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Synthetic musks in the aquatic environment and personal care products in Shanghai, China

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ABSTRACT

The concentrations and distributions of six polycyclic musks and two nitro musks in Suzhou Creek, influent/effluent of a sewage treatment plant (STP), and household commodities were investigated and discussed in this study. The levels of 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta(g)-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) in Suzhou Creek were 3–78 ng g^{-1} (dry weight) and 2–31 ng g^{-1} (dry weight) in sediments, while 20–93 ng l^{-1} and 8–20 ng l^{-1} in surface waters. The results indicated a low proportion of wastewater burden in this river. The concentrations of HHCB and AHTN in the effluent of the STP were 5- to 6-fold higher than those in Suzhou Creek. The amounts discharged into the aquatic environment from sewage in Shanghai are 1.26 t (HHCB) and 0.38 t (AHTN) in 2007, and the input into the STPs is estimated to be HHCB 0.2 g y^{-1} and AHTN 0.06 g y^{-1} per inhabitant, respectively. A broad concentration range of HHCB and AHTN could be observed in household commodities. The distributions are in accordance with the profiles of musks in aquatic environment, with HHCB and AHTN being the major components.

1. Introduction

Synthetic musks are widely used as fragrances in a variety of consumer products, including detergents and personal care products (Roosens et al., 2007). After use, most of them are released into the sewer. Hence, musks are present in raw sewage (Simonich et al., 2000; Artola-Garicano et al., 2003; Horii et al., 2007), sewage sludge (Herren and Berset, 2000; Yang and Metcalfe, 2006; Shek et al., 2008) and surface water (Dsikowitzky et al., 2002; Buerge et al., 2003; Peck and Hornbuckle, 2004; Moldovan, 2006). The continuous use of musks in household products causes their steady input into the environment via sewage treatment plant (STP) effluents.

Nitro musks were identified for the first time in Japan in 1981 (Yamagishi et al., 1981). More recently, synthetic musks have been detected in almost every environmental compartment, including surface water, sediment, sewage, sludge, air and biota such as fish, shrimp (Kallenborn et al., 1999; Stevens et al., 2003; Peck and Hornbuckle, 2004; Duedahl-Olesen et al., 2005). And they have been detected even in breast milk and human adipose tissues (Rimkus and Wolf, 1996; Kannan et al., 2005; Raab et al., 2008). The biotransformation of two polycyclic musks, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta(g)-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), were also investigated (Franke et al., 1999; Bester, 2005; Martin et al., 2007). Due to its bioaccumulation potency in aquatic environment and the toxicity to organisms, 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX) was banned in Japan in 1980s as an ingredient in domestic products (Maekawa et al., 1990).

There are few studies on musks in China (Chen et al., 2007; Zeng et al., 2007, 2008). Little is known about the occurrence and distribution of these compounds in Shanghai, a typical urban region and densely populated city with 18.6 million inhabitants. The Suzhou Creek is considered as the 'mother river' of Shanghai, which flows through the city all year around, with 23.8 km in the urban area and 29.3 km in the suburb. The river is 40–50 m wide in Shanghai, with an average flow velocity of 0.1–0.2 m s^{-1}, nearly 5 million inhabitants living in its catchment. Raw sewage is discharged into the Suzhou Creek directly as a result of the lack of wastewater gathering system in some rural areas, while untreated wastewater is discharged on heavy rainy days in urban areas. The river is also affected by its polluted tributaries to some extend. It is of great significance to study the occurrence and distributions of musks in Suzhou Creek, since these compounds have been used as molecular tracers indicating domestic sewage contamination of surface water (Standley et al., 2000). The goal of this study is to determine the

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concentrations of main synthetic musks, and assess the impact of domestic sewage on aquatic environment in Shanghai.

