Concentrations and distribution of synthetic musks and siloxanes in sewage sludge of wastewater treatment plants in China

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HIGHLIGHTS

- High levels and detection frequencies of SMs and siloxanes were found in sludge.
- SM levels were correlated with the TOC of the sludge and serving population of WWTPs.
- Cyclic siloxane levels had a positive correlation with the treatment capacity of WWTPs.
- Linear siloxane concentrations had correlation with the TOC of the sludge in WWTPs.
- When using treated sewage sludge as bio-solids, negligible effect was observed.

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ABSTRACT

In this study, we assessed the occurrence and distribution patterns of seven synthetic musks (SMs) and 17 siloxanes in anaerobic digested sludge samples collected at the dewatering process from 42 wastewater treatment plants (WWTPs) in China. SMs in sludge from different WWTPs exhibited similar composition profiles, and their total concentrations ranged from 47.3 ng/g to 68.2 µg/g dry weight (dw). On average, galaxolide (HHCB, 63.8%) and tonalide (AHTN, 31.7%) accounted for 95.5% of $\sum$ SMs. The total concentrations of cyclic siloxanes ranged from <LOQ (limit of quantitation) to 36.1 µg/g dw (mean: 1.98 µg/g), while from <LOQ to 13.2 µg/g dw (mean: 0.937 µg/g) for linear siloxanes. On average, cyclic siloxanes accounted for 68% of the total siloxanes. High concentrations and detection frequencies of SMs and siloxanes in sewage sludge indicated that both of them were widely used in China. Among the sludge samples from 42 WWTPs, the concentrations of both $\sum$ SMs and $\sum$ siloxanes had considerable variations. We investigated the influence of potential factors (wastewater and sludge characteristics, the treatment capacity, serving population, and the treatment techniques of WWTPs) on the levels of target compounds in sludge, and found that SMs were significantly ($p < 0.05$) correlated with the total organic carbon (TOC) of the sludge and the serving population of WWTP. There were also strong correlations ($p < 0.05$) between the treatment capacity of WWTPs and cyclic siloxanes, as well as between the TOC of the sludge and linear siloxanes. In addition, the ecological risks of SMs and siloxanes in sewage sludge addressed to land application were assessed, which suggested that there was a low risk to the soil environment.

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1. Introduction

As the low-cost substitutes for natural musks, synthetic musks (SMs) have been widely used as fragrances in most of detergents, cleaning agents and various cosmetic products due to their typical musky scents and fixative properties (Lu et al., 2011a). With a high production rate of SMs (8000 tons/year) in the last 5 years, China has been a major producer of musk compounds in the world (Guo et al., 2012). SMs can be mainly divided into nitro musks (NMs) and polycyclic musks (PCMs) according to their chemical structures. Musk xylene (MX) and musk ketone (MK) are the main NMs, while galaxolide

(HHCB) and tonalide (AHTN) are the most commonly used PCMs. It was estimated that HHCB and AHTN represented about 95% of the market share in Europe for all PCMs (Upadhyay et al., 2011). Since the late 1980s, the production of NMs has been dramatically decreased and even banned in some countries due to their potential toxicity to human health and environment (Nakata et al., 2007). Both HHCB and AHTN have been featured as high production volume (HPV) chemicals by the US Environmental Protection Agency (EPA) and the 2007 OECD (Organization for Economic Co-operation and Development). More than 1000 tons/year of these two chemicals are produced or imported in at least one country/region among the OECD members (Kubwabo et al., 2012; Lu et al., 2011b). Due to their widespread use and low rates of degradation, SMs have been found not only in various environmental matrices (air, water and sediment, etc.), but also in many biota

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even in human milk, blood, fat and adipose tissue (Guo et al., 2010; Moon et al., 2012).

Siloxane, another class of HPV chemicals, is used not only in a broad range of consumer products, but also in industrial products, such as automotive polishes, fuel additives and anti-foaming agents due to their special properties such as low surface tension, physiologic inertness, high thermal stability and smooth texture (Companioni-Damas et al., 2012; Sanchis et al., 2013; Xu et al., 2012b). The annual production of octamethylcyclotetrasiloxane (D4) is about 45–227 thousand tons, indicating a great potential for widespread presence of siloxanes in the environment (Hori and Kannan, 2008). Several studies have reported the occurrence of siloxanes in various environmental and biota matrices (Borga et al., 2012; Hanssen et al., 2013; Krogseth et al., 2013). Owing to their potential toxic effects on organisms, SMs and siloxanes were of concern from their ubiquitous environmental occurrence (Parrott et al., 2012; Schnell et al., 2009).

