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Spatial and temporal distribution characteristics of synthetic musk in Suzhou Creek

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Abstract Contamination levels and distribution of seven synthetic musks in Suzhou Creek were investigated in this study. Two 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, 1, 3, 4, 4, 6-hexamethyl-1, 2, 3, 4-tetrahydronaphthalene (AHTN), were found in all samples. The ranges of HHCB and AHTN were from 8 ng/L to 138 ng/L and from 1 ng/L to 25 ng/L in surface waters, and from 2 ng/g to 77 ng/g (dry weight) and from 1 ng/g to 31 ng/g (dry weight) in sediments respectively. The total concentration of HHCB and AHTN showed obvious spatial change in surface waters: the upper reaches (suburb) 13 less than the lower course (urban area); and in sediments, the musk levels were also higher in urban area. The distribution pattern also showed seasonaly varied characteristics both in surface waters and sediments. The distribution coefficient (Kp) and standardized distribution coefficient (Koc) were calculated through musk concentrations and octanol-water partition coefficient (Kow). The results showed that AHTN was more easily absorbed in sediments. The adsorption of musk was increased with the increasing of total organic carbon (TOC) in Suzhou Creek. The significant positive correlation of HHCB and AHTN was found in this study, which indicated the same pollution source: the use and discharge of flavoring substances.

Keywords musk, Suzhou Creek, surface waters, sediments

Introduction

Synthetic musk, as a new type of environmental contaminants, was widely used in cosmetics, detergents, shower gel, shampoo, *etc.*[1−3] As the most widely used synthetic musk, 7-acetyl-1, 1, 3, 4, 4, 6-hexamethyl-1, 2, 3, 4-tetrahydronaphthalene (AHTN) and 1, 3, 4, 6, 7, 8-hexahydro-4, 6, 6, 7, 8, 8-hexamethylcyclopenta(g)-2-benzopyran (HHCB) were two kinds of commonly used polycyclic musk, both of them were strong hydrophobic lipophilic, easily bio-enrichment and widely existed in environment[4]. They were found in raw sewage[5], sewage sludge[6] and surface water in many countries[7−8]. As a molecular tracer, musk concentrations could indicate the sewage impact on water environment[9]. However there were only few studies conducting in China[10−11].

Suzhou Creek, as the largest tributary of the Huangpu River, is a tidal river in the alluvial plain of the Yangtze River Delta region. It has 6 tributaries in the urban area. Suzhou Creek had been polluted by plenty of organic pollutants as sewage was discharged directly in the last hundred years. In this study, eight sampling points evenly located in the urban and suburban sections of Suzhou Creek were selected and the polycyclic musk concentrations in surface water and sediment samples were analyzed, their spatial and seasonal distribution, and the influence factors on musk pollution in Suzhou Creek were discussed.

1 Materials and methods

1.1 Sample collection

Eight sediments and surface water samples were collected from the Suzhou Creek, of which four samples (1-4) were taken from the urban, and the other four (5-8) from the rural-urban fringe. Considering the impact of surface runoff, we conducted sampling on sunny days

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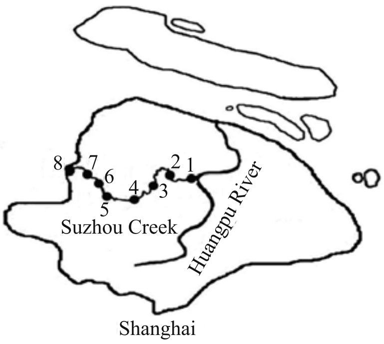
of March, June, September and December. Surface water samples were kept at 4 °C with a certain amount of methanol added to prevent microbial growth, and then analyzed within 7 d. Sediment samples were stored at −20 °C after collected. The specific locations of sampling sites are listed in Fig.1.