2. Materials and methods

2.1. Chemicals and materials

Dichloromethane (DCM) and *n*-hexane were of analytical grade and redistilled prior to use, methanol was HPLC grade. Glass fiber filters (GF/F, average retention diameter: 47 mm) were purchased from Whatmann, USA, and heated at 450 °C for 4 h before use. C_{18} discs were from Supelco, USA. Anhydrous sodium sulfate was baked at 450 °C for 4 h prior to use. Silica gel (80–100 mesh) and neutral alumina (100–200 mesh) were Soxhlet extracted with DCM for 72 h firstly, actived at 180 °C and 250 °C for 12 h, respectively, deactived with 3% redistilled water, then kept in *n*-hexane before use.

HHCB, AHTN, MX, 4-acetyl-1-tert-butyl-3,5-dimethyl-2,6-dinitrobenzene (MK), 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one (DPMI), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan (ATII), 6-acetyl-1,1,2,3,3,5-hexamethylindan (AHMI) and 4-acetyl-1,1-dimethyl-6-tert-butylindan (ADBI) were purchased from Promochem, Germany. The purity of HHCB is 75% (GC), and the others are of 99% purity (GC). AHTN-d_3 and hexamethylbenzene (HMB) were obtained from Dr. Ehrenstorfer, Germany.

2.2. Samples characterization

Influents and effluents were collected at a municipal STP with a conventional activated sludge system, comprising a screen, a grit chamber, a primary clarifier, an aeration tank and a secondary clarifier. It serves a population of 250 000 and receives 56 000 m^3 of domestic wastewater only per day. Sampling was conducted on four dry days (two weekdays and two weekends) between 9:00 a.m. and 10:30 a.m. during April 12–April 22, 2007. A 1000 ml of influents and effluents ($n = 4$ each) were grab sampled, kept at 4 °C with 0.5% methanol (v/v) added, and then analyzed within 5 days after collection.

A 1000 ml of surface water ($n = 8$) and 30 g sediments ($n = 8$) were collected from Suzhou Creek on March 20 and 26, 2007. The sampling sites S1–S4 are located in the urban areas, and S5–S8 are in the suburb (Fig. 1). The surface waters were treated in the same way above. The sediments were frozen at −20 °C after collection and then freeze-dried, ground finely to pass through an 80-mesh sieve, finally kept in the dark before extraction.

According to the market share reported in detergent and cosmetics during 2003–2005, 31 frequently used household commodities were chosen including personal care and sanitary products. All were purchased from supermarkets in Shanghai. The liquid samples include perfume, bath gel, liquid hand soap, liquid facial soap, shampoo, fabric softener and detergent; while the solid samples contain laundry detergent, toothpaste and facial/body cream.

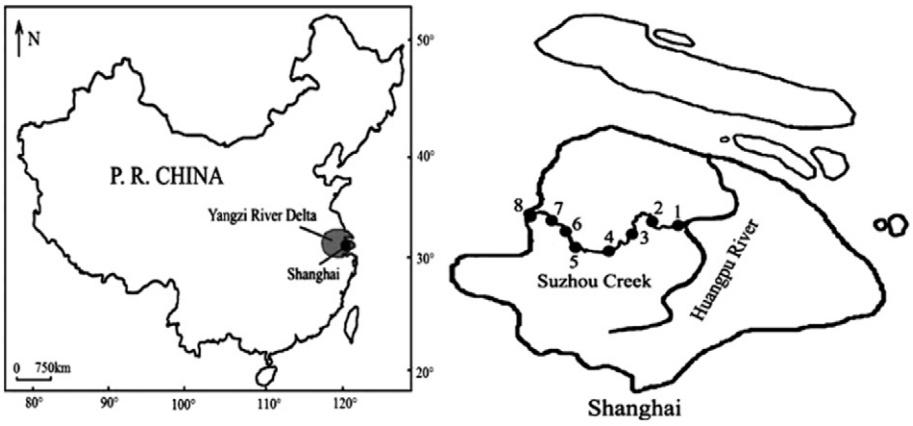
2.3. Extraction and clean-up

The influents were separated into dissolved and particulate phase through glass fiber filters, both phases were analyzed. The effluents and surface waters were filtered in the same way, and only the dissolved phases were analyzed.