As their widespread use in daily life, SMs and siloxanes are likely to be discharged into sewage systems with the applied “rinse-off” products (Whelan, 2013). For example, the total mass of siloxanes draining into wastewater was estimated at 17,000 tons/year in the USA (Dewil et al., 2006). Moreover, SMs and siloxanes tend to be preferentially adsorbed onto sludge in WWTPs because of their poor water solubility and high octanol–water partition coefficients (Hanssen et al., 2013; Heberer, 2003). Due to the low degradability, considerable amounts of SMs and siloxanes remain in sludge rather than complete elimination after treatment with common technologies in WWTPs (Hori et al., 2007; Parker et al., 1999; Xu et al., 2012a). Previous studies showed that the absorption of HHCb and AHTN onto sludge contributed 50%–90% of the removal efficiencies, while 77% for D4 and 73.2%–94% for decamethylcyclopentasiloxane (D5) (Brooke et al., 2009; Guo et al., 2010; Sanchis et al., 2013). Moreover, the excess sludge is often applied as fertilizer in agriculture, which could lead to the potential dispersal of pollutants to soils, and then transferred to different environmental compartments (air and surface water, for instance) and biota (Arvaniti et al., 2012; Zeng et al., 2005). The annual amount of WWTP

sludge is estimated to be up to 1.3×10^6 tons dw, which keeps increasing at a rate of approximately 10% per year in China (Lu et al., 2012). Sewage sludge is one important transitional sink and a reservoir that should be of special concern to investigate the level, distribution, fate and release of siloxanes. So it is essential to assess the occurrences, distribution, and ecological risks of siloxanes in the sewage sludge on a large scale in China. However, to the best of our knowledge, relevant studies are scarce.

Here we investigated the levels and composition profiles of SMs and siloxanes in sewage sludge from 42 WWTPs collected from 23 representative cities in China. Then the potential factors affecting their levels in sewage sludge were assessed. Finally, we evaluated the ecological risks of SMs and siloxanes when sewage sludge was addressed to land application.

2. Materials and methods

2.1. Sample collection

The sampling map and sites are shown in Fig. 1. From October 2010 to March 2011, a total of 42 sewage sludge samples were collected from different WWTPs in 23 cities, most of which are located in relatively developed provinces in China. Freshly anaerobic digested sludge samples were collected at the dewatering process, packed in aluminum foil and sealed in polypropylene bags. The field blanks were also collected during the sampling procedure. Subsequently, the samples and the filed blanks were freeze-dried, homogenized and finally stored at -20°C prior to further analysis. Detailed information of the investigated WWTPs is given in Table 1, regarding the serving population, treatment capacity, treatment technique, and sources of effluents.

2.2. Standards and reagents

The analytes in this study included five polycyclic musks and two nitro musks, three cyclic siloxanes and 13 linear siloxanes (Table S1). NMs (MK and MX), PCMs including HHCb (Galaxolide®), AHTN (Tonalide®), ADBI

Fig. 1. Sampling locations of municipal sewage sludge samples in China.

Table 1
Details of selected wastewater treatment plants.

