

Distribution and fate of synthetic musks in the Songhua River, Northeastern China: influence of environmental variables

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Abstract Contamination levels and spatial and temporal distributions of six typical synthetic musks (SMs) in water and sediment of the Songhua River in Northeastern China were investigated. Experimental data for 72 water and 52 sediment samples collected at 29 sampling sites over 12 months spanning 2011–2012 showed that the Songhua River had been contaminated to different degrees at various sites separately from the river's source. The polycyclic musks 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran (HHCB) (Galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) (Tonalide) were found most frequently and at the highest levels. Concentrations of HHCB were <2–37 ng/L in water and <0.5–17.5 ng/g dry weight (dw) in sediment. AHTN was <1–8 ng/L in water and <0.5–5.7 ng/g dw in sediment. Statistical relationships between SM concentrations and four environmental variables (temperature, illumination, runoff, and population density) in the Songhua River Basin were formulated. Concentration levels varied proportionately with the size of the city along the river, while the distribution patterns showed clear seasonal variations. HHCB/AHTN ratios mirrored the transfer and transmitting process of SMs. Concentrations of target compounds were correlated with

each other, suggesting similar exposure sources. Environmental risk assessment of SMs presented seasonal variations and provided baseline information on SM exposure in the Songhua River Basin.

Keywords Synthetic musk · Spatial and temporal distribution · Fate · Risk assessment · Surface water and sediment

Introduction

Synthetic musks (SMs) as emerging persistent organic pollutants are receiving increasing concern due to their potential environmental impacts (Heberer 2002; Tanabe 2005; Peck et al. 2006; Liu et al. 2013). SMs are used extensively as fragrant ingredients in a variety of scented household and personal care products (Balk and Ford 1999a; Rimkus, 2004; Lignell et al. 2008; Zhang et al. 2008; Lu et al. 2011). The most widely used SMs include polycyclic musks—1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran (HHCB) (Galaxolide), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) (Tonalide), 4-acetyl-1,1-dimethyl-6-tert-butylindan (ADBI) (Celestolide), and 6-acetyl-1,1,2,3,3,5-hexamethylindan (AHMI) (Phantolide)—and nitro musks—1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (musk xylene (MX)) and 4-acetyl-1-tert-butyl-3,5-dimethyl-2,6-dinitrobenzene (musk ketone (MK)) (Rimkus, 2004; Peck et al. 2006; Zhang et al. 2008).

Most SMs are discharged into sewage treatment plants (STPs) (Bester 2005; Yang and Metcalfe 2006). Due to continuous use and incomplete removal during the treatment processes, SMs are steadily introduced into the environment via STP effluent and sludge (Zeng et al. 2005; Yang and Metcalfe 2006; Zhang et al. 2008). Though used at low

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concentrations, consumption of large volumes and lengthy environmental persistence contribute to SM detection in almost every environmental compartment (Lv et al. 2009). Since the first detection of MX and MK in freshwater fish from Japan (Yamagishi et al. 1981), these compounds have been investigated in various environmental matrices, including sewage influent and effluent (Lv et al. 2009), sewage sludge (Zeng et al. 2005), surface water (Hu et al. 2011), suspended particulate matter (Dsikowitzky et al. 2002), sediment (Wang et al. 2010), soils (Chase et al. 2012), air (Peck and Hornbuckle 2004), precipitation (Hu et al. 2012), dust (Liu et al. 2013), and groundwater and drinking water (Benotti et al. 2009). As SMs are hydrophobic and lipophilic (Tanabe 2005; Schramm et al. 1996), they tend to accumulate in various biological matrices such as fish (Reiner and Kannan 2011), crustaceans and bivalves (Nakata et al. 2012), marine mammals (Kannan et al. 2005), plant tissues (Chase et al. 2012), earthworms (Rimkus, 2004), and birds (Kannan et al. 2005). In addition, SMs have been detected in human tissues (Kannan et al. 2005), blood (Hu et al. 2010), and breast milk (Lignell et al. 2008).

The ubiquitous occurrence (Peck et al. 2006), relative persistence (Tanabe 2005), bioconcentration tendency, and potential toxicological effects (carcinogenicity, genotoxicity, mutagenicity, physiological ecotoxicity, and environmental hormone toxicity [Schramm et al. 1996]) raise significant concerns about the distribution and fate of SMs in the aquatic environment. Studies have been conducted in developed countries and regions such as the European Union (Sumner et al. 2010), USA (Reiner and Kannan 2011), and Korea (Lee et al. 2010; Yoon et al. 2010); however, little information is available for developing countries (Zeng et al. 2008; Hu et al. 2011). With increased economic development, the usage volume of SMs in these regions has increased (Liu et al. 2013; Wang et al. 2013). Although the SM usage patterns in developing countries are largely unknown, these patterns are suspected to be very different from those in developed nations (Villa et al. 2012). Moreover, in developing countries, sewage treatment is only partial or, in many places, completely lacking (Liu et al. 2013; Wang et al. 2013). To clarify the global transport, distribution, and fate of SMs in the natural environment, SM monitoring in developing countries should be increased (Nakata et al. 2012).

Preliminary investigations have shown that environmental variables can affect spatial and temporal distributions of SMs in the aquatic environment (Fono et al. 2006; Peck et al. 2006; Zeng et al. 2008; Wang et al. 2010; Hu et al. 2011). However, most of these studies are limited to a very short time period or cover only a few sampling sites, some of which are uncorrelated (Quednow and Püttmann 2008; Sumner et al. 2010; Gómez et al. 2012; Villa et al. 2012). Limited data are available for large-scale and long-term monitoring of an entire river basin, especially in developing countries (Dsikowitzky et al.

2002; Bester 2005). Furthermore, little is known about the statistical relationships between SM levels and environmental variables.

As the third largest river in China, the Songhua River covers a watershed area of 556,800 km² and has 66 million inhabitants with a population density that varies greatly along the river (Wang et al. 2012, 2013). It is an important flowing freshwater body intensively utilized not only for commercial fisheries but also for water supply, industrial production, and agricultural irrigation (Wang et al. 2012). In rural areas and some urban areas, raw sewage is discharged into the Songhua River directly due to the lack of wastewater gathering and treatment systems, while in urban areas, untreated wastewater is discharged into the river directly during heavy rains. The river is also affected by its polluted tributaries to some extent (Wang et al. 2012). Recently, the increased emission intensity has contributed to aggravated pollution levels (Wang et al. 2012).

