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Levels and distribution of synthetic musks and polycyclic aromatic hydrocarbons in sludge collected from Guangdong Province

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The levels and distribution of six polycyclic musks, three nitromusks and 15 polycyclic aromatic hydrocarbons (PAHs) were investigated in sludge collected from 19 municipal wastewater treatment plants (WWTPs) in six cities in Guangdong Province, China. PAHs were detected in all of the sludge samples, and the levels of the total 15 PAHs ranged from 177.2–4421.8 μg/kg dry weight (dw). Four polycyclic musks, 4-acetyl-1,1-dimethyl-6-*tert*-butylindan (ADBI), 6-acetyl-1,1,2,3,3,5-hexamethylindan (AHMI), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta (*g*) -2-benzopyran (HHCB) and 7-acetyl -1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydro naphthalene (AHTN), were found in these samples. The total concentrations of polycyclic musks varied from 794.4–12960.3 μg/kg dw, with HHCB and AHTN being the main components. Of the three nitromusks, 2,6-dinitro-3-methoxy-4-*tert*- butyl - toluene (MA) was only found in one sludge sample at the limit of detection (LOD) level, while 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) were found at levels ranging from the LOD to 65.8 μg/kg dw and LOD to 172.7 μg/kg dw, respectively, in most of the sludge samples. The PAHs, polycyclic musks and nitro musks were also shown to have various distribution patterns, possibly due to their different wastewater sources and wastewater treatment technology.

Keywords: Polycyclic musks, nitromusks, polycyclic aromatic hydrocarbon, sludge.

Introduction

PAHs are primarily produced from the incomplete combustion of organic matter during natural or anthropogenic processes, such as fossil fuels, and biomass, and are distributed extensively in all parts of the environment. Generally, PAHs in wastewater originate from industrial wastewater, domestic sewage, atmospheric precipitation, road runoff, etc. Synthetic musks are one group of emerging contaminants that have attracted increased concern from researchers and the general public due to their ubiquitous occurrence in the environment and their potential toxicity.[1]

Synthetic musks, including two major classes known as nitro musks and polycyclic musks, are widely used fragrance materials in detergents, cosmetics, shampoo, perfume, food and cigarette additives. After application, these compounds were discharged into sewage and then into surface water through effluent or into soil via sludge,[2] after which they diffused to all parts of the environment. For example, HHCB has been detected in blubber of fur seal pups and skua eggs in Antarctica.[3, 4] Consequently, synthetic musks could be used as indicators for domestic sewer contaminants.[5]

Due to their low water solubility and high hydrophobicity, PAHs and synthetic musks tend to be adsorbed onto particulates and transferred into sludge during the wastewater treatment process, which causes elevated loads in sludge.[6–8] Thomas et al.[9] further verified that synthetic musks tended to be adsorbed onto sludge during the wastewater treatment processes in laboratory-scale sorption experiments using HHCB as a representative compound.

Because sludge contains many nutrients for plants, the most effective and economic disposal of sludge is application to agricultural soil as fertilizers. When sludge is applied to soil, the pollutants contained in the sludge

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are transferred into the soil, where they can be retained for months or years because of their sorption to the soil and persistence in the environment, or bio-accumulated via food-chains.[10–12] As a result, sludge containing higher levels of contaminants is not suitable for agricultural application.

For example, sludge containing Benzo(a)pyrene (Bap) >3 mg/kg dw has already been prohibited for agricultural application by Chinese law (GB18989–2002). It is also necessary to monitor the occurrence and levels of organic/inorganic pollutants in sludge and to assess their risk for land use as well as their potential risk to human health. In this study, we determined the levels and distribution of 15 PAHs, six polycyclic musks and three nitromusks in 19 municipal WWTPs in six cities located in Guangdong Province (GD), China. In addition, their source apportion is also simply discussed based on the results of principal component analyses.