Sequence	Province	City	WWTPs	Treatment techniques	Sewage source	Treatment capacity (10 ⁴ m ³ /d)	Population (10 ⁴)	TOC (%)	
1	Beijing	Beijing	BJ-1	AO	Dom/ind	10	40	39	
2			BJ-2	AAO	Dom/ind	100	240	39.1	
3			BJ-3	OD	Dom/ind	108	48	37	
4			BJ-4	AAO	Dom	40	81.4	35.5	
5	Hubei	Wuhan	BJ-5	SBR	Dom	8	18	40.6	
6			WH-1	AO	Dom	24	63	7.1	
7			WH-2	AAO	Dom/ind	15	30	13.6	
8			Lanzhou	LZ	AO	Dom/ind	16	80	40.2
9	Hebei	Baoding	BD	AO	Dom/ind	16	30	16.5	
10	Heilongjiang	Jiamusi	JMS	OD	Dom/ind	20	20	35.5	
11	Shanghai	Shanghai	SH	SBR	Dom/ind	6	20	45	
12	Guangdong	Zhongshan	ZS	OD	Dom/ind	10	25	28.8	
13	Shandong	Dongying	DY	AO	Dom/ind	5	10	30.7	
14		Rizhao	RZ	SBR	Dom/ind	5	10	34	
15		Yantai	YT-1	AAO	Dom/ind	4	21	36.6	
16			YT-2	AAO	Dom/ind	2	9	37.4	
17		Qingdao	QD-1	AAO	Dom/ind	10	30	35.8	
18				QD-2	OD	Dom/ind	4	10	34.8
19		Linyi	LY-1	OD	Dom/ind	15	50	35.9	
20			LY-2	AAO	Dom/ind	5	42	29.6	
21		Laiwu	LW-1	AO	Dom/ind	4	10	20	
22				LW-2	AO	Dom	1.5	8	20.2
23		Dezhou	DZ-1	AO	Dom/ind	2	10	10.4	
24				DZ-2	AAO	Dom	2	10	16.2
25		Jining	JN-1	AAO	Dom	20	40	13.9	
26				JN-2	AAO	Dom/ind	4	20	17.2
27			JN-3	OD	Dom/ind	3	25	22.5	
28		Hunan	Changsha	CS-1	AO	Dom/ind	18	50	7.8
29			CS-2	AAO	Dom/ind	16	47.5	13.8	
30			Henan	Puyang	PY	OD	Dom/ind	10	22
31			Xinxiang	XX	AO	Dom	15	20	34.4
32		Shanxi	Xi'an	XA-1	OD	Dom/ind	8	15	29.9
33			XA-2	AAO	Dom/ind	25	50	39.1	
34				XY	OD	Dom/ind	10	15	36
35		Anhui	Hefei	HF-1	OD	Dom/ind	18	30.4	28.1
36				HF-2	OD	Dom/ind	30	30	32.4
37			HF-3	SBR	Dom	5.5	17	25.8	
38			Zhejiang	Ningbo	NB-1	AO	Dom/ind	3	5
39				NB-2	AO	Ind	–	–	–
40				NB-3	AAO	Dom	12	15	22.6
41		Hangzhou	HZ-1	AAO	Dom/ind	115	250	24.9	
42				HZ-2	AAO	Dom/ind	40	100	21.7

(Celestolide®), AHMI (Phantolide®), ATII (Traseolide®) standards and the internal standard HCB-¹³C₆ were all obtained from Dr. Ehrenstorfer (Augsburg, Germany). Surrogate standard d₁₀-fluoranthene was purchased from Supelco (Bellefonte, PA, USA). Cyclic siloxane standards (purity > 98%) including D4, D5 and dodecamethylcyclotrisiloxane (D6), linear siloxane standards (purity > 98%) including octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), polydimethylsiloxane mixture (PDMS, L5–L16), and tetrakis(trimethylsiloxy)silane (M₄Q, purity > 97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Solvents, including dichloromethane (DCM), n-hexane (HEX) and ethyl acetate and acetone, were all of high-performance liquid chromatography (HPLC) grade. Anhydrous sodium sulfate (Na₂SO₄) and silica gel (100–200 mesh) were baked at 450 °C for 4 h prior to use.

2.3. Sample pre-treatment and quantitative analysis

2.3.1. Pretreatment for SMs

The sample pretreatment procedure is similar to previously reported methods (Hu et al., 2011). Freeze-dried sludge samples were sieved through a stainless steel 50-mesh (0.3 mm) sieve, after which the weighed sample (0.1 g) was spiked with 20 µL of d₁₀-fluoranthene (100 µg/L, Surrogate standard), and then mixed with 4 g of activated silica (100–200 mesh) and 28 g anhydrous sodium sulfate. The mixture was placed into a 34 mL stainless steel extraction cell. The cells were extracted with HEX/DCM (1:1, v/v) under conditions of 60 °C and

1500 psi within two static extraction cycles (15 min of each) using an accelerated solvent extractor (ASE 350, Dionex Corporation). All extracts were concentrated to 2 mL by rotary evaporation and loaded onto a chromatography column (packed with glass wool, 3 g activated silica gel and 0.5 g anhydrous Na₂SO₄ consecutively), which was pre-conditioned by 8 mL HEX. All analytes were subsequently eluted with 5 mL HEX, 15 mL HEX/DCM (2:1), 15 mL HEX/DCM (1:2) and 20 mL HEX/DCM (1:3). The eluant was concentrated, and the solvent was exchanged with HEX into 1 mL. Finally, 100 ng internal standard (HCB-¹³C₆) was added before instrumental analysis.