The Songhua River Basin is located at the joint section of a temperate zone and a cold temperate zone with the greatest temperature variation (−38.1 to 39.2 °C) in China. As a typical semi-moist, continental monsoon climate region, it has a long cold winter, a rainy torrid summer, and a windy dry spring. Precipitation is concentrated from June to September, which accounts for 85 % of annual rainfall in this basin (Wang et al. 2013). For approximately 5 months annually, the river is covered with ice and snow (from mid-November to early April) with episodes of severe organic pollution each winter (Wang et al. 2012).

The Chinese Ministry of Environmental Protection has focused significantly on emerging persistent organic pollutants in the Songhua River following the Songhua River benzene spill in December 2005 (Wang et al. 2013). Densely distributed monitoring sections have been established, and an extensive monitoring database (including organic properties, physical and chemical properties, nutrients, inorganic constituents, and heavy metals) has been put in place through the ministry's programs (Wang et al. 2013). A recent screening survey showed that SM concentrations in human blood in Harbin were the highest in China (Hu et al. 2010).

The monitoring of SMs and determination of their fate in the Songhua River Basin deserve considerable attention. While it is of great significance to study the occurrence, fate, transport, and risk assessment of SMs in this river, no information has been available until this study. The primary objectives of this study were to (1) investigate baseline contamination levels and spatial and temporal distributions of SMs in the Songhua River, (2) analyze main correlative factors (runoff, temperature, illumination, and population density) affecting SM pollution in dissolved phase (water) and sediments, (3) investigate the relationships among different ingredients and different matrices, and (4) evaluate the potential risk to the environment of SMs during four seasons. These results will

help fill information gaps regarding the potential sources and long-term fate of SMs in large-scale rivers.

Materials and methods

Chemicals and materials

Six SMs were selected to survey based on levels of use in China, reported aquatic toxicity effects, and the ability to analyze for the compounds at low levels (Hu et al. 2010; Liu et al. 2013). The musk standards for HHCB, AHTN, ADBI, AHMI, MX, and MK were purchased from Promochem, Germany. All reagents were 99 % pure (GC), except HHCB with purity of 75 % (GC). Hexamethylbenzene (HMB) and d_3 -AHTN were obtained from Dr. Ehrenstorfer, Germany.

All solvents (dichloromethane, *n*-hexane, and methanol) were of high-performance liquid chromatography (HPLC) grade and were obtained from Dikma, China. The C18 columns used in this study were purchased from Supelco, USA. Glass fiber filters (GF/F, average retention diameter 47 mm), anhydrous sodium sulfate, neutral Al_2O_3 (100–200 mesh), and silica gel (80–100 mesh) were baked at 450 °C for 4 h prior to use.

Sampling

As shown in Fig. 1, nine key sampling sites (S1 to S9) and 20 auxiliary sampling sites (AS1 to AS20) were selected for this study. Water and bottom sediment samples were collected in the middle of 12 months spanning 2011–2012. The detailed sampling program is listed in the supplementary materials.

The equal-width-increment (EWI) method (US Geological Survey 2006) was employed to collect the isokinetic, depth-integrated samples at each stream cross section sampled (see Fig. 1). After collection, mixed water samples were immediately transferred to precleaned 5-L amber glass bottles and sealed (free of air bubbles) using glass stoppers. Samples were kept on ice during transit to the laboratory, preserved by the addition of 0.5 % methanol (*v/v*) and stored in the dark at 4 °C until extraction. All samples were extracted within 10 days of collection. Relevant data for river runoff were supplied by the Harbin Station of Environmental Monitoring, Heilongjiang Province, China.

A bottom-sediment sampling location was located just below each water sampling location (shown in Fig. 1). At each sampling point in the transversal section of the river, the top sediment samples (a mixture of sediments from the upper 10 cm shown in Fig. 1) were collected by a box-like grab sampler (manufactured by the Harbin Station of Environmental Monitoring, Heilongjiang Province, China). After sampling, the top 5 cm of sediment was transferred using a precleaned, stainless steel scoop into precleaned 1-L amber

glass containers. The collected samples were then homogenized and sealed on-site and transported on ice to the laboratory immediately, where the samples were stored at –20 °C prior to chemical analysis (Smyth et al. 2007). All containers in contact with samples were previously washed with deionized water, acetone, dichloromethane, and the river sample in the stated sequence.

Analytical methods

Water samples were extracted using C18 columns. Sediments were extracted with a Soxhlet extraction system. GC–MS analysis was carried out with a Hewlett–Packard (HP) 6890GC/5973MS system operating in the selected ion monitoring (SIM) mode. Detailed extraction and analytical information is presented in the supplementary materials.

Quality control and assurance

The surrogate standard for the water and sediment samples was d_3 -AHTN, while HMB was used as the internal standard to quantify the musk concentrations in samples. The sample concentrations were corrected with the recovery of surrogate standards. The blanks, recoveries, and deviations were within acceptable ranges, and detailed materials are listed in the supplementary materials. The limit of detection (LOD) and limit of quantification (LOQ) were determined from a signal to noise ratio of 3 and 6, respectively. In the Songhua River, LOQs of water samples were 2 ng/L for HHCB, MX, and MK and 1 ng/L for AHTN, ADBI, and AHMI. LOQs of sediment samples were 0.5 ng/g for HHCB, AHTN, MX, and MK and 0.2 ng/g for ADBI and AHMI, respectively.

Environmental risk assessment

Environmental risk assessment was carried out based on an exposure concentration to predicted no-effect concentration (PNEC) ratio, namely the risk characterization ratio (RCR). If the RCR is ≥ 1 , a high risk is expected, while $RCR \leq 0.01$ indicates no environmental risk (Balk and Ford 1999b).

Results and discussion

SM levels in water and sediment phases of the Songhua River

The SM concentration ranges and detection frequencies in water and sediment of the Songhua River are listed in Table 1. The concentration details are listed in Tables S1, S2, S3, and S4 in the supplementary materials.