Materials and methods

Standards and chemicals

The analytes measured in this study include 16 PAHs, six polycyclic musks and three nitromusks. The 16 PAHs specified in EPA Method 610 include Naphthalene (Nap), Acenaphthylene (Ace), Acenaphthene (Dih), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoramthene (BkF), Bap, Indeno(1,2,3-cd)pyrene (IncdP), Dibenzo(a,h)anthrancene (Dib), and Benzo(g,h,i)perylene (BghiP). These standards and five perdeuterated PAHs (Nap-d_8, Ace-d_{10}, Phe-d_{10}, Chr-d_{12}, Perylene-d_{12}) were purchased from Supelco, USA (Bellefonte, PA, USA), while internal standard hexamethylbenzene (HMB) was obtained from Dr. Ehrenstofer-Schäfer. Bgm-Schlosser (Augsburg, Germany). Six polycyclic musks, 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4*H*-inden-4-one (DPMI), ADBI, AHMI, 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan (ATII), HHCB and AHTN, as well as three nitromusks (MA, MX and MK) were purchased from LGC Promochem GmbH (Mercatorstrasse, Wesel, Germany).

Dichloromethane (DCM) and *n*-hexane were of analytical grade and redistilled prior to use, while methanol was HPLC grade. Anhydrous sodium sulfate was baked at 450°C for 4h prior to use. Silica gel (80–200 mesh) and neutral alumina were Soxhlet extracted with DCM for 72h, after which they were activated at 180°C and 250°C, respectively, for 12h, deactivated with 3% redistilled water, and kept in *n*-hexane until use.

Sludge samples were collected from 19 municipal WWTPs located in six cities in GD, nine of which treated domestic sewage, two of which treated mainly industrial wastewaters, and eight of which treated mixtures of domestic and industrial wastewater with different ratios. Detailed information regarding these WWTPs is listed in Table 1.

Table 1. Information regarding the 19 studied wastewater treatment plants.

Sampling date	*Sample name*	*Composition of wastewater*	*Daily capacity (Tons/day)*	*Service area (km^2)*	*Treatment technology*	*Habitants*
2008.01.9	DTS	60% domestic wastewater	150000	12.89	A/A/O	600,000
2008.01.9	FSD	90% domestic wastewater	200000	31.8	UNITANK	237,000
2008.01.9	NHPZ	100% domestic wastewater	50000	32.5	BAF	290,000
2008.01.9	FSZA	100% domestic wastewater	200000	28.55	A/A/O	390,000
2008.01.9	NH	100% domestic wastewater	25000	15	OD	80,000
2008.01.9	LD	100% domestic wastewater	750000	66.5	AB	1,200,000
2008.01.9	SGSC	almost industrial wastewater	100000	9.9	A/A/O	79,000
2008.01.9	ZHGB	almost domestic wastewater	128000	25	A/A/O	250,000
2008.01.17	JMWC	100% domestic wastewater	200000	23	A/A/O	350,000
2008.01.17	JM	100% domestic wastewater	40000	10.8	UBAF	130,000
2008.01.17	SZLF	75% domestic wastewater	350000	16.25	AB	650,000
2008.01.17	ZHGD	70% domestic wastewater	48000	7	SBR	150,000
2008.01.17	SZBH	91.5% domestic wastewater	300000	27.5	OD	540,000
2008.01.17	SZNS	60% domestic wastewater	736000	103	MUCT	121,6800
2008.03.13	DG	100% domestic wastewater	200000	62.95	SBR	499,600
2008.03.13	KFQD	20% domestic wastewater	25000	7	SBR	23,100
2008.03.13	KFQ	25% domestic wastewater	30000	7.86	AS	60,000
2008.03.13	XT	100% industrial wastewater	100000	1.4	OD	unconfirmed
2008.03.13	FSSG	100% domestic wastewater	50000	13	CASS	150,000

AS-Activated sludge; OD-oxidation ditch; SBR-sequencing batch reactor; CASS-cyclic activated sludge system; MUCT-modified University of Cape Town; A/A/O-anaerobic/anoxic/oxic; BAF-biological aerated filter; AB-adsorption biodegradation; UBAF-upflow-biological aerated filter.

Sample clean-up and determination

About 1 g of dried sludge from each sample was spiked with five perdeuterated PAHs as surrogates, after which the samples were Soxhlet-extracted with DCM for 72 hours. Activated copper was then added to the flask for desulphurization. The extracts were then concentrated with an evaporator rotator to approximately 1 mL, after which the solvent was exchanged with *n*-hexane and reduced to 0.5–1 mL. The achieved extracts were then loaded on a combined column of silica gel and alumina (2:1), after which they were eluted with organic solvents of different polarity. A detailed description of the elution and concentration process has been published elsewhere.[13] The collected fractions were added with a known aliquot of HMB as internal standard before instrumental analysis.