S1:	121°55'19.5"(E)	31°05'20.3"(N)
S2:	121°26'13.0"(E)	31°15'17.1"(N)
S3:	121°24'48.1"(E)	31°13'42.3"(N)
S4:	121°23'32.0"(E)	31°13'15.3"(N)
S5:	121°22'48.2"(E)	31°13'42.1"(N)
S6:	121°19'19.1"(E)	31°13'54.8"(N)
S7:	121°17'02.3"(E)	31°14'27.9"(N)
S8:	121°09'09.5"(E)	31°14'58.3"(N)

Fig.1 Specific location of samples

1.2 Materials and reagents

Five polycyclic musk standards: celestolide (4-acetyl-1,1-dimethyl -6-tert-butylindan, ADBI), phantolide (6-acetyl-1, 1, 2, 3, 3, 5-hexamethylindan AHMI), traseolide (5-acetyl-1, 1, 2, 6-tetramethyl-3-isopropylindan, ATII), AHTN, HHCB and two nitro musk standards: musk xylene (1-tert-butyl-3, 5-dimethyl-2, 4, 6-trinitrobenzene, MX), musk ketone (4-acetyl-1-tert-butyl-3, 5-dimethyl-2, 6-dinitrobenzene, MK) were purchased from Promochem, Germany. The purity of HHCB is 75% (GC), and the others are 99% (GC). AHTN-d_3 and hexamethylbenzene (HMB) were obtained from Dr. Ehrenstorfer, Germany.

Analytical-grade dichloromethane (DCM) and *n*-hexane were redistilled in glass before use. Silica gel (80–100 mesh) and neutral alumina (100–200 mesh) were Soxhlet-extracted with DCM for 72 h, then activated at 180 °C and 250 °C for 12 h, respectively, deactivated with 3% redistilled water and kept in *n*-hexane before use. Anhydrous sodium sulfate was baked at 450 °C for 6 h. C18 discs were from Supelco, USA.

1.3 Determination of synthetic musk

1.3.1 Pre-treatment of samples

The surface water samples (1L) were separated into aqueous and particulate phases directly through glass fiber filters, only the aqueous phase was analyzed. Samples were spiked with AHTN-d_3 and extracted using C18 discs which was fully cleaned by DCM/methanol, methanol, distilled water sequentilly. After dried under high purity N_2 stream, the discs were eluted with 20 mL *n*-hexane and 10 mL *n*-hexane/DCM (1:1, v/v) consecutively. Then the latter fraction was collected and concentrated. HMB was added as internal standard prior to gas chromatography mass spectrometry (GC/MS) analysis.

Sediments were freeze-dried, ground, and homogenized by sieving through an 80 mesh sieve. Approximately 20 g sediments were Soxhlet-extracted for 72 h with DCM. Activated copper granules were added to the extraction flasks during the extraction to desulphurization. The concentrated extract was purified on a silica/alumina column, and was separated into three fractions. The fractions containing musks were collected and concentrated. Internal standard HMB was added prior to GC/MS analysis.

Sediments used for the determination of total organic carbon (TOC) were homogenized by sieving through an 80 mesh sieve. HCl was added to remove inorganic carbon and the sample was dried to constant weight at low-temperature prior to Multi N/C 2100 analysis.

1.3.2 Instrumental analysis

Musks analysis was carried out on an HP6890 gas chromatograph equipped with HP 5975 mass spectrometric detector. The separation was carried out on an HP-5 MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm), with a carrier gas flow rate of 1 mL/min and 1 μL by manual splitless injection. The inlet temperature was 290 °C and the oven temperature was programmed as follows: 100 °C hold for 1 min, 7 °C/min up to 160 °C, and then 3 °C/min up to 180 °C, 0.5 °C/min up to 190 °C and 30 °C/min up to 290 °C hold for 10 min. The mass spectromentry (MS) was operated in an electron impact selected ion monitoring mode (EI-SIM). Target compounds were qualified by retention time and characteristic ions. The quantification ion and reference ions of ADBI, AHMI, ATII, HHCB, AHTN, MX, MK are 229, 244, 173; 229, 244, 187; 215, 258, 173; 243, 258, 173; 243, 258, 201; 282, 128, 297; 279, 294, 128 amu respectively.

TOC analysis was carried out on Multi N/C 2100.

1.4 Quality control and quality assurance

AHTN-d_3 was added to each sample to control the entire analysis process and the recovery rate range was (76.7 ± 16.7)%. For each batch of 12 samples, a spiked blank, a matrix spiking sample, were processed and recovery was (88.5 ±3.6)%–(113.2 ± 4.8)%. None target compounds were detected in procedural blanks, hence blank values could be overlooked. The limits of detection (LOD) and limits of quantification (LOQ) were based on a signal-to-noise ratio of 5 and 10, respectively. The LOQ of MX, MK, ATII, HHCB and AHTN were 1 ng/g and that of ADBI, AHMI were 0.6 ng/g.