2.3.2. Pretreatment for siloxanes

An ultrasound-assisted extraction procedure was employed based on a previously described method with minor modifications (Xu et al., 2012a). Briefly, 0.1 g of the sieved sample was spiked with 100 µL of 1 mg/L M₄Q solution as the internal standard. The spiked sample was extracted with 10 mL of ethyl acetate/HEX mixture (1:1) for 15 min in an ultrasonic bath, and the mixture was then centrifuged at 3500 rpm for 10 min. The collected supernatant was transferred to a new glass tube. The extraction procedure was repeated three times. The total extract was concentrated to 2 mL under a gentle stream of N₂ and then purified by passing through a cartridge packed with 1.0 g anhydrous Na₂SO₄. Finally, the eluent was concentrated to 1 mL under a gentle stream of N₂ before GC–MS analysis.

2.3.3. Instrument analysis

All target compounds were determined using a GC/MS system (Agilent 7890A GC/5975C MSD) with an electron-impact (EI) ionization source. The target analytes were separated by a 5% phenyl methyl siloxane capillary column (HP-5 ms; 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m).

The temperature of the GC injector port (splitless mode) was set as follows: 250 °C for SMs; 200 °C for L3, L4 and D4–D6; 300 °C for L5–L16, and 230 °C for the ionization source (except for L5–L16: 280 °C). Table S1 summarized mass-to-charge ratios of ions used to monitor the signal of each compound.

2.4. Quality assurance and quality control (QA/QC)

Due to the extensive use of SMs and siloxanes in consumer and laboratory products and their broad distribution in environment, a series of precautions were taken during the sample collection, pre-treatment and analysis: (1) all participants in sample extraction and analysis refrained from using PCPs (perfumes, cosmetic products and hand cleaners), and powder free nitrile gloves were used throughout the experiment; (2) sampling or storage device during field collection was made of non-silica gel materials, and all glassware was rinsed with acetone before use; (3) due to the volatility of cyclic siloxanes, the mass losses of targets during freeze-drying process were also investigated, and the results showed that the recoveries of target compounds were more than 96%. Besides, the blank samples showed that there was little cross-contamination during freeze-drying process (the levels of targets in blank samples were all below LOQ); (4) during GC/MS analysis (especially for D4, D5 and D6), low injector port temperature (200 °C) and low-bleed capillary columns (HP-5MS) were selected to minimize targets bleeding from inlet septum and capillary columns.

Good recoveries were found for the SMs (55%–107%) and siloxanes (69%–104%) in matrix spiked samples. Levels of targets in procedural blanks were 1.3–2.8 ng/g for HHCB and AHTN, and 1.0–1.7 ng/g for (D4, D5 and D6). Procedural blanks of every batch were subtracted during the quantification of concentration in sludge samples. For these above-mentioned compounds, limit of quantitation (LOQ) was determined as 10 times the standard deviation of the laboratory blank signals ($n = 7$). For compounds not detected in procedural blanks, the limit of detection (LOD) and LOQ were determined based on a signal-to-noise ratio of 3 and 10. LOQs ranged from 0.4 to 2.2 ng/g for SMs and siloxanes. The detailed materials are listed in Table S1.

2.5. Data analysis

2.5.1. Statistical analyses

Statistical analyses were performed using the statistical software SPSS 18.0. Pearson correlation analysis was used to assess the correlations among either the seven SMs or the 17 siloxanes in sludge samples. Kruskal–Wallis test and multiple linear regressions were employed to assess the impact of nonparametric and parametric variables on target concentrations in sludge samples, respectively. For all comparisons, $p < 0.05$ was considered significant.

2.5.2. Ecotoxicological risk assessment

Risk quotient (RQ) values were utilized for ecotoxicological risk assessment in digested-sludge amended soil, which are expressed as Eq. (1):

$$RQ = \frac{PEC_{soil}}{PNEC_{soil}} \quad (1)$$

where $PNEC_{soil}$ is defined as the predicted no observed effect concentration on organisms and often derived from NOEC (no observed effect concentration). PEC_{soil} values are estimated as the concentration of pollutant in soil since one year after sludge-dose application. In general,

$RQ \geq 1$ means a high risk; $0.1 \leq RQ < 1$ represents a medium risk; and $0.01 \leq RQ < 0.1$ indicates a low risk (Sañchez-Bayo et al., 2002).