Determination and quantification of synthetic musks were conducted using a Shimadzu 2010 gas chromatography equipped with a mass spectra detector and a DB-5 ms column (30 m × 0.32 mm I.D × 0.25 μm film) (Agilent Technology). The oven temperature was programmed as follows: 80°C for 1 min, followed by an increase of 5°C /min to 150°C, then 1°C /min to 180°C and 10°C /min to 300°C, where it was held for 15 min. N_2 was applied as the carrier gas at 37 cm/sec, and the injection was at split/splitless mode at 270°C. The mass spectrometer was operated in selected ions mode with EI-mode, and the source temperature was set at 180°C.

Determination and quantification of PAHs was also conducted using the same instrument under similar conditions, except that the following temperature program was used: 70°C hold for 2 min, followed by an increase at 3°C /min to 295°C, where it was held for 15 minutes.

Quality assurance and quality control

For quality assurance and quality control, method blanks ($n = 4$), spiked blanks ($n = 6$, spiked standards into solvent), spiked matrix ($n = 6$, spiked standards into pre-extracted sediment) and duplicate samples ($n = 4$) were analyzed with real samples in each batch of ten samples. Ten microliters of a mixture of five perdeuterated PAHs at a concentration of 20 μg/mL were spiked into every sample as surrogate standards. The recoveries of the perdeuterated PAHs were 71.15±9.35% for Ace-d_{10}, 74.18±7.95% for Phe-d_{10}, 83.37±10.58% for Chr-d_{12} and 63.51±7.50% for Perylene-d_{12}. Because the recoveries of Nap-d8 were low, the values of Nap were not reported in this study.

Except for Phe, which was detected at levels below the limit of detection (LOD) in one of the four method blank samples, no other individual PAH was detected in the blank samples. For synthetic musks, no D_3-AHTN was added as a surrogate because partial D-H exchange occurred during GC-MS analysis.[14] Therefore, the method performance was evaluated based on the recoveries of synthetic musks from spiked blank samples ($n = 6$, spiked standards into solvent) and spiked matrix samples ($n = 6$, spiked standards into pre-extracted sediment), which were spiked with 10μL mixture of analytes at concentration of 20μg/mL. The recoveries ranged from 50.90±5.64%–97.19±5.67% depending on the compounds.

Results and discussion

Levels and source of synthetic musks in sludge samples

The levels and distribution of six polycyclic musks and three nitromusks are listed in Table 2. Among the six polycyclic musks, no ATII or DPMI was found in any of the samples, while traces of AHMI at the LOD level were measured in all samples. ADBI was found in all of the sludge samples at levels ranging from the LOD–43.4 μg/kg dw, and HHCB and AHTN were the predominant components in the sludge samples, being present at levels ranging from 270.0 to 8421.2 μg/kg dw and 524.4 to 4498.4 μg/kg dw, respectively.

The highest total polycyclic musks concentration was detected from KFQ (12,960.3 μg/kg dw), followed by those from JM (8316.8 μg/kg dw) and SZNS (5886.5 μg/kg dw). The lowest level was found from XT (794.0 μg/kg dw), which primarily treated industrial wastewater. The levels of total polycyclic musks observed in this study were comparable to those in Canada and Germany,[15–17] but almost one magnitude lower than those observed in Hong Kong.[18]

The three nitromusks analyzed in this study were MX, MK and MA, which are two- or three-fold nitrated benzene derivatives with an additional substituent group (alkyl, keto, or methoxyl, respectively). Nitro musks have attracted increasing attention due to their occurrence in the environment and their toxicity to aquatic life. In 1998, MX was included in the third list of contaminants for priority action of the EU and the OSPAR Commission due to its being carcinogenic to animals, while MK is suspected to improve carcinogenic effects of other chemicals; consequently, nitromusks have gradually been replaced by polycyclic musks.[19]

However, their addition to some inexpensive cosmetic and domestic products still occurs due to their low cost.[20, 21] Indeed, it has been reported that two nitromusks (MX and MK) and two polycyclic musks (HHCB and AHTN) accounted for 95% of the musks used in perfume market,[15] therefore, these nitromusks are still detected in environmental samples and in humans.[15,16, 22–24] In this study, MK was detected at the LOD–172.7 μg/kg dw in all of the WWTPs except for XT, while MX was found at the LOD–65.8 μg/kg dw in all of the WWTPs except for SGSC. MA was only detected in one sample (KFQD) at the LOD level. The concentrations and use patterns of nitromusks were comparable to those of previously conducted studies.[15,24]

Table 2. Concentration and distribution of synthetic musks in sludges (μg/kg dw).