1.5 Calculation

$$K_{\mathrm{p}} = \frac{C_{\mathrm{s}}}{C_{\mathrm{w}}}, \tag{1}$$

where K_{p} is the partition coefficient, C_{s} the balance concentration in sediment, C_{w} the balance concentration in water.

$$K_{\mathrm{oc}} = \frac{K_{\mathrm{p}}}{X_{\mathrm{oc}}}, \tag{2}$$

where K_{oc} is the standardized distribution coefficient, X_{oc} the mass fraction of organic carbon in sediment.

$$\mathrm{lg}K_{\mathrm{oc}} = 0.74\ \mathrm{lg}D_{\mathrm{ow}} + 0.15, \tag{3}$$

$$\mathrm{lg}D_{\mathrm{ow}} = \mathrm{lg}K_{\mathrm{ow}}, \tag{4}$$

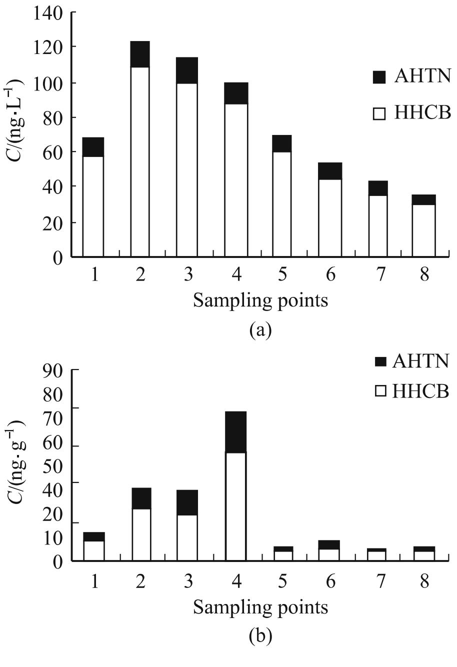
where D_{ow} is the pH-dependent octanol-water partition coefficient, K_{ow} is octanol-water partition coefficient[12].

2 Results and discussion

2.1 Contamination levels

2.1.1 Water

HHCB and AHTN are detected in all samples while the remaining 3 polycyclic and 2 nitro musk are below the detection limit (see Fig.2). The concentration ranges of HHCB and AHTN are from 8 ng/L to 138 ng/L (average 65 ng/L) and from 1 ng/L to 25 ng/L (average 10 ng/L) respectively, which indicate that HHCB is the main contaminant. In 1998, the use volumes of HHCB and AHTN were respectively 1473 t and 385 t in Europe. The use of HHCB is more popular in perfumed products compared to AHTN[14].



(a)

(b)

Fig.2 Spatial distribution of synthetic musk in surface water (a) and sediments (b)

The musk concentrations show spatial change, the concentrations in the upper reaches (suburb) are lower than those in the lower reaches (urban) except S1. The average levels are 98 ng/L HHCB, 14 ng/L AHTN in urban area, and 46 ng/L, 7 ng/L in suburb. The pollution level in urban area is more serious, and this may be resulted by larger population density in urban. As sewage is the main source of musk compounds, the large usage of perfumed household products in urban area may result large emissions of domestic sewage. Previous studies in the Pearl River and Liverpool River have drawn the same conclusion as ours[11,15]. S1 was an exception, which was located near creek mouth, the musk concentrations were deeply influenced by the dilution of the Huangpu River. When the water control gate was open or closed, the musk concentrations in S1 changed a lot.

Compared with the concentrations in other regions, the musk contamination level in Suzhou Creek is relatively low (see Table 1). This result is reasonable since the musk concentrations in perfumed household products are low in China, and musks consumption in Shanghai is only $\frac{1}{6}$–$\frac{1}{4}$ of that in EU countries[16].

