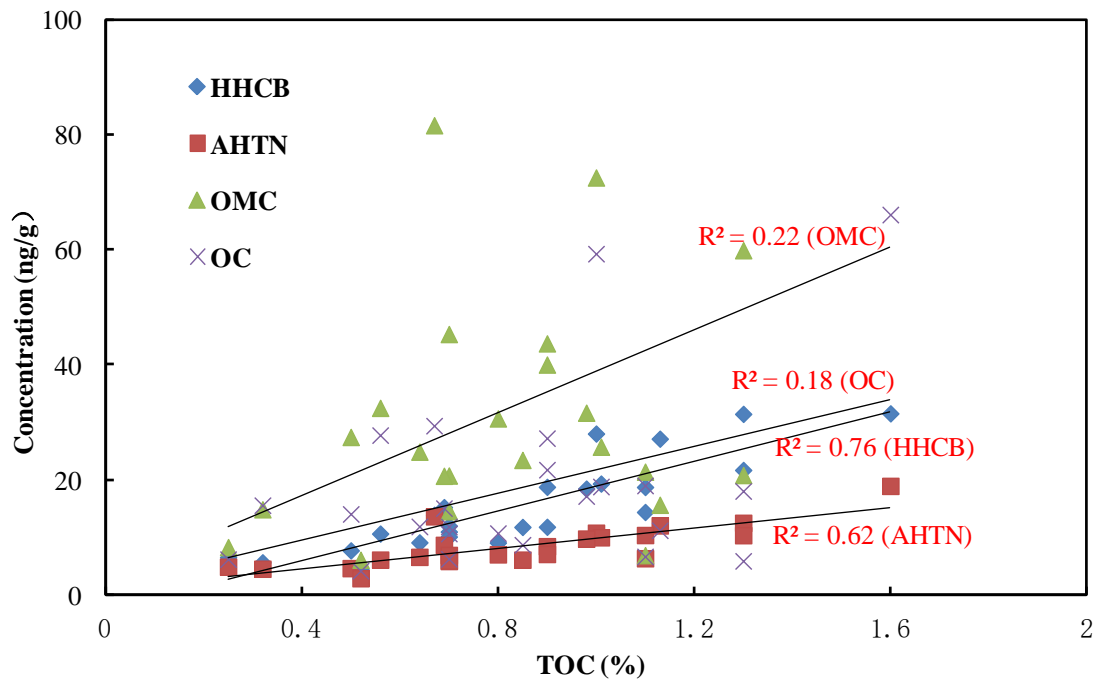


Fig.4 Correlations between the selected compounds and TOC content

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