SM levels varied widely in both matrices depending on the chemical compound considered, sampling location, and time

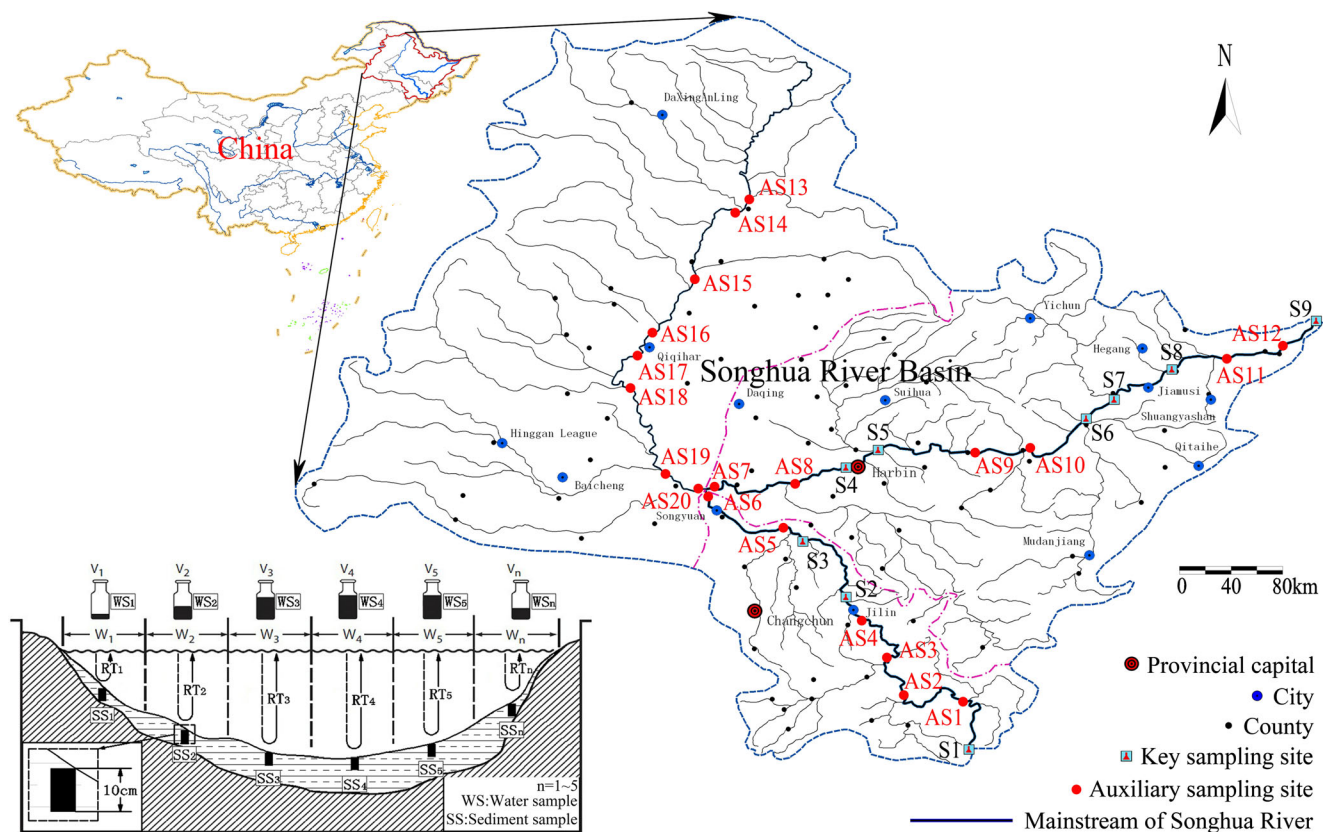


Fig. 1 Sampling sites of synthetic musks in the Songhua River Basin and schematic diagram illustrating sampling methods. Equal-width-increment method (US Geological Survey 2006). *RT* transit rate, *W* width, *V* volume

collected at each vertical proportional to the discharge of each increment. The value of *n* varied between 1 and 5 according to the river's width and the distance from inflowing tributary

of sampling. The total concentrations of six target compounds at different sampling times are listed in Fig. S1 in the supplementary materials, where the concentration levels in January 2012 and April 2012 distinctly dominated. HHCB and AHTN were detected in the majority of water and sediment samples. ADBI, AHMI, and MK were also detected in several samples. However, MX was not detected in all the water and sediment samples. The concentrations of HHCB and AHTN clearly dominated, which was consistent with the results detected in STP effluents (Salgado et al. 2010; Lu et al. 2014), and

therefore, this study and the following discussion focused on these two compounds.

Table S5 compares this work and previous works. In general, SM contamination levels in the Songhua River were in the normal ranges found in previous works. Concentrations of HHCB and AHTN in water were similar to those reported in the Hudson River, USA (HHCB 3.95–25.80 ng/L; AHTN 5.09–22.80 ng/L) (Reiner and Kannan 2011), Haihe River, China (HHCB 3.5–32.0 ng/L; AHTN 2.3–26.7 ng/L) (Hu et al. 2011), Tamar estuarine, England (HHCB 6.0–28.0 ng/

Table 1 SM concentration ranges and detection frequencies in water (ng/L) and sediment (ng/g) of the Songhua River at sampling sites S1 to S9 in the middle of August 2011, October 2011, January 2012, and April 2012

Compounds	Water		Sediment	
	Concentration range (ng/L)	Detection frequency (%)	Concentration range (ng/g, dw)	Detection frequency (%)
HHCB	<2–37	66.7	<0.5–17.5	83.3
AHTN	<1–8	55.6	<0.5–5.7	77.8
ADBI	<1–2	33.3	<0.3–2.8	27.8
AHMI	<1–3	27.8	<0.3–2.9	16.7
MX	ND	ND	ND	ND
MK	<2–4	16.7	<0.5–3.3	16.7

ND not detected

L; AHTN 3.0–10.0 ng/L) (Sumner et al. 2010), and Lake Zürich, Switzerland (HHCB <2–47 ng/L; AHTN <1–18 ng/L) (Buerge et al. 2003). HHCB and AHTN levels in sediment were similar to those measured in the Haihe River, China (HHCB 1.5–32.3 ng/g dry weight (dw); AHTN 2.0–21.9 ng/g dw) (Hu et al. 2011), and Lake Erie and Lake Ontario, USA (HHCB 3.2–16.0 ng/g dw; AHTN 0.96 ng/g dw) (Peck et al. 2006).