	AHMI	*ADBI*	*HHCB*	*AHTN*	*MK*	*MA*	*MX*
DTS	LOD	43.4	3299.1	2533.6	60.48	ND	6.97
FSD	LOD	13.4	1037.8	746.9	15.70	ND	4.20
NHPZ	LOD	11.9	1018.1	1164.5	LOD	ND	11.7
FSZA	LOD	18.5	1470.8	1301.6	32.8	ND	4.9
NH	LOD	18.9	1678.1	1198.3	14.8	ND	2.7
LD	LOD	25.9	2167.5	1609.7	45.7	ND	3.7
SGSC	LOD	6.2	624.9	709.8	LOD	ND	ND
ZHGB	LOD	19.1	1771.2	1460.3	58.2	ND	11.4
JMWC	LOD	15.9	2889.7	2579.7	51.4	ND	6.3
JM	LOD	22.6	4427.3	3866.9	21.2	ND	2.8
SZLF	LOD	34.1	2256.1	2095.9	80.4	ND	7.6
ZHGD	LOD	21.2	2540.5	1763.0	LOD	ND	3.8
SZBH	LOD	36.2	2328.0	1653.8	64.4	ND	4.4
SZNS	LOD	46.5	3146.4	2693.6	88.3	ND	29.4
DG	LOD	20.4	1862.1	1709.1	62.6	ND	16.2
KFQD	LOD	21.1	4155.8	3863.2	172.7	LOD	65.8
KFQ	LOD	40.7	8421.2	4498.4	101.2	ND	13.7
XT	LOD	LOD	270.0	524.4	ND	ND	1.2
FSSG	LOD	4.9	1857.8	1768.5	10.4	ND	LOD

AHMI:6-acetyl-1,1,2,3,3,5-hexamethylindan
ADBI:4-acetyl-1,1-dimethyl-6-*tert*-butylindan
HHCB:1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyran
AHTN:7-acetyl -1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydro naphthalene
MX: 1-*tert*-butyl- 3,5-dimethyl-2,4,6 -trinitro benzene
MK: 4-acetyl-1-*tert*-butyl- 3,5-dimethyl -2,6- dinitrobenzene
MA-2,6-dinitro-3-methoxy-4-*tert*-butyl– toluene

Principal components analysis of synthetic musks

Principal components analysis (PCA) was conducted using SPSS software 13.0 to assess the synthetic musks loading in these sludge samples. It should be noted that AHMI was excluded because it was only present at the LOD level. The PCA results (Fig. 1a) indicated that 86.8% of the variance could be explained by two principal components. Principal component 1 (PC1) represented 68.1% of the total variance, while PC2 represented 18.7%. PC1 represented the polycyclic musks HHCB and AHTN, which are widely used as fragrance materials in household products and personal products. PC2 represented the nitromusks MX and MK, which are still added to inexpensive cosmetics and detergents due to their low cost.

The 19 WWTPs could be divided into three distinctive groups based on the two principal components (PC1 and PC2). The PCA results (Fig. 1b) indicated that 99.95% of the variance could be explained by two principal components. PC1 represented 97.6% of the total variance, which was related to the contribution of HHCB to the total concentrations of synthetic musks detected in sludges. In addition, PC2 represented 2.35% of the total variance, which was related to the contribution of nitromusks (MK and MX) to the total concentrations of synthetic musks detected in sludges. Specifically, Group 1 included one WWTP (KFQD), in which higher levels of nitromusks (MK and MX) were detected.

Specifically, MK and MX accounted for approximately 3% of the total loading of the synthetic musks. These results can be ascribed to the fact that there is a large amount of industrial wastewater from detergent and household products manufacturing factories. KFQ belongs to Group 2, from which the percentage of HHCB accounted for more than 64% of the total synthetic musks. This WWTP received 70% industrial wastewater, much of which was from several cosmetic plants. Previously, we have found high loading of HHCB (33.54μg/L) and AHTN (5.97 μg/L) in effluent from one of these cosmetic plants.[25] Group 3 consists of the remaining WWTPs, which originated from different sources showing different compositions of polycyclic musks and nitromusks.