The $PNEC_{soil}$ levels were 0.28 mg/kg wet weight (ww) for AHTN and HHCB (HERA, 2004). An indicative $PNEC_{soil}$ about D5 has been estimated as 0.15 mg/kg ww according to previous study (Brooke et al., 2009). $PNEC_{soil}$ about D4 was assumed as 0.15 mg/kg ww due to the long-term exposure of a similar level of toxicity in D4 and D5.

PEC_{soil} values were measured via Eq. (2) according to the European Commission Technical Guidance Document on Risk Assessment EUR 20418 EN/2 (Arvaniti et al., 2012):

$$PEC_{soil} = \frac{C_{sludge} \times APPL_{sludge}}{DEPTH_{soil} \times RHO_{soil}} \quad (2)$$

where C_{sludge} (g/kg dw) is the detected concentration of the target compound in digested sludge; $APPL_{sludge}$ is the application rate of dry sludge onto agricultural soils (usually 0.5 kg/m² year); $DEPTH_{soil}$ is the mixing depth (usually 0.20 m for agricultural soils); and RHO_{soil} is the bulk density of wet soil (usually 1.5×10^3 kg/m³ for agricultural soils).

3. Results and discussion

3.1. Concentrations and composition profiles of SMs in sludge

Concentrations of the total SMs in 42 sludge samples were in the range of 47.3 ng/g to 68.2 μ g/g dw (mean: 5.52 μ g/g) (Fig. 2). The detection frequencies (DFs) of target analytes were distinct: HHCB (95%), AHTN (98%), ATII (38%), ADBI (29%), AHMI (19%), MK (29%) and MX (14%). Spearman's correlation analysis showed strong correlations ($p < 0.01$) among PCMs (except for AHMI), as well as between PCMs and NMs (Table 2), which could suggest common sources and similar environmental fates of SMs.

We found that the composition profiles of SMs in sludge were similar in spite of different sewage sources and different districts of the WWTPs (Fig. 3a and Table 2). HHCB (63.8%) and AHTN (31.7%) were the predominant SMs in these sludge samples. This result agreed with a previous report showed that HHCB and AHTN represent approximately 90–95% of the SMs market globally, and the percentages of HHCB and AHTN were high in personal care and sanitation products (Upadhyay et al., 2011). In this study, concentrations of HHCB and AHTN varied in sludge samples from different WWTPs, ranging from <LOQ to 41.4 (mean: 3.52 μ g/g) and <LOQ to 22.0 μ g/g dw (mean: 1.75 μ g/g), respectively. The mean concentrations of HHCB and AHTN in this study were at the same levels as those from one previous study, which reported that the values of HHCB and AHTN in sludge from some WWTPs in Guangdong Province of China were 2.49 (0.270–8.42) and 1.99 μ g/g (0.524–4.50 μ g/g dw), respectively (Zeng et al., 2012). However, these mean levels were lower than those from Korea (31.2 for HHCB and 9.56 μ g/g for AHTN), New York State (88.6 for HHCB and 12.6 μ g/g for AHTN) and Hong Kong (27.1 for HHCB and 5.85 μ g/g for AHTN) (Guo et al., 2010; Reiner et al., 2007; Shek et al., 2008). The large variability in concentrations might be attributed to different consumption patterns of PCMs in fragrance products in different areas and countries.

NMs contributed little to the total SMs. Concerns over the toxicity and bioaccumulation of NMs lead to restrictions on their appliance in cosmetics. However, they were still added in many cheap consumer products, leading to their presence in environmental samples and biota (Raab et al., 2008; Smyth et al., 2008). Compared with one previous study, which reported that the mean concentrations of MX (DF: 80%) and MK (DF: 90%) were 10.4 and 46.3 ng/g in sludge from Guangdong Province of China (Zeng et al., 2012), while these two compounds in our study had lower DFs (14% for MX and 29% for MK) but higher mean concentrations exceeding LOQ (382 for MX and 359 ng/g dw for MK). The maximum levels of MX (0.362 μ g/g dw) and MK (2.54 μ g/g dw) were found in sludge from the 2nd WWTP in

Fig. 2. Concentrations of Σ SMs and Σ siloxanes in sludge samples collected from 42 WWTPs.