Seasonal variations in HHCB and AHTN levels in water and sediment of the Songhua River

Seasonal variation in HHCB and AHTN levels at different sampling sites had the same tendencies (see Tables S1, S2, S3, and S4). Therefore, the data at sampling sites S5 and S8 were selected for further analysis because the SM levels were comparatively higher and detailed environmental parameters were known. As shown in Fig. 2, concentrations collected from sites S5 and S8 tended to be higher in cold months than

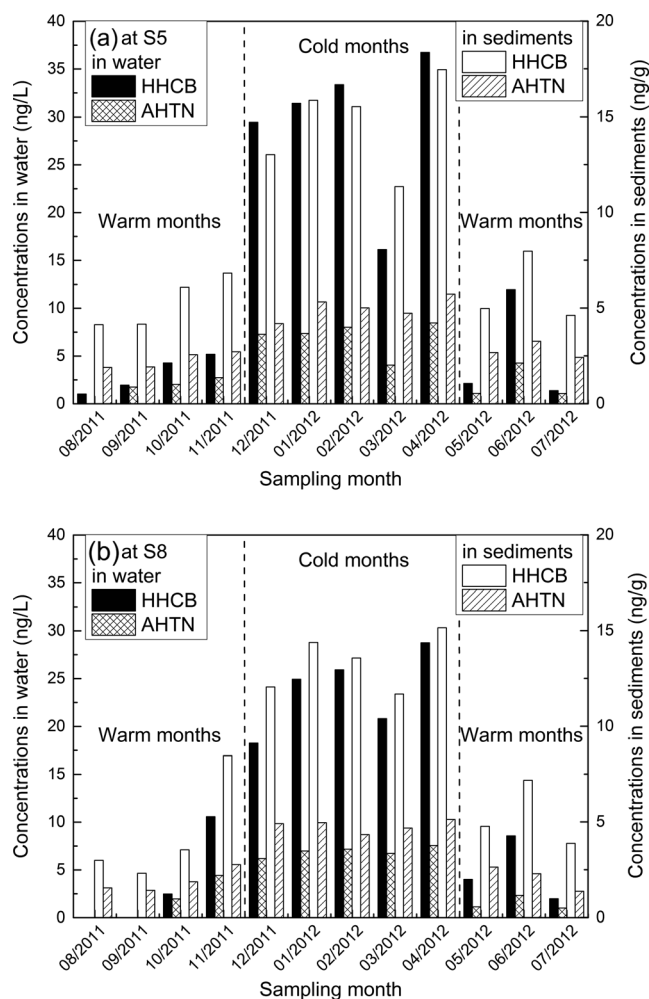


Fig. 2 Concentrations of HHCB and AHTN in water (ng/L) and sediment (ng/g dw) at sampling sites S5 and S8 from August 2011 to July 2012

in warm months. This phenomenon has been seen recently in four small freshwater river systems in Hessen, Germany, although there have also been conflicting results for seasonal variation of SMs in other studies (Quednow and Püttmann 2008).

Due to stable inputs (Dzikowitzky et al. 2002; Salgado et al. 2011), SM levels in rivers are primarily determined by temperature, illumination, and runoff, which can affect the rate and pattern of sedimentation, volatilization, degradation, photolysis, and dilution (Heberer 2002; Peck et al. 2006; Wang et al. 2012, 2013). Relationships between SM concentrations (HHCB and AHTN) and environmental variables (monthly average temperatures, illumination, and runoff) at sampling sites S5 and S8 are presented in Fig. S2. These temperatures and SM levels have a slightly negative correlation (Fig. S2 [a2] and [a3]). Similarly, illumination and SM levels also have a slightly negative correlation (Fig. S2 [b2] and [b3]). River runoff and SM concentration have a clear negative correlation (Fig. S2 [c2] and [c3]), which indicates that flow velocity has an important impact on both distribution and variance of SM concentrations (Fono et al. 2006; Reiner and Kannan 2011; Chase et al. 2012; Wang et al. 2012). For instance, at site S5, the STP discharge was 3.36 to 3.70 m³/s (Lu et al. 2014), while the Songhua River runoff (299.01 to 2368.74 m³/s) was much greater. Clearly, the most important factor controlling SM concentration was the volume of river runoff, which diluted the pollutants (Wang et al. 2012; Lu et al. 2014).

As shown in Fig. S2 (c1), the overall flow of the Songhua River occurs in three distinct hydrological seasons: a 6-month low-flow period (from November to April), moderate-flow periods (May, June, and October), and a high-flow period (from July to September) (Wang et al. 2012). In addition, runoff in the cold season was just 1/6 to 1/16 of that in the warm season. For example, in April 2012, the smallest runoff volume corresponded to the highest SM concentrations. In contrast, the largest runoff occurred with the lowest concentrations. In addition, SM concentrations were found to be higher in January and April, due to decreasing river flow, low temperatures, and low illumination in the low-flow period compared to other periods. The winter ice-bound period of almost 5 months greatly aggravated the SM levels, partly because low flow and low temperatures hampered dilution and degradation in reducing pollutant concentration and partly because fugacity tends to rise inversely proportional to environmental temperature and enhances the capacity of “holding” pollutants in the aquatic environment as temperatures decrease. Finally, the river went through a thawing phase in April 2012, with SM concentrations reaching a maximum after the low-flow period (see Table S3).

Correlations of normalized concentrations and normalized runoffs for HHCB and AHTN in water and sediment at sites S5 and S8 are shown in Fig. 3 and can be determined by the

following equation:

$$C_t/C_{t,max} = A + K_t \cdot e^{((-R/R_{max})/B)} \tag{1}$$

where C_t is the predictive concentration of HHCB or AHTN in different sampling periods at one given sampling site (ng/L or ng/g dw); $C_{t,max}$ is the maximum concentration in 1 year at this site (ng/L or ng/g dw); R is the monthly average runoff at this site (m^3/s); R_{max} is the minimum monthly average runoff corresponding to $C_{t,max}$; and A , B , and K_t are three fitting parameters. For eight sets of data shown in Fig. 3, the fitting parameters and R^2 can be found in Table S6. From the R^2 and the fitting curves in Fig. 3, we found that the nonlinear regressions were satisfactory. Using Eq. (1), we can easily estimate the SM concentrations in different months at one location.

From Fig. 3, we can also see that normalized SM concentrations in water are closer to 0 than those in sediment in the high runoff periods, which indicates that SM levels in water are more susceptible to the impact of runoff.

Spatial profiles of HHCB and AHTN in water and sediment of the Songhua River

Spatial distributions of HHCB and AHTN detected in water and sediment phases are shown in Fig. 4, which shows that HHCB and AHTN have the same spatial profile. The spatial variation of HHCB concentrations was consistent with that of AHTN (Fig. 4). Similarly, Fig. 5 shows that there was a solid positive correlation between concentrations of HHCB and AHTN in water and sediment.