Water was spiked with AHTN-d_3 and extracted using C_{18} discs at a flow rate of 10–15 ml min^{-1}. 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. The second fraction was collected and concentrated to 0.2 ml. HMB was added as internal standard prior to GC/MS analysis.

Particulates and sediments were analyzed according to the method reported earlier (Zeng et al., 2005). Briefly, samples were spiked with AHTN-d_3 and Soxhlet extracted with DCM. 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 was added prior to GC/MS analysis.

Household commodity samples were spiked with AHTN-d_3, and then extracted with *n*-hexane for three times. The combined *n*-hexane layers were concentrated and then cleaned up by a silica/alumina column. The fraction containing musks was collected



S1— N: 31°05'20.3" E: 121°55'19.5" S2— N: 31°15'17.1" E: 121°26'13.0"

S3— N: 31°13'42.3" E: 121°24'48.1" S4— N: 31°13'15.3" E: 121°23'32.0"

S5— N: 31°13'42.1" E: 121°22'48.2" S6— N: 31°13'54.8" E: 121°19'19.1"

S7— N: 31°14'27.9" E: 121°17'02.3" S8— N: 31°14'58.3" E: 121°09'09.5"

Fig. 1. Sampling sites of the Suzhou Creek.

and concentrated. Internal standard was added prior to GC/MS analysis.

2.4. GC/MS analyses

Musks were analyzed using a Hewlett-Packard 6890N GC equipped with a 5975 mass selective detector. The separation was carried out on a HP-5MS (30 m × 0.25 mm × 0.25 μm) fused-silica capillary column. The oven temperature was programmed as follows: 100 °C hold for 1 min, raised at 7 °C min^{-1} to 160 °C, then 3 °C min^{-1} to 180 °C, 1 °C min^{-1} to 190 °C, and finally 10 °C min^{-1} to 280 °C. The flow rate of the carrier gas (Helium) was 1.0 ml min^{-1}, the injection was set to a splitless mode at 280 °C. The MS was operated in an electron impact selected ion monitoring mode (EI-SIM). Target compounds were qualified by retention time and characteristic ions (Table 1). AHTN-d_3 showed partial D-H exchange during GC-MS analysis (Buerge et al., 2003; Bester, 2005), thus the effect was evaluated and subtracted from the peak of AHTN in data analysis.

2.5. Quality assurance and quality control

Because of the widespread use of polycyclic musks in many household products, great care was taken to avoid contamination during sample treatment and analyses. For each batch of 15 samples, a procedural blank, a spiked blank, a matrix spiking sample, and a matrix spiking duplicate sample were processed. The spiked samples contained 6 polycyclic musks and 2 nitro musks. Reported concentrations were not surrogate recovery corrected. Only low concentration of HHCB was detected in a procedural blank, hence blank values were not subtracted from the sample measurements. In this study, concentrations of polycyclic musks in sediment samples are reported on a dry weight (dw) basis. The limits of detection (LODs) and limits of quantification (LOQs) were based on a signal-to-noise ratio of 5 and 10, respectively. LOQs were listed in Table 1, while LODs were 1/2 of LOQs. Concentration of musks was obtained by the internal standard calibration method based on a 6-point calibration curve.

2.6. Calculation

The total amount of HHCB and AHTN discharged into aquatic environment is estimated as follows:

$$M = C_e \cdot Q_t \cdot R + C_i \cdot Q_t \cdot (1 - R)(ng) \quad (1)$$

where C_e and C_i are the concentrations of HHCB and AHTN in effluent and influent (ng l^{-1}), Q_t is the amount of sewage in Shanghai, and R is the average treatment rate of wastewater in Shanghai. According to the data provided by Shanghai Water Authority, Q_t is 1.5×10^{12} l y^{-1} in 2007, R is about 73%.