Hangzhou city, which indicated the presence of point source pollution of NMs nearby this WWTP.

3.2. Concentrations and composition profiles of siloxanes in sewage sludge

The total concentration in sludge extended from <LOQ to 36.0 (mean: 1.98) for cyclic (DF: 93%–95% for D4–D6), and <LOQ to 13.0 $\mu\text{g/g dw}$ (mean: 0.937 $\mu\text{g/g dw}$) for linear (L3–L16) siloxanes, respectively (Fig. 3b). The mean concentration of the total cyclic siloxanes in sludge from this study was about one order of magnitude lower than those in Nordic countries (26.0 $\mu\text{g/g}$) and Greece (20.2 $\mu\text{g/g}$) (Bletsou et al., 2013; Kaj et al., 2005). Previous studies mainly focus on the occurrence of cyclic siloxanes in sludge, whereas studies on linear siloxanes were scarce (Wang et al., 2012; Whelan, 2013). The mean value of Σ L4–L16 (0.937 $\mu\text{g/g}$) in 42 sludge samples was lower than that detected from Greece (Σ L3–L14, 53.9 $\mu\text{g/g}$) (Bletsou et al., 2013). Different consumption quantities of siloxanes among these countries or regions might explain the remarkable variance of siloxanes levels in sludge. In addition, the samples in this study were anaerobic digested sludge. Losses caused by the volatilization and degradation of siloxanes during anaerobic digestion should be the other reason for lower concentrations of siloxanes in studied sludge (Brooke et al., 2009; Dewil et al., 2006).

Generally, the cyclic siloxanes (D4–D6) had (68%) dominant concentrations in total siloxanes in this study. This result was inconsistent with the previous study which reported that the total concentrations of

linear siloxanes (L3–L14) were roughly twice higher than those of cyclic siloxanes (D3–D7) in sludge from Greece (Bletsou et al., 2013). Generally speaking, cyclic siloxanes are primarily used in daily commodities and health care products, while linear siloxanes are widely used in industrial products (Zhang et al., 2011). In this study, higher concentrations of cyclic siloxanes than linear compounds in sludge might be caused by the dominance of domestic sewage in the studied WWTPs.

The average proportions in the total cyclic siloxanes were 45%, 34% and 21% for D4, D5 and D6, respectively (Fig. 3b), which indicated that D4 was the major cyclic siloxane. The observation in this work was discordant with some previous studies: Bletsou et al. (2013) reported that the average proportion of D4 in cyclic compounds (D4–D6) was only 0.54% in sludge, and the other study from Spain showed that the shares of D4 were 20% (Companiononi-Damas et al., 2012). One significant cause might be that the production of D4 has been limited in many developed countries due to its estrogenic activity (information available in English at: <http://www.ec.gc.ca/planp2-p2plan/default.asp?lang=En&n=51567C93-1>), while there is no any restriction measure in China till now.

In this study, the median concentrations of linear siloxanes (L6–L16, excepted L11) increased with the Si–O chain length ($p < 0.05$) (Fig. 3b). The total concentration of L11–L16 (DF = 81%–95%) accounted for 84% of all the studied linear siloxanes, which might be because the adsorption capacities of linear siloxanes would increase with their Si–O chains (Kaj et al., 2005).

Table 2
Spearman's rank correlations among SMs in 42 sludge samples.

	HHCB	AHTN	ADB1	AHMI	ATII	MX	MK	Polymusks	Nitromusks
HHCB	1								
AHTN	0.996**	1							
ADB1	0.890**	0.898**	1						
AHMI	0.009	−0.016	0.141	1					
ATII	0.923**	0.927**	0.951**	−0.023	1				
MX	−0.079	−0.074	0.017	0.231	−0.053	1			
MK	0.886**	0.902**	0.942**	−0.019	0.957**	−0.008	1		
Polymusks	0.999**	0.998**	0.898**	0.003	0.930**	−0.076	0.897**	1	
Nitromusks	0.863**	0.879**	0.934**	0.018	0.938**	0.153	0.987**	0.874**	1

** Correlation is significant at the 0.01 level (2-tailed).

Fig. 3. Box-and-whisker plots of SMs and siloxanes in sludge samples collected from 42 WWTPs in China. a: SMs; b: siloxanes. The horizontal black line in the box represented the median value and the low and upper edges of the box mark, the 25th and 75th percentiles. The whiskers extending from the box show the highest and lowest values. “O” represents extreme values, which were beyond the triplication of the difference between 25th and 75th percentiles, and singular values are represented by “O”, which were beyond the 150th percentile of the difference between 25th and 75th percentiles.