As presented in Fig. 4, sampling sites along the Songhua River were polluted to a certain extent separately from the river’s source (sampling sites S1 and AS13). Higher

concentrations of HHCB and AHTN were detected at S5 (the maximum), S8, AS5, S2, and AS17, which were all located downstream of cities with dense populations (Fig. 4) and large wastewater discharges (Dsikowitzky et al. 2002; Fono et al. 2006; Chase et al. 2012). Lower levels of SMs in water and sediment were found at S1, AS13, AS1, AS14, and S7, likely owing to the sparse population around the sites (Fig. 4) along with dilution effects from adjoining branches of the river (Buerge et al. 2003; Wang et al. 2010). The concentrations of HHCB and AHTN in surface water and sediment show an obvious spatial distribution feature: concentrations downstream of cities were distinctly higher than those found upstream (Dsikowitzky et al. 2002; Bester 2005). Furthermore, the levels of SM concentrations in water and sediment depended on the distance of the sampling sites to the pollution source (Fig. 4) (Dsikowitzky et al. 2002; Yoon et al. 2010; Gómez et al. 2012).

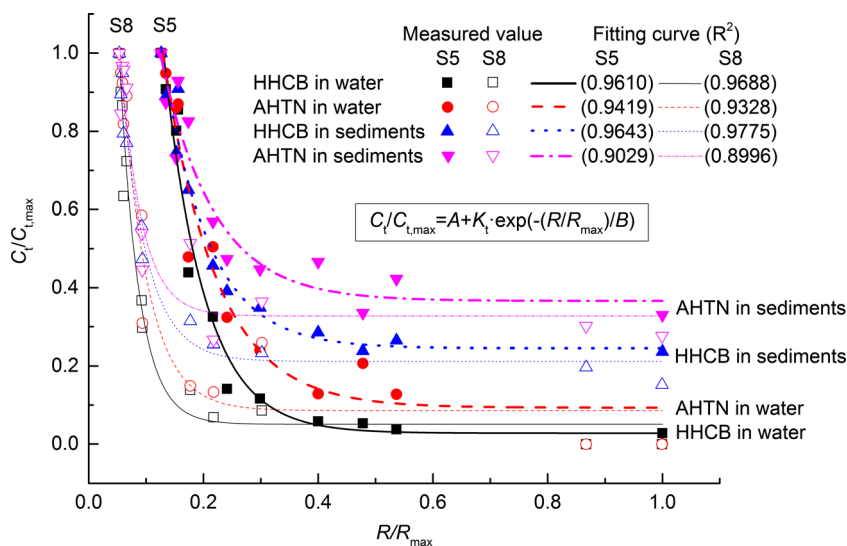
The pollution levels in the Songhua River are related to population density (Dsikowitzky et al. 2002; Wang et al. 2010). As presented in Fig. 4, the greater the population density, the higher the contamination levels. Figure S3 presents positive correlations between concentrations of HHCB and AHTN and population densities around sampling sites in water and sediment in April 2012. Similar relationships can be found in other monitored seasons. Experimental data reported in Fig. S3 can be fitted with the following equations:

$$C_s/C_{s,max} = K_s \cdot \ln D - D_0 \tag{2}$$

$$D_0 = D_{0,max} - 1 \tag{3}$$

where C_s is the predictive concentration of HHCB or AHTN (ng/L or ng/g dw), $C_{s,max}$ is the maximum value of C_s , D is the

Fig. 3 Correlations of normalized concentrations and normalized runoffs for HHCB and AHTN in water and sediment at sampling sites S5 and S8



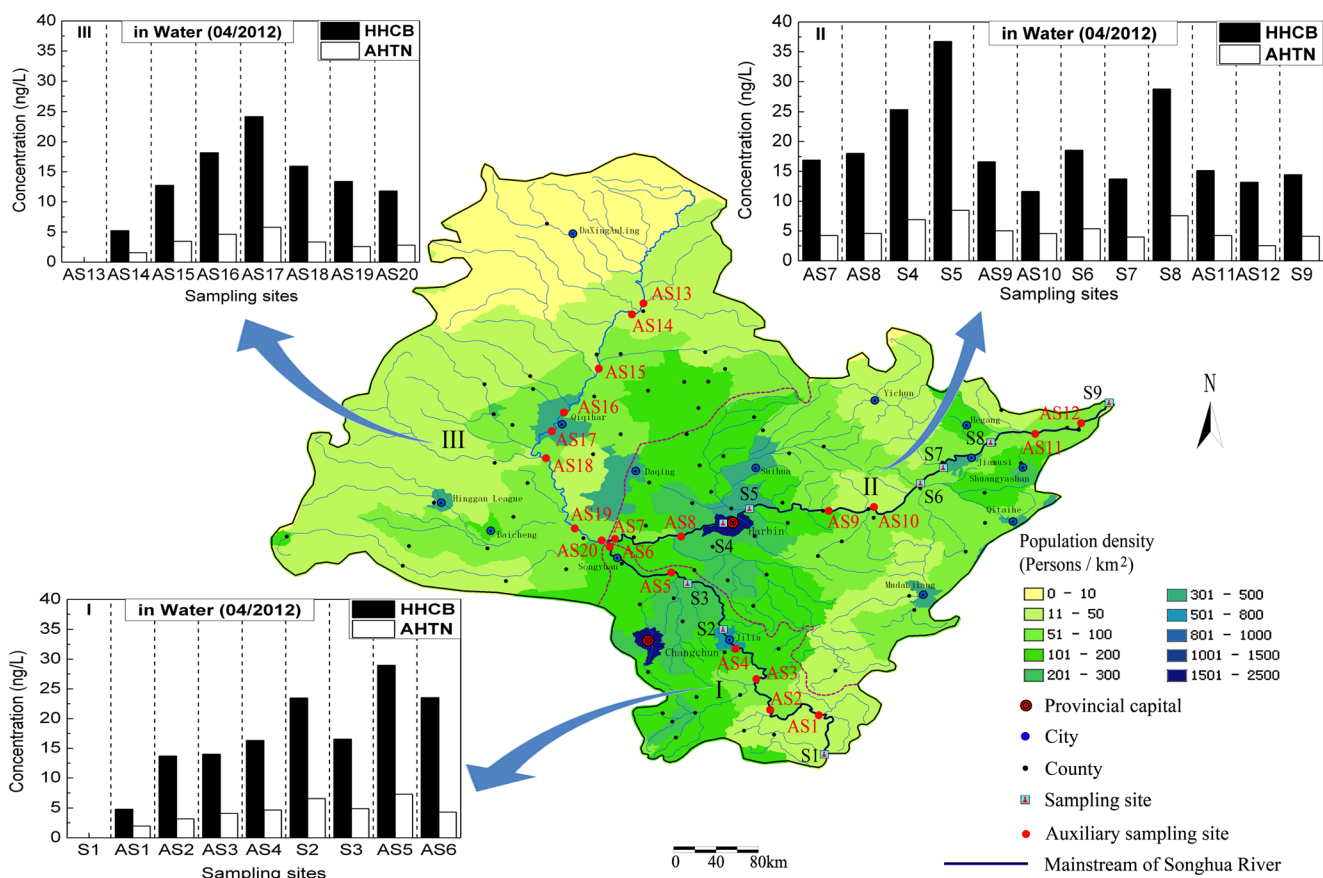


Fig. 4 Population densities and spatial profiles of HHCB and AHTN in water in April 2012