Table 1
Method quality data for the quantification

	QI (amu)	RI (amu)	ARR (%)	RSD (%)	LOQ		
					Water (ng l^{-1})	Sediment (ng g^{-1})	Commodity (ng g^{-1})
DPMI	191	206, 168	79.2	12.6	4	1	6
ADBI	229	244, 173	73.8	16.0	2	0.6	4
AHMI	229	244, 187	75.4	15.8	2	0.6	4
ATII	215	258, 173	71.1	14.9	4	1	6
HHCB	243	258, 213	77.8	14.4	4	1	6
AHTN	243	258, 201	83.4	11.7	4	1	6
MK	279	294	68.7	23.1	4	1	6
MX	282	297	62.3	19.7	4	1	6
AHTN-d_3	246	243	76.6	12.5			

QI = quantification ion; RI = reference ion; ARR = average recovery rate; RSD = relative standard deviation; LOQ = limit of quantification.

The special input into the STPs can be determined by Eq. (2) (Kupper et al., 2004)

$$I_{sp} = \frac{C_i \cdot Q \cdot 365}{1000,000 \cdot n} \quad (\text{mg cap}^{-1}\ \text{y}^{-1}) \quad (2)$$

where I_{sp} is the special input, the yearly input per inhabitant connected (capita); C_i is the concentrations of HHCB and AHTN in influent (ng l^{-1}), n is the inhabitants that STP serves (n = 250000), Q is the receiving capacity of the STP (Q = 56000000 l d^{-1}).

The concentrations of musks in influent from STPs are estimated as follows:

$$C_1 = \frac{\sum(C \cdot m) \cdot n}{Q} \quad (3)$$

where C_1 is the estimated concentration in influent (ng l^{-1}), C is the average concentration detected in commodities (ng g^{-1}), m is the consumption of commodities (14.5, 12.8 and 10.4 g d^{-1} for body lotion, shampoo and laundry detergent, respectively) (Loretz et al., 2006), n, Q see notes of formula (2).

3. Results and discussion

3.1. Synthetic musk in Suzhou Creek

3.1.1. Surface water

HHCB and AHTN were detected in surface waters of Suzhou Creek at concentrations of 20–93 ng l^{-1} (mean 60 ng l^{-1}), 8–20 ng l^{-1} (mean 14 ng l^{-1}), respectively (Fig. 2). The concentrations of DPMI, AHMI, ADBI, ATII, MK and MX were below the LODs in all samples. HHCB is the main contaminant among them. Higher concentration of HHCB was found in the urban areas (urban 83 ng l^{-1}, rural 38 ng l^{-1}), while concentrations of AHTN were similar (urban 15 ng l^{-1}, rural 13 ng l^{-1}) in all sites.

The musk concentrations in surface water depend on the distance of the sampling sites to pollution sources. In this study, the highest concentrations of both HHCB and AHTN in Suzhou Creek were detected at S3 (urban) and S6 (rural). S3 was located in the campus of a university and S6 was in the neighborhood of a village, where some of the untreated domestic wastewater may be discharged directly, causing higher levels of musk pollution.

As an urban river, Suzhou Creek was polluted by HHCB and AHTN. The concentrations of both polycyclic musks reflect the

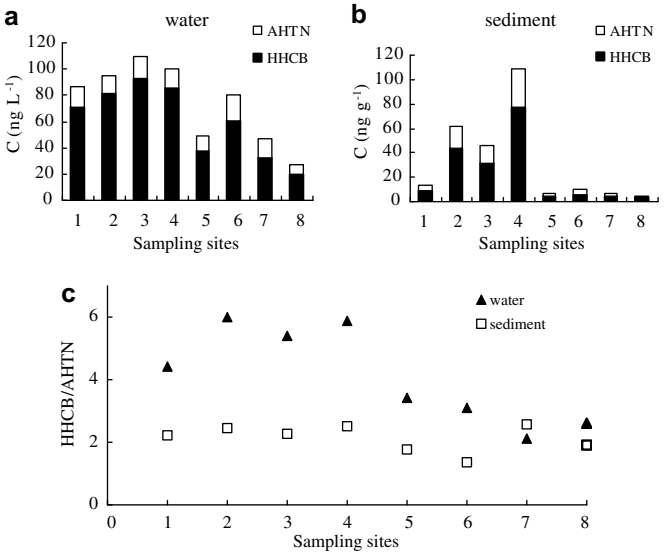


Fig. 2. Levels of musks in (a) water, (b) sediment and HHCB/AHTN (c).

impact of wastewater discharge into the river (Standley et al., 2000; Buerge et al., 2003; Quednow and Püttmann, 2008). Fromme et al. (2001) reported mean concentrations of HHCB and AHTN in surface water from rivers with low wastewater input, which are 70 ng l^{-1} and 20 ng l^{-1}, respectively. The musk concentrations in Suzhou Creek are at the same level, while the levels are 5–8 times lower than those in Somes River in Romania (Table 2).