Levels and source of PAHs in sludge samples

Due to the poor recoveries of Nap from the blank-spiked samples and matrix-spiked samples, the concentrations of Nap in sludge samples were not reported in this study. The concentrations and distribution of 15 PAHs were given in Table 3. The sum of the total 15 PAHs ($\sum$PAHs) ranged from 177.2 to 4421.8 μg/kg dw with an average value of 1276.1 μg/kg dw. The highest level, 4421.8 μg/kg dw, was measured at FSD, which collected almost 90% domestic sewage combined with 10% of industrial wastewater from ceramic factories and stainless steel factories. The second

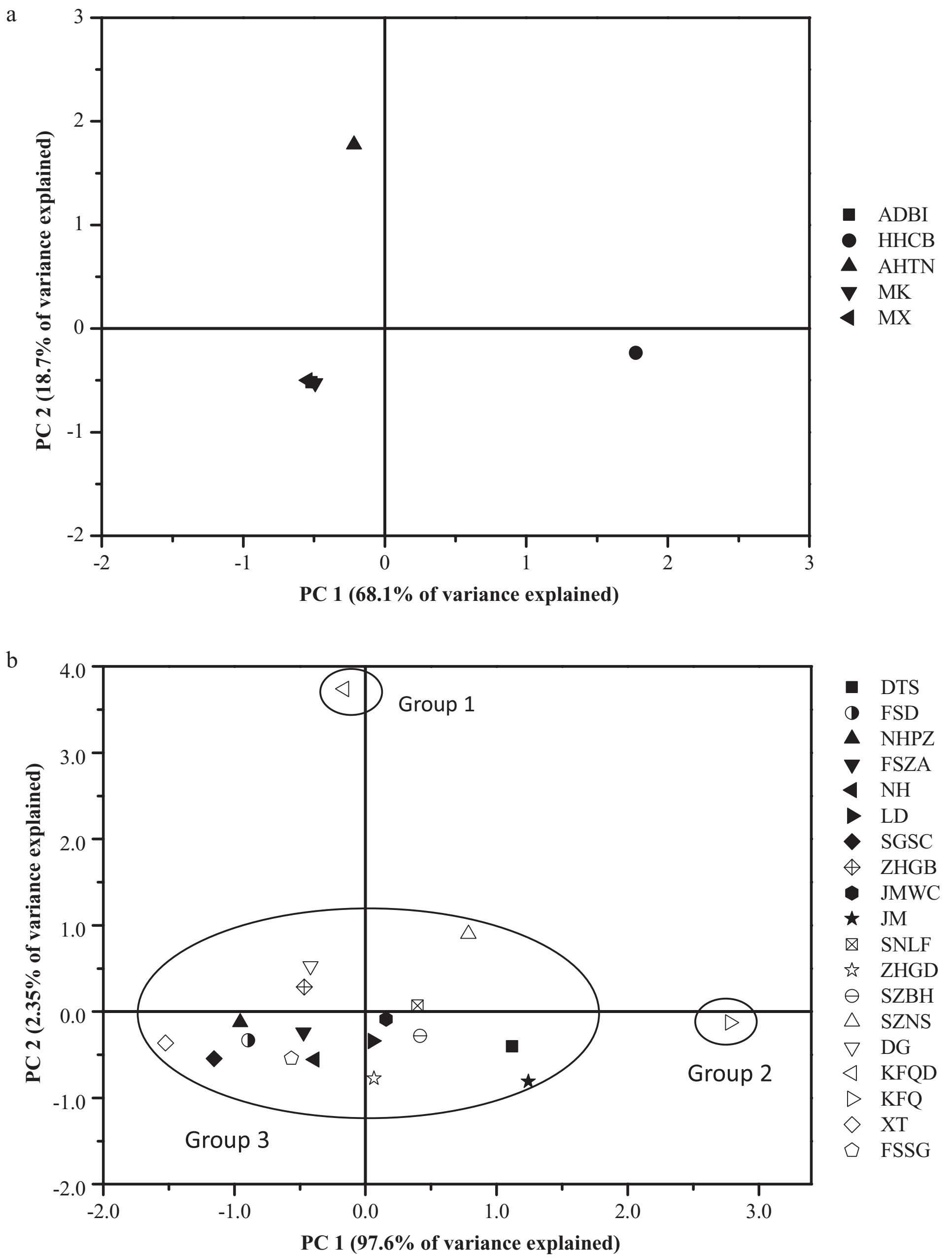

Fig. 1. Principal component analyses for the distribution of synthetic musks (a) 5 synthetic musks; and (b) 19 WWTPs.