population density around the sampling site (number of persons/km²), and $D_{0,max}$ is the maximum no-effect population density that can be determined by survey or regress. K_s is a fitting parameter. For four sets of data shown in Fig. S3, the fitting parameters are provided in Table S7. The coefficients of determination (R^2) are 0.8492 and 0.8221 to HHCB and AHTN for water and 0.6311 and 0.7162 for sediment, respectively. Through Eq. (2), we can estimate the maximum SM concentrations in different locations along the Songhua River.

Combining Eqs. (1) and (2), we can preliminarily predict the SM levels in the entire mainstream of the Songhua River at any time and place. Furthermore, the overall environmental risk assessments for aquatic organisms can be performed based on these predicted SM levels. Nevertheless, in order to provide a more realistic forecast and assessment, a dynamic multimedia fate model of SMs in the Songhua River is needed (Wang et al. 2012).

HHCB/AHTN ratios in water and sediment of the Songhua River

The ratios of the concentrations of HHCB and AHTN in different aquatic compartments have been used as a tool to characterize differences in partitioning (Dsikowitzky et al. 2002). As illustrated in Fig. S4, HHCB/AHTN ratios ranged

from 1.1 to 4.3 (mean=3.1) and 1.7 to 3.1 (mean=2.3) in water and sediment, respectively, which are in close agreement with results from studies in other regions (HHCB/AHTN=2.9–5.8) (Buerge et al. 2003; Peck and Hombuckle 2004). The mean HHCB/AHTN ratios in water are higher than those in sediment mainly as a result of the higher photolysis rate of AHTN relative to that of HHCB (Buerge et al. 2003; Peck et al. 2006) and the degradation of HHCB to HHCB-lactone in sediment (Bester 2005). Variations of HHCB/AHTN ratios are possibly due to variations in ongoing discharge and SM degradation along the river (Lu et al. 2011).

Figure 5 presents the significant positive correlation between HHCB and AHTN concentrations in water and sediment samples ($R^2=0.9039, 0.9584, p<0.05$), suggesting the coexposure of HHCB and AHTN in the Songhua River Basin (Wang et al. 2010). Moreover, the positive correlation between HHCB/AHTN ratios and SM concentrations suggests that the HHCB/AHTN ratio could be used as a tracer for source discrimination and for the degree of degradation in the environment (Buerge et al. 2003; Zeng et al. 2008). Positive correlations were also found between concentrations of HHCB and other SMs (ADBI, AHMI, and MK, $p<0.05$, see Table S1, S2, S3 and S4), which indicate potential feasibility to predict levels of other SMs based on levels of HHCB (Lee et al. 2010).

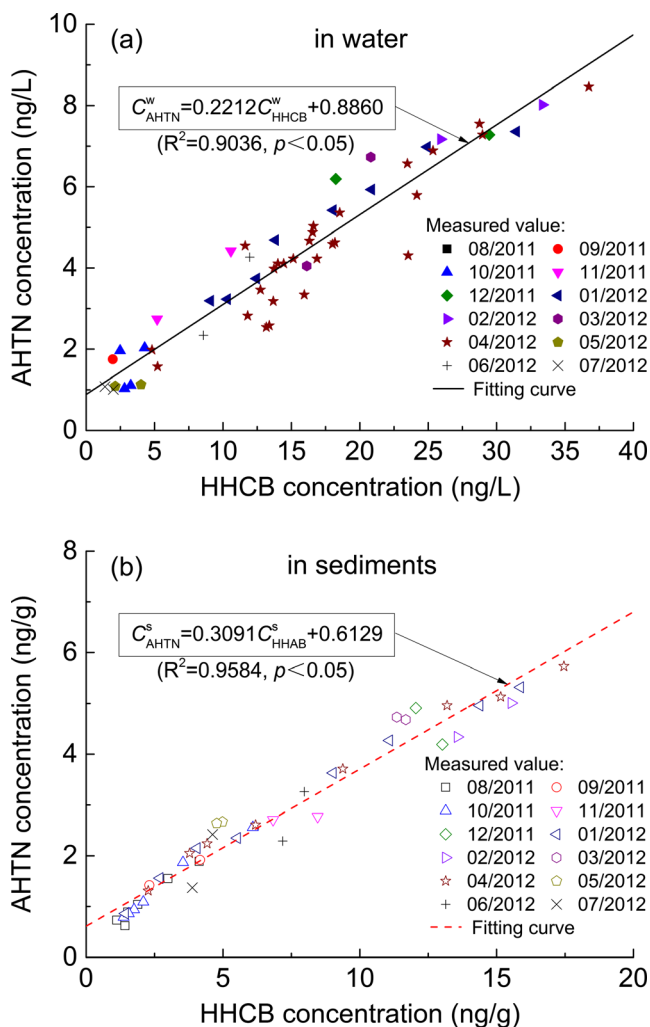


Fig. 5 Positive correlation between concentrations of HHCB and AHTN in **a** water and **b** sediment

Linear regression analysis was performed between the concentrations of HHCB and AHTN in water and sediment samples with Eqs. (4) and (5) as follows:

$$C_{\text{AHTN}}^w = 0.2212C_{\text{HHCB}}^w + 0.8860 \tag{4}$$

$$C_{\text{AHTN}}^s = 0.3091C_{\text{HHCB}}^s + 0.6129 \tag{5}$$

where C_{AHTN}^w and C_{AHTN}^s are the predictive concentrations of AHTN in water (ng/L) and sediment (ng/g dw) and C_{HHCB}^w and C_{HHCB}^s are the measured concentrations of HHCB in water (ng/L) and sediment (ng/g dw).