Variations of HHCB/AHTN ratios are possibly due to the ongoing supply of them along the river. The HHCB/AHTN ratios ranged from 2.1 to 6.0 in surface waters from Suzhou Creek (Fig. 2), which are close to the previous results in other regions (HHCB/AHTN: 2.9–5.8) (Dsikowitzky et al., 2002; Buerge et al., 2003; Peck and Hornbuckle, 2004; Moldovan, 2006).

3.1.2. Sediment

The concentrations of HHCB and AHTN in sediments from Suzhou Creek varied from 3 to 78 ng g^{-1} dw (mean 23 ng g^{-1} dw) and 2–31 ng g^{-1} dw (mean 10 ng g^{-1} dw), respectively (Fig. 2). The concentrations of DPMI, AHMI, ADBI, ATII, MK and MX were below the LODs in all samples.

The highest concentrations of musks were detected at S4, which was 1.8 to 24-fold higher than those at the other sites, and this may be attributed to the heavily polluted upstream tributary. In contrast, the concentrations of HHCB and AHTN decreased at S1, which is near the creek mouth and affected by the relatively clean runoff of the Huangpu River. The lowest concentrations of musks in both surface water and sediments were found at S8, owing to the sparse population around.

The levels of musks in Suzhou Creek are slightly below those observed in sediments from Zhujiang River, China, while the concentrations of them are similar to those measured in sediments from rivers receiving low proportion of wastewaters in Germany (Table 2). The results in this study indicated a low anthropogenic burden by domestic wastewater in Suzhou Creek. Due to the continuous input, the pollution of musks in Suzhou Creek should be concerned. In order to better understand the distribution of musks, further detailed studies are necessary to obtain data about temporal trends and seasonal variation in Suzhou Creek.

Table 2
Comparison of levels of HHCB and AHTN

	HHCB	AHTN	Wastewater proportion	Reference
Water (ng l^{-1})				
Rivers in Berlin (Germany)	70 230 1590	20 70 530	Low Moderate High	Fromme et al. (2001)
Ruhr River (Germany)	<3–600	<1–120		Bester (2005)
Streams in Hessen (Germany)	5–678	3–299	15–50%	Quednow and Püttmann (2008)
Rivers and Streams (Switzerland)	5–564	2.3–186		Buerge et al. (2003)
Somes River (Romania)	300–314	102–106	5–10%[a]	Moldovan (2006)
Suzhou Creek (China)	20–93	8–20		This study
Sediment (ng g^{-1} dw)				
Rivers in Berlin (Germany)	220 920	20 260 1100	Low Moderate High	Fromme et al. (2001)
Lippe River (Germany)	151[b]	44[b]		Heim et al. (2004)
Ontario Lake (USA)	16.0	0.960		Peck et al. (2006)
Zhujiang River (China)	3–121	7–167		Zeng et al. (2008)
Suzhou Creek (China)	3–78	2–31		This study

[a] Calculated by dilution factor.
[b] Maximum concentration.

3.2. Synthetic musks in influent and effluent of STP

The main source of musks in aquatic environment is sewage, the occurrence characteristics in STPs were also examined in this study. In the STP, HHCB, AHTN, MK and MX were identified in the influent and effluent. The total concentration of the influent and the soluble concentration of the effluent were measured in this study. As is found in surface water and sediments in Suzhou Creek, HHCB was the dominant musk with concentrations of 2.30×10^3 ng l^{-1} in the influent, and 300 ng l^{-1} in the effluent, followed by AHTN and MK, while the concentration of MX was below LOQ in sewage (Table 3). In USA and EU countries, the concentrations of HHCB and AHTN in wastewater influent were measured at 1420–16600 ng l^{-1} and 540–12500 ng l^{-1}, respectively (Simonich et al., 2002; Artola-Garicano et al., 2003; Bester, 2004), which are higher than those found in Shanghai.