3.3. Distribution patterns of SMs and siloxanes in different WWTPs and influence factors

The highest concentration of $\sum$ SMs (68.2 $\mu\text{g/g dw}$) was detected in the sludge sample from the 2nd WWTP in Hangzhou city (Fig. 2). The lowest concentration (47.3 ng/g dw) was observed in one WWTP which serves a water purification company in Dezhou city, followed by one WWTP primarily treating industrial wastewater, which serves an electroplating factory in Ningbo city (153 ng/g dw).

The highest concentrations of $\sum$ siloxanes (38.0 $\mu\text{g/g dw}$) were found in the municipal WWTPs located in Dongying city (Fig. 2). The lowest one (22.1 ng/g dw) was detected in one WWTP, which was the same WWTP with the lowest concentration of $\sum$ SMs.

Levels of SMs and siloxanes considerably varied in sludge collected from different WWTPs in this study. In order to investigate potential factors affecting target compound levels in sewage sludge, we examined related information about WWTPs, including the TOC of sludge, sources of sewage [domestic ($n = 9$), industrial ($n = 1$) and combined ($n = 32$)] and the operational conditions of WWTPs (treatment technique, treatment capacity and serving population) (Table 1).

3.3.1. SMs

Using the nonparametric Kruskal–Wallis Test, we assessed the variation of SM concentrations in sludge samples grouped by two sewage sources of WWTPs, including domestic and the combined sewage sources [WWTP serving industrial source was excluded for too limited sample ($n = 1$)]. The test showed that SM concentrations in sludge had no significant differences ($p > 0.05$) between two types of WWTPs (Table S2). Meanwhile, the SM concentration (0.153 $\mu\text{g/g dw}$) in sludge from WWTP treating industrial sewage was an order of magnitude lower than the those from other two types of WWTPs (mean: 5.48 for domestic and 3.68 $\mu\text{g/g dw}$ for the combined). A previous

study reported that SMs were mainly used as fragrances in daily life and 77% of them would be drained into the sewer system (Reiner et al., 2007). Therefore, our results indicated that through afflux of industrial wastewater, domestic wastewater might be the primary source in these WWTPs with combined sewage. In addition, we found that the mean concentrations of $\sum$ SMs in sludge samples typed by four treatment processes were within the same order of magnitude: 7.69 for AAO, 4.78 for OD, 7.89 for SBR and 2.91 $\mu\text{g/g dw}$ for AO. Furthermore, the Kruskal–Wallis vales ($p > 0.05$) showed no significant differences of their sludge concentrations among these four groups, showing that the treatment processes in the studied WWTPs had no significant effect on the SM levels in sludge.

We also examined the relationships between SM concentrations in sludge samples and parameter variables about WWTPs (TOC of the sludge, treatment capacity and serving population) by multivariate linear regression analysis (Table 3). In the multivariate models, strong positive correlations were found between SM concentrations and the serving population (standardized coefficient 0.413, $p = 0.034$) as well as TOC (standardized coefficient 0.489, $p = 0.001$). The present results might be attributed to the fact that WWTPs serving larger population are commonly situated in larger cities, where people might use more fragrance products. In addition, the lipophilicity of SMs might result in the significant influence of TOC of the sludge on SM levels.

3.3.2. Siloxanes

Similar with SMs, the nonparametric tests showed that siloxane concentrations in sludge had no significant differences ($p > 0.05$) between two groups of WWTPs with different sewage sources. According to the above result coupled with the dominance of cyclic siloxanes in sludge (68%, Section 3.2), which were mainly used in personal care product, we also could deduce that combined sewage in the studied WWTPs might be mainly from domestic wastewater.

Table 3

Coefficients from multivariate regression of total-SMs, cyclic siloxanes and linear siloxanes.