Partitioning of SMs between dissolved and sedimentary phases

The partition characteristics in water and sediment for selected SMs in the Songhua River were determined. A positive

correlation between concentrations in water and those in sediment was observed for HHCB and AHTN, and the relationships were determined using Eqs. (6) and (7):

$$C_{\text{HHCB}}^s = 0.4055C_{\text{HHCB}}^w + 1.8681 \tag{6}$$

$$C_{\text{AHTN}}^s = 0.5051C_{\text{AHTN}}^w + 0.9015 \tag{7}$$

The R^2 s are 0.7717 and 0.6803. According to the above relationships, SM levels in sediment can be roughly estimated based on those in water (Lee et al. 2010).

Results also indicated that HHCB and AHTN have similar tendencies to partition between aqueous and solid matrices, which can be explained by the similar $\log K_{oc}$ values of 4.65 and 4.74, respectively. Previous studies have indicated that sediment is the final destination of SMs and the overlying water is a significant factor affecting SM concentrations in sediment (Hu et al. 2011; Reiner and Kannan 2011), which can explain the positive correlations between concentrations in sediment and water (Wang et al. 2010).

Environmental risk assessment to aquatic organisms

This study found that HHCB and AHTN are the primary musk contaminants found in the Songhua River, with both SMs being present at levels of nanogram per liter. The PNECs of HHCB and AHTN for aquatic organisms were estimated to be 6.8 and 3.5 $\mu\text{g/L}$ (Balk and Ford 1999b). All RCRs calculated based on this data were below 0.01 as shown in Fig. S5, suggesting that these substances will not pose an environmental risk in the near future (Balk and Ford 1999b).

The spatial distribution maps for the environmental risk from HHCB and AHTN in four seasons are shown in Fig. S6. From the spatial distribution patterns, there appears to be a high degree of spatial variability in the SM RCRs. One hot-spot area was observed at S5, downstream of Harbin city, which is the most developed region along the Songhua River, with a population of about 4.65 million. Here, the river mainstream receives the greatest pollution from both point (STP effluent) and nonpoint (directly draining urban domestic sewage) sources (Wang et al. 2013). Moreover, due to the higher RCR value in the cold season, it is critical to select effective STP treatment processes for SM elimination under conditions of extreme cold.

Conclusion

SMs are widespread in water and sediment of the Songhua River. HHCB and AHTN were found to be the principal pollutants. Temporal profiles were found to be seasonal,

which is mainly attributed to seasonal changes of environmental variables. Higher contamination in the cold season is most likely caused by the following: (1) low dilution, (2) low microbial degradation rate of SMs, (3) low volatilization and photolysis of SMs prevented by ice and snow layers, (4) low levels of dissolved oxygen below the ice layer that reduces SM degradation, (5) relatively large STP emission of SMs, most likely caused by the relatively lower STP removal efficiency at low temperatures particularly for biological oxidation processes (Lu et al. 2014).

Spatial differences of SM levels in the Songhua River mainly were found in total SM emission rates, related to population densities around the sampling sites. SM concentrations downstream of cities were distinctly higher than those found upstream. Peak concentrations were measured downstream of Harbin city (site S5), which has a high population density and considerable volume of direct drainage of urban domestic sewage into the river. Environmental risk assessment to aquatic organisms was performed, and all RCRs were calculated to be below 0.01, indicating that SMs are unlikely to pose an environmental risk in the near future.

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References

- Balk F, Ford RA (1999a) Environmental risk assessment for the polycyclic musks, AHTN and HHCb in the EU: I. Fate and exposure assessment. *Toxicol Lett* 111:57–79
- Balk F, Ford RA (1999b) Environmental risk assessment for the polycyclic musks, AHTN and HHCb: II. Effect assessment and risk characterisation. *Toxicol Lett* 111:81–94
- Benotti MJ, Trenholm RA, Vanderford BJ, Holady JC, Stanford BD, Snyder SA (2009) Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol* 43:597–603
- Bester K (2005) Polycyclic musks in the Ruhr catchment area—transport, discharges of waste water, and transformations of HHCb, AHTN and HHCb-lactone. *J Environ Monit* 7:43–51
- Buerge IJ, Buser HR, Müller MD, Poiger T (2003) Behavior of the polycyclic musks HHCb and AHTN in lakes, two potential anthropogenic markers for domestic wastewater in surface waters. *Environ Sci Technol* 37:5636–5644
- Chase DA, Kamjanapiboonwong A, Fang Y, Cobb GP, Morse AN, Anderson TA (2012) Occurrence of synthetic musk fragrances in effluent and non-effluent impacted environments. *Sci Total Environ* 416:253–260
- Dsikowitzky L, Schwarzbauer J, Littke R (2002) Distribution of polycyclic musks in water and particulate matter of the Lippe River (Germany). *Org Geochem* 33:1747–1758
- Fono LJ, Kolodziej EP, Sedlak DL (2006) Attenuation of wastewater-derived contaminants in an effluent-dominated river. *Environ Sci Technol* 40:7257–7262
- Gómez MJ, Herrera S, Solé D, García-Calvo E, Fernández-Alba AR (2012) Spatio-temporal evaluation of organic contaminants and their transformation products along a river basin affected by urban, agricultural and industrial pollution. *Sci Total Environ* 420:134–145
- Heberer T (2002) Occurrence, fate, and assessment of polycyclic musk residues in the aquatic environment of urban areas—a review. *Acta Hydrochim Hydrobiol* 30:227–243
- Hu ZJ, Shi YL, Niu HY, Cai YQ, Jiang GB, Wu YN (2010) Occurrence of synthetic musk fragrances in human blood from 11 cities in China. *Environ Toxicol Chem* 29:1877–1882
- Hu ZJ, Shi YL, Cai YQ (2011) Concentrations, distribution, and bioaccumulation of synthetic musks in the Haihe River of China. *Chemosphere* 84:1630–1635
- Hu ZJ, Shi YL, Niu HY, Cai YQ (2012) Synthetic musk fragrances and heavy metals in snow samples of Beijing urban area, China. *Atmos Res* 104:302–305
- Kannan K, Reiner JL, Yun SH, Perrotta EE, Tao L, Johnson-Restrepo B, Rodan BD (2005) Polycyclic musk compounds in higher trophic level aquatic organisms and humans from the United States. *Chemosphere* 61:693–700
- Lee IS, Lee SH, Oh JE (2010) Occurrence and fate of synthetic musk compounds in water environment. *Water Res* 44:214–222
- Lignell S, Damerud PO, Aune M, Cnattingius S, Hajslova J, Setkova L, Glynn A (2008) Temporal trends of synthetic musk compounds in mother's milk and associations with personal use of perfumed products. *Environ Sci Technol* 42:6743–6748
- Liu N, Shi Y, Xu L, Li W, Cai Y (2013) Occupational exposure to synthetic musks in barbershops, compared with the common exposure in the dormitories and households. *Chemosphere* 93:1804–1810
- Lu Y, Yuan T, Wang W, Kannan K (2011) Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China. *Environ Pollut* 159:3522–3528
- Lu BY, Feng YJ, Gao P, Zhang ZH (2014) Occurrence behavior and removal efficiencies of synthetic musks in a sewage treatment plant. *Desalination and Water Treatment (in submittal process)*
- Lv Y, Yuan T, Hu JY, Wang WH (2009) Simultaneous determination of trace polycyclic musks and nitro musks in water samples using optimized solid-phase extraction by gas chromatography and mass spectrometry. *Anal Sci* 25:1125–1130
- Nakata H, Shinohara RI, Nakazawa Y, Isobe T, Sudaryanto A, Subramanian A, Tanabe S, Zakaria MP, Zheng GJ, Lam PKS, Kim EY, Min BY, We SU, Viet PH, Tana TS, Prudente M, Frank D, Lauenstein G, Kannan K (2012) Asia-Pacific mussel watch for emerging pollutants: distribution of synthetic musks and benzotriazole UV stabilizers in Asian and US coastal waters. *Mar Pollut Bull* 64:2211–2218
- Peck AM, Hornbuckle KC (2004) Synthetic musk fragrances in Lake Michigan. *Environ Sci Technol* 38:367–372
- Peck AM, Linebaugh EK, Hornbuckle KC (2006) Synthetic musk fragrances in Lake Erie and Lake Ontario sediment cores. *Environ Sci Technol* 40:5629–5635
- Quednow K, Püttmann W (2008) Organophosphates and synthetic musk fragrances in freshwater streams in Hessen/Germany. *Clean Soil Air Water* 36:70–77
- Reiner JL, Kannan K (2011) Polycyclic musks in water, sediment and fishes from the Upper Hudson River, New York, USA. *Water Air Soil Pollut* 214:335–342