The removal efficiencies of HHCB and AHTN were 87% and 88% in this study, and the reported overall removal rates ranged from 63% to 88% for HHCB, and 64–89% for AHTN, respectively (Simonich et al., 2002; Bester, 2004; Berset et al., 2004; Kupper et al., 2004, 2006). Horii et al. (2007) reported a high removal rate (72–98%) of HHCB and AHTN in USA, which may be caused by the grab sampling. A high removal rate (98–99%) was also found in Canada, when only the soluble concentrations in wastewater were analyzed (Lishman et al., 2006). The removal efficiency in this study might be overestimated since the total concentration was determined in influent and only the soluble concentration in effluent was examined. The difference between the soluble and the total concentration can be substantial even in effluent (Artola-Garicano et al., 2003). The elimination of synthetic musks in STPs is incomplete, HHCB and AHTN are discharged with effluent into the aquatic environment, and thus STPs are the major source for musks in receiving water.

The total amounts of HHCB and AHTN discharged into aquatic environment in Shanghai are estimated by Eq. (1). About 1.26 t HHCB and 0.38 t AHTN were discharged into aquatic environment in 2007. According to Eq. (2), the special input into the STPs is estimated to be HHCB 0.2 g cap^{-1} y^{-1} and AHTN 0.06 g cap^{-1} y^{-1}, respectively. The values are 3-fold lower than those in Switzerland (Kupper et al., 2004), which may indicate the different usage pattern of musks: the consumption rates of HHCB and AHTN connected to per inhabitant in Shanghai are lower than that in EU countries.

Table 3
Concentrations of synthetic musks in wastewater (ng l^{-1})

	DPMI	ADBI	AHMI	ATII	HHCB	AHTN	MK	MX
Influent								
04/12/07	N.D	N.D	N.D	N.D	2464	762	418	<LOQ
04/15/07	N.D	N.D	N.D	N.D	1840	627	566	<LOQ
04/16/07	N.D	N.D	N.D	N.D	1467	435	1010	<LOQ
04/21/07	N.D	N.D	N.D	N.D	3430	1043	979	<LOQ
Average	N.D	N.D	N.D	N.D	2300	717	743	<LOQ
Effluent								
04/12/07	N.D	N.D	N.D	N.D	233	74	43	<LOQ
04/15/07	N.D	N.D	N.D	N.D	331	94	82	<LOQ
04/16/07	N.D	N.D	N.D	N.D	289	81	101	<LOQ
04/21/07	N.D	N.D	N.D	N.D	336	93	95	<LOQ
Average	N.D	N.D	N.D	N.D	297	86	80	<LOQ

N.D: below LODs.

3.3. Synthetic musk in household commodities

Many of the household products contain musks. After use, they may enter the sewage system. The 31 household commodities were analyzed for the distribution characteristics of the six polycyclic musks and two nitro musks. Three replicates were measured for each sample, and the average concentrations were reported.

The results indicated that many of the household commodities contain musks. HHCB was found in 61% of the total samples analyzed while AHTN was detected in 36%. A few samples contained nitro musks, the occurrence frequency of MK and MX was 16% and 6%. Though the percentage distribution may vary with the selection of household commodities, the results are consistent with the relatively higher production of HHCB and AHTN in fragrance industries (Salvito, 2005). The usage patterns are in accordance with the distributions of musks which were found in influent/effluent, surface water and sediment in this study.