Table 1 Concentration level in different regions

	HHCB	AHTN	References
Surface Water/(ng·L^{-1})			
Berlin Waterways (Germany)	70–1590	20–530	[17]
Ruhr River (Germany)	< 3 – 600	< 1 – 120	[18]
Hessen River (Germany)	5–678	3–299	[19]
Rivers in Swiss	5–564	2.3–186	[9]
Somes River (Romania)	300–314	102–106	[8]
Suzhou Creek (China)	8–138 (65)	1–25 (10)	This study
Sediment/ (ng·g^{-1} dright weight)			
Berlin Waterways (Germany)	220–920	20–1100	[17]
Lippe River (Germany)	151	44	[20]
Ontario Lake (USA)	16	0.96	[21]
Pearl River (China)	3–121	7–167	[11]
Suzhou Creek (China)	0.34–62	0.3–20.9	This study

2.1.2 Sediments

According to the statistics of Shanghai Water Authority, Suzhou Creek has a long history of direct emissions of sewage along the river. Peck, *et al.* claimed that the overlying water was a main factor affecting musk concentrations in sediment[21]. In Suzhou Creek, the concentrations of HHCB and AHTN in sediment samples are from 2 ng/g to 77 ng/g (average 18 ng/g), and from 1 ng/g to 31 ng/g (average 7 ng/g), respectively.

Unlike the situation in surface water samples, the highest concentrations of HHCB and AHTN are appeared at S4, which is 11 times higher than the lowest. Those may be caused by its location. S4 is closed to one of polluted tributaries of Suzhou Creek, and is seriously influenced by the tributary, which has been confirmed in the previous study[11]. In addition, as a tidal river, S4 is less diluted than other sample sites.

Comparing the musk concentration ratio in surface water and sediments, we find that the ratio of HHCB concentration is much higher than that of AHTN (HHCB: 3.6, AHTN: 1.4), indicating that the adsorption of AHTN in sediment is stronger than that of HHCB.

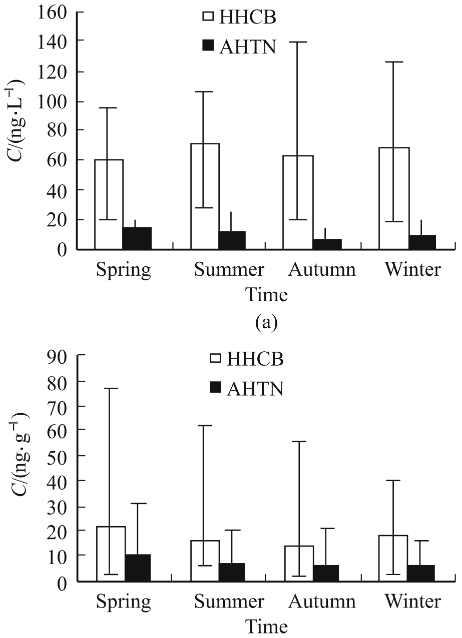
2.2 Seasonal distribution

The seasonal distribution characteristics of synthetic musk concentration in surface water are not obvious. From Fig.3(a), we can see the concentration turn of HHCB is: June (70 ng/L)> December (68 ng/L)> October (62 ng/L)> March (60 ng/L), while that of AHTN is: March (15 ng/L) > June (12 ng/L) > December (8 ng/L) > October (6 ng/L). In Fig.3(b), the average concentrations in sediments are: HHCB: March(22 ng/g) > December(18 ng/g)> June(16 ng/g) > October(13.5 ng/g); while AHTN is: March(10 ng/g) > June(6.5 ng/g) > December(6 ng/g) = October(6 ng/g). Seasonal variations of AHTN in surface water are significant (p=0.027) through One-Way ANOVA analysis, while other variations are not so obvious. The significant variations in surface water may be caused by the direct emission and the dilution factors, emission may increase in summer as many perfumed household products are used in this period, however, dilution factors, rain and tide, may also increase since summer is a rainy season in Shanghai.

The main factors affecting the concentrations of synthetic musk in sediment are the pollution in the overlying sewage. The concentrations in sediments and surface water are proportional when the other conditions are equal because sediments are the final destination of synthetic musk. However, tidal effect may accelerate the rate of conversion in the sediment-suspended solids-water phase, a lot of musk substances in sediments are discharged into the water phase again. Quednow and Püttmann analyzed water samples of all the year in Germany and found that the concentration of synthetic musk in June was much smaller than that in December[19]. That differs from our conclusions, and it needs further study.