highest value (3294.1 μg/kg dw) was found at NHPZ, followed by SZNS (1749.9 μg/kg dw). The lowest level of 177.2 μg/kg dw was measured at ZHGB.

The levels of PAHs were similar to those detected in six WWTPs from Guangzhou City in our previous study,[13] as well as those of previously conducted studies.[12, 26–31] We also found that the PAH levels in this study were much lower than those in previously published studies. For example, Cai et al.[30] studied the occurrence and distributions of 16 PAHs in sludge samples collected in 11 cities in China including four cities in GD, including Guangzhou, Foshan, Zhuhai and Shenzhen, and found considerably higher concentrations of 15 PAHs (1400–31,900 μg/kg) in these WWTPs. Ju et al.[32] reported rather high concentrations of 1240–44,900 μg/kg dw with a mean of 10,400 μg/kg dw in six sludge samples collected along the Nakdong River in Korea.

The European Union (EU) has suggested a limited value for 10 PAHs ($\sum$10PAHs) of 6000 μg/kg dw for sludge application to agricultural land, which includes Ace, Phe, Flu, Flua, Pyr, BkF, BbF, BaP, BghiP and Ind. In this study, the concentrations of the $\sum$10PAHs in these sludges

Table 3. Concentration and distribution of PAHs found in sludges (μg/kg dw).

	Ace	*Dih*	*Flu*	*Phe*	*Ant*	*Flua*	*Pyr*	*BaA*	*Chry*	*BbF*	*BkF*	*BaP*	*Ind*	*BghiP*	*DiB*	$\sum PAHs$
DTS	10.6	6.4	29.9	138.5	26.3	168.8	158.8	82.3	183.5	152.8	42.3	72.2	27.9	16.2	6.7	1123.2
FSD	21.1	5.2	37.8	112.7	65.4	135.1	144.2	287.6	391.8	927.3	899.8	573.6	296.1	418.2	106.0	4421.8
NHPZ	11.7	21.4	122.9	798.4	70.3	498.0	668.0	146.9	449.6	190.2	47.9	78.6	69.6	101.1	19.4	3294.1
FSZA	13.7	3.3	12.0	43.8	12.1	28.2	34.4	21.4	99.9	164.2	27.7	94.8	106.9	154.4	27.8	844.9
NH	3.0	7.1	11.4	36.1	7.9	25.7	40.6	24.9	63.7	41.8	10.0	21.6	23.6	33.6	6.3	357.4
LD	6.2	2.5	10.7	76.3	12.2	92.7	97.6	52.0	120.2	103.4	27.5	49.3	48.2	66.9	12.3	778.2
SGSC	2.1	0.9	3.6	20.6	3.5	15.0	21.6	9.8	49.9	28.5	27.9	16.3	14.3	21.0	5.3	240.4
ZHGB	3.0	1.0	4.5	21.6	3.5	12.5	17.6	7.5	37.6	19.0	4.4	12.9	10.9	17.7	3.5	177.2
JMWC	8.0	2.7	18.8	120.3	17.4	88.5	99.1	49.5	186.0	133.1	33.9	113.8	60.9	52.4	16.5	1000.8
JM	6.3	7.9	51.4	267.6	28.6	180.1	193.3	55.3	137.0	88.0	19.3	40.7	41.9	63.6	8.8	1189.9
SNLF	6.1	3.2	12.1	69.7	9.7	99.1	98.7	33.5	93.6	84.1	24.5	49.7	41.3	52.7	9.0	687.0
ZHGD	10.9	5.5	31.8	246.8	32.9	168.0	343.3	68.8	245.3	129.8	34.2	74.6	61.8	84.8	15.8	1554.3
SZBH	7.5	6.2	44.1	247.6	36.3	168.6	201.3	65.2	121.3	103.3	23.0	50.1	41.1	49.6	11.6	1176.7
SZNS	10.5	11.5	60.8	474.8	51.1	268.4	311.7	80.8	159.3	102.6	27.4	61.9	48.2	68.2	12.5	1749.9
DG	12.1	5.2	22.0	118.2	22.8	81.1	85.0	46.2	195.5	172.2	46.9	99.8	90.6	142.1	20.2	1159.7
KFQD	6.9	5.8	30.5	191.1	24.2	120.8	486.3	55.8	172.7	73.4	47.4	36.9	23.1	43.3	8.2	1326.5
KFQ	10.2	5.9	32.5	185.2	18.1	93.9	149.9	30.6	75.9	55.3	11.2	25.4	22.4	41.3	5.2	762.9
XT	5.9	16.5	46.5	277.8	47.5	127.9	329.1	96.8	198.7	51.5	15.7	66.8	12.3	32.2	15.0	1340.1
FSSG	8.9	3.0	16.4	94.1	17.6	71.7	101.5	47.9	239.4	134.8	34.8	82.3	70.7	110.9	27.3	1061.2