- Rimkus GG (2004) Synthetic musk fragrances in the environment. In: The handbook of environmental chemistry, Part X; Springer-Verlag, Berlin Heidelberg, 338 p
- Salgado R, Noronha JP, Oehmen A, Carvalho G, Reis MAM (2010) Analysis of 65 pharmaceuticals and personal care products in 5 wastewater treatment plants in Portugal using a simplified analytical methodology. *Water Sci Technol* 62:2862–2871
- Salgado R, Marques R, Noronha JP, Mexia JT, Carvalho G, Oehmen A, Reis MA (2011) Assessing the diurnal variability of pharmaceutical and personal care products in a full-scale activated sludge plant. *Environ Pollut* 159:2359–2367
- Schramm KW, Kaune A, Beck B, Thumm W, Behechti A, Kettrup A, Nickolova P (1996) Acute toxicities of five nitro musk compounds in *Daphnia*, algae and photoluminescent bacteria. *Water Res* 30: 2247–2250
- Smyth SA, Lishman L, Alaei M, Kleywegt S, Svoboda L, Yang JJ, Lee HB, Seto P (2007) Sample storage and extraction efficiencies in determination of polycyclic and nitro musks in sewage sludge. *Chemosphere* 67:267–275
- Sumner NR, Guitart C, Fuentes G, Readman JW (2010) Inputs and distributions of synthetic musk fragrances in an estuarine and coastal environment; a case study. *Environ Pollut* 158:215–222
- Tanabe S (2005) Synthetic musks—arising new environmental menace? *Mar Pollut Bull* 50:1025–1026
- U.S. Geological Survey (2006) Collection of water samples (ver. 2.0): U.S. geological survey techniques of water-resources investigations, book 9, chap. A4, September 2006. Accessed 25 September 2014.
- Villa S, Assi L, Ippolito A, Bonfanti P, Finizio A (2012) First evidences of the occurrence of polycyclic synthetic musk fragrances in surface water systems in Italy: spatial and temporal trends in the Molgora River (Lombardia Region, Northern Italy). *Sci Total Environ* 416: 137–141
- Wang FL, Zhou Y, Guo YW, Zou LY, Zhang XL, Zeng XY (2010) Spatial and temporal distribution characteristics of synthetic musk in Suzhou Creek. *J Shanghai Univ* 14:306–311
- Wang C, Feng YJ, Gao P, Ren NQ, Li BL (2012) Simulation and prediction of phenolic compounds fate in Songhua River. *China Sci Total Environ* 431:366–374
- Wang Y, Wang P, Bai YJ, Tian ZX, Li JW, Shao X, Mustavich LF, Li BL (2013) Assessment of surface water quality via multivariate statistical techniques: a case study of the Songhua River Harbin region, China. *J Hydro Environ Res* 7:30–40
- Yamagishi T, Miyazaki T, Horii S, Akiyama K (1981) Identification of musk ketone in freshwater fish collected from the Tama River, Tokyo. *Bull Environ Contam Toxicol* 26:656–662
- Yang JJ, Metcalfe CD (2006) Fate of synthetic musks in a domestic wastewater treatment plant and in an agricultural field amended with biosolids. *Sci Total Environ* 363:149–165
- Yoon Y, Ryu J, Oh J, Choi BG, Snyder SA (2010) Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). *Sci Total Environ* 408:636–643
- Zeng XY, Sheng GY, Xiong Y, Fu JM (2005) Determination of polycyclic musks in sewage sludge from Guangdong, China using GC-EI-MS. *Chemosphere* 60:817–823
- Zeng XY, Mai BX, Sheng GY, Luo XJ, Shao WL, An TC, Fu JM (2008) Distribution of polycyclic musks in surface sediments from the Pearl River Delta and Macao coastal region, South China. *Environ Toxicol Chem* 27:18–23
- Zhang XL, Yao Y, Zeng XY, Qian GR, Guo YW, Wu MH, Sheng GY, Fu JM (2008) Synthetic musks in the aquatic environment and personal care products in Shanghai, China. *Chemosphere* 72: 1553–1558