Concentrations of HHCB and AHTN in household commodities varied greatly from non-detectable to several hundred ng g^{-1} (Fig. 3). The highest mean concentrations (8.04×10^5 ng g^{-1}) of HHCB was found in perfume, while the highest AHTN concentration (4.69×10^4 ng g^{-1}) was detected in shampoo. The average concentrations of HHCB and AHTN found in household commodities in this study are much lower than those found in USA and Belgium (Reiner and Kannan, 2006; Roosens et al., 2007). Due to the induction of metabolizing enzymes and carcinogenicity of nitro musks, the European Union established the maximum authorized concentrations for MK and MX (0.03–1% MX and 0.042–1.4% MK depending on the consumer product) (Brunn et al., 2004). The concentrations of MK and MX did not exceed these levels, but high concentrations were determined in some of the products. The concentrations of HHCB, AHTN, MK and MX are not correlated to each other, and ratios of musks differ by manufacturers, depending on their formulations.

Daily use of certain household commodities results in the release of musks via rinsing or washing down the drain, leading to discharge into the sewage system (Bester, 2005). Household commodities, especially body washes (including bath gel, liquid hand soap and facial soap), shampoo and laundry detergents are the major source of musks in STPs. The average concentrations in body washes, shampoos and laundry detergents were 5.9×10^4, 5.2×10^4, 2.4×10^4 ng g^{-1} for HHCB and 2.5×10^3, 1.2×10^4, 8.8×10^3 ng g^{-1} for AHTN, respectively. According to Eq. (3), the concentrations of HHCB and AHTN in influent were estimated to be 7.9×10^3 ng l^{-1} and 1.3×10^3 ng l^{-1}, respectively, which were 1.8–3.4 times higher than the measured ones. Taking into account of the large difference in usage patterns, the estimated concentrations are reasonable. The estimated concentration of MK in the influent is lower than the measured level, suggesting that there might be other sources besides the commodities we studied.

The contributions of certain commodities in STP influent are different: shampoo is the main contributor (HHCB: 38%, AHTN: 55%); followed by body wash (HHCB: 48%, AHTN: 13%) and laundry detergent (HHCB: 14%, AHTN: 32%).

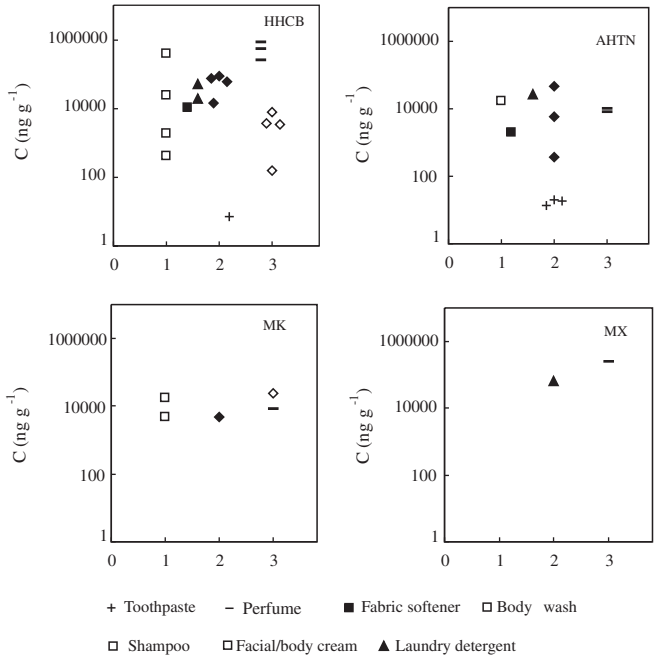


Fig. 3. Distribution of musks in household commodities.

4. Conclusions

Synthetic musks can be used as anthropogenic makers to assess the impacts of domestic wastewater in Suzhou Creek. The concentrations of musks indicate a low proportion of wastewater burden in this river.

Household products, especially shampoo, are the main source of musks. The distributions detected in aquatic environment are in accordance with the usage pattern of household commodities in Shanghai.

The consumption rates of HHCB and AHTN connected to per inhabitant are low in Shanghai, compared with those found in USA and EU countries. As a densely populated city, still a large amount of musks (1.26 t HHCB and 0.38 t AHTN) were discharged into aquatic environment, and this should be paid attention to.

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