2.3 Partition coefficient

According to the calculated value of distribution coefficient (K_p) and standardized distribution coefficient (K_oc) (see Table 2), we find that logK_p (AHTN) > logK_p (HHCB), logK_oc (AHTN) > logK_oc (HHCB), which shows that AHTN is more easily absorbed in the sediment than HHCB. The same result was also proposed in the previous studies of Winkler[22] and Carballa[23], *et al.*



(a)

(b)

Fig.3 Seasonal distribution of synthetic musk in surface water (a) and sediment (b)

Table 2 Estimated and calculated values of logK_p and logK_oc

	Estimated value		Calculated value	
	logK_p	logK_oc	logK_p	logK_oc
HHCB	6.4	4.5	1.7–3	4.1–4.6
AHTN	6.3	4.4	2.1–4.3	4.1–5.1

Calculated K_p and K_oc in this study are lower than the reported value in the related literature. That indicates (3) and (4) may be not very applicable and need further to be improved.

2.4 Correlation analysis

2.4.1 HHCB and AHTN

As shown in Fig.4, HHCB and AHTN in surface water samples and sediments reveales a significant positive correlation (r = 0.723, 0.951, p <0.001). That indicates the synthetic musk in water and sediments may have the same source: directly from the discharge of domestic sewage and industrial effluent and indirectly from the emissions of sewage plant effluents without sufficient treatment. Reiner and Shek reported a significant positive correlation of these two substances in the sludge and suggested their common source was the use and emission of commodities with fragrances[14,24].

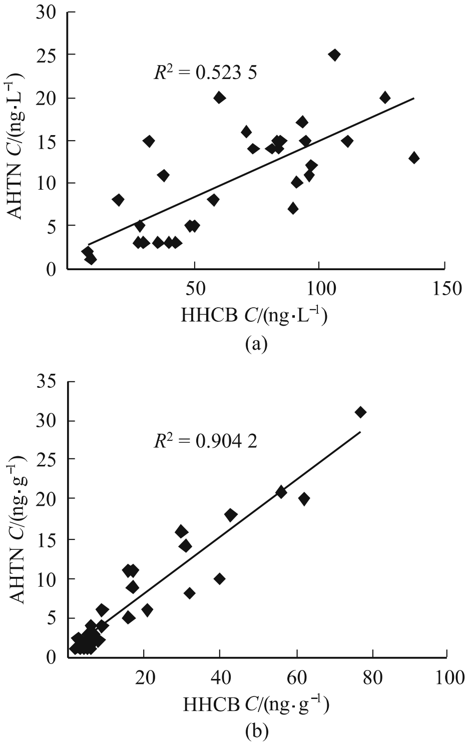


Fig.4 Correlation analysis of HHCB and AHTN in water (a) and sediment (b)

2.4.2 TOC and musk concentrations

In Fig.5, TOC and the total musk concentrations in sediment show a significant positive correlation: $r = 0.823$, $p < 0.001$ (except S8). Synthetic musk is lipophilic and hydrophobic, and easily adsorbed in the organic substances in sediment. The adsorption is increased with the increasing of TOC.

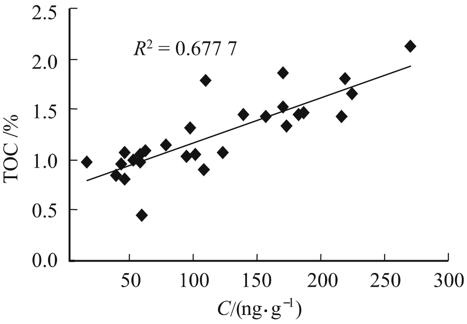


Fig.5 Correlation analysis of TOC and musk concentrations

3 Conclusions

(i) HHCB and AHTN are detected in all surface water and sediment samples, and this indicates that HHCB and AHTN are the main musk contaminants.

(ii) The concentration of HHCB and AHTN in surface water and sediments show obvious spatial distribution feature: the upper reaches (suburb) < the lower course (urban), while the seasonal distribution is not so obvious. The polluted level in Suzhou Creek is related to the population density.

(iii) K_{p} and K_{oc} are both calculated through musk concentrations. The results indicate that AHTN is more absorbed in sediment than HHCB.

(iv) The significant positive correlation of HHCB and AHTN expresses their same source, *i.e* the use and discharge of flavoring substances. TOC and the total concentrations in sediment are also positively correlated.

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