Outcome	Independent variate	Coef	Std. err.	Standardized coef	t	p
Total-SMs	TOC	173.429	45.887	0.489	3.779	0.001**
	Treatment capacity	−25.415	47.077	−0.100	−0.540	0.593
	Service population	43.669	19.800	0.413	2.205	0.034*
Cyclic siloxanes	TOC	21.768	16.341	0.160	1.332	0.191
	Treatment capacity	91.672	15.757	1.023	5.818	0.000**
	Service population	−3.182	8.491	−0.046	−0.375	0.710
Linear siloxanes	TOC	36.374	11.961	0.461	3.041	0.004**
	Treatment capacity	2.896	11.534	0.056	0.251	0.803
	Service population	1.145	4.913	0.052	0.233	0.817

* Statistically significant ($p < 0.05$).** Statistically significant ($p < 0.01$).

The mean concentrations of total siloxanes in sludge samples grouped by four treatment processes were within the same order of magnitude: 4.39 for AO, 2.75 for AAO, 2.06 for SBR and 1.80 $\mu\text{g/g}$ dw for OD, respectively. In addition, no significant difference ($p > 0.05$) of siloxane concentrations was found among those four groups. These results suggested that siloxane concentrations in sludge were not affected by these four treatment techniques, which was consistent with the SMs.

Generally, cyclic siloxanes are primarily used in daily life, while linear siloxanes mainly in industry. In our study, the main source of sewage in studied WWTPs was identified as domestic wastewater. These reasons could explain the result that cyclic but not linear siloxanes had the positive associations (*standardized coefficient* 1.203, $p = 0.000$) with treatment capacity (Table 3). The correlations between linear siloxanes and TOC in sludge samples were statistically significant (*standardized coefficient* 0.461, $p = 0.004$). However, no similar result

was observed for cyclic siloxanes. These results indicated that TOC of the sludge would have a greater impact on linear siloxanes than cyclic siloxanes, which might be because the linear siloxanes could bind to sludge with a higher affinity than cyclic siloxanes (Bletsou et al., 2013; Zhang et al., 2011).

3.4. Risk assessment

In the present study, SMs and siloxanes were detected in all digested sludge samples with high DFs and concentrations. Therefore, it was necessary to assess the ecological risk of the recycled sewage sludge to soil compartments. In this study, HHCb, AHTN, D4 and D5 were selected as the representative compounds.

The results showed that all of RQs were lower than 0.1 except for two RQs about HHCb (0.247) and AHTN (0.131) in the 2nd WWTP of

Fig. 4. RQs about HHCb, AHTN, D4 and D5 calculated from sludge as bio-soil. a: HHCb; b: AHTN; c: D4; d: D5.

Hangzhou and two RQs about D4 (0.148) and D5 (0.178) in the WWTP of Dongying city. In particular, most of RQs (17/42 for HHCB, 33/42 for AHTN, 32/42 for D4 and 39/42 for D5) were lower than 0.01 (Fig. 4a–d). Taken together, only four RQs were in the range of $0.1 \leq \text{RQ} < 1$, indicating a medium risk when the sludge in these WWTPs is recycled to farm. However, to sum up, these four studied compounds might present very low risk to the soil compartment from biosolids land application.

4. Conclusions

In this study, we investigated the levels and distribution patterns of SMs (5 PCMs and 2 NM)s and siloxanes (3 cyclic siloxanes and 14 linear siloxanes) in sewage sludge samples collected from 42 WWTPs in 23 cities of China. SMs were detected in all of the sludge samples at concentrations ranging from 47.3 ng/g to 68.2 µg/g dw. The two main components, HHCB and AHTN, accounted for 95.5% of Σ SMs. Very similar composition profiles of SMs were found in sludge samples from the all studied WWTPs, revealing their similar consumption models and extensive pollution in China. Cyclic siloxane concentrations ($< \text{LOQ} - 36.1 \mu\text{g/g dw}$) accounted for 68% of the total siloxanes, and on average, they were > 2 folds higher than linear siloxanes ($< \text{LOQ} - 13.2 \mu\text{g/g dw}$), suggesting that domestic sewage might account for significant proportions in 42 WWTPs. High concentrations and DFs of SMs and siloxanes in sewage sludge disclosed the wide-ranging pollution caused by the extensive usages of these pollutants in China. Moreover, the levels of SMs and siloxanes in sewage sludge were associated with the potential factors including TOC of the sludge, sewage composition, treatment capacity and serving population of the studied WWTPs. Also, risk assessments of the excess sludge applied as fertilizer in agriculture were performed and negligible effect was observed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.12.124>.

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