Ace-Acenaphthylene; Dih-Acenaphthene; Flu-Fluorene; Phe-Phenanthrene; Ant-Anthracene; Flua-Fluoranthene; Pyr-Pyrene; BaA-Benzo(a)anthracene; Chr-Chrysene; BbF-Benzo(b)fluoranthene; BkF-Benzo(k)fluoramthene; Bap-Benzo(a)pyrene; IncdP-Indeno(1,2,3-cd)pyrene; Dib-Dibenzo(a,h)anthrancene; BghiP-Benzo(g,h,i)perylene.

ranged from 124.2–3565.8 μg/kg dw. Moreover, no sludge samples had Bap values exceeding the maximum limit of 3000 μg/kg dw as suggested by Chinese legislation (GB18989–2002). Taken together, these results implied a relatively low risk associated with their agricultural land use.

The concentrations of the individual PAHs can be seen in Table 3. For most of these samples, 3-ring and 4-ring PAHs such as Phe, Flua, Pyr and Chry were the abundant components, which reflected their main origin of extensive traffic.[13,33] Conversely, in the sludge samples collected from FSD and FSZA located in Foshan, 5-ring and 6-ring PAHs accounted for more than 60% of the $\sum$15PAHs, suggesting that they have similar wastewater sources. In 2009, Ju et al.[32] also observed that Pyr, BbF and BaP were dominant in two of six sludge samples.

Principal component analysis for PAHs

PCA for PAHs was also conducted using the SPSS software 13.0 to assess the PAHs profile in these sludge samples. The results (Fig. 2a) indicated that 92.2% of the variance could be explained by two principal components. Specifically, PC1 represented 58.4% of the total variance, while PC2 represented 33.8%. PC1 might be ascribed to higher molecular weight PAHs, such as BghiP, IncdP, BaP, BaA and Flua, which are formed by pyrogenic processes at high temperature.[13,34, 35]

In addition, PC2 was likely primarily associated with 2-ring and 3-ring PAHs, including Dih, Flu, Ace, Ant, and Phe. It has been reported that Phe was a very thermodynamically stable compound primarily derived from uncombusted petroleum products such as gasoline, diesel and fuel oil. Additionally, Dih, Ace and Flu are known to be produced from the combustion of organic materials at low temperature. Based on this information, PC1 might represent PAHs originating from petroleum and household activities.

The 19 WWTPs studied could be divided into three groups based on the results of PCA. PC1 was related to the contribution from 5-ring and 6-ring PAHs to the average values from 19 sludge samples, while PC2 was related to those of 3-ring and 4-ring PAHs in these sludges. FSD showed a distinct pattern of PAHs, with higher levels of the total 5-ring and 6-ring PAHs accounting for more than 70% of the $\sum$15PAHs. These results implied that the water they treated had obviously different origins from the other WWTPs; however, its source has yet to be identified.

Higher contents of 2-ring and 3-ring PAHs were detected for NHPZ, such as Phe, followed by Flua and Pyr. These results suggested that PAHs in this sludge sample primarily originated from petroleum. The remaining WWTPs could be grouped in one class, which were dominated by 4-ring and 5-ring PAHs, with BbF, BkF and BghiP being the representative compounds. These findings indicated that their primary source was pyrogenic processes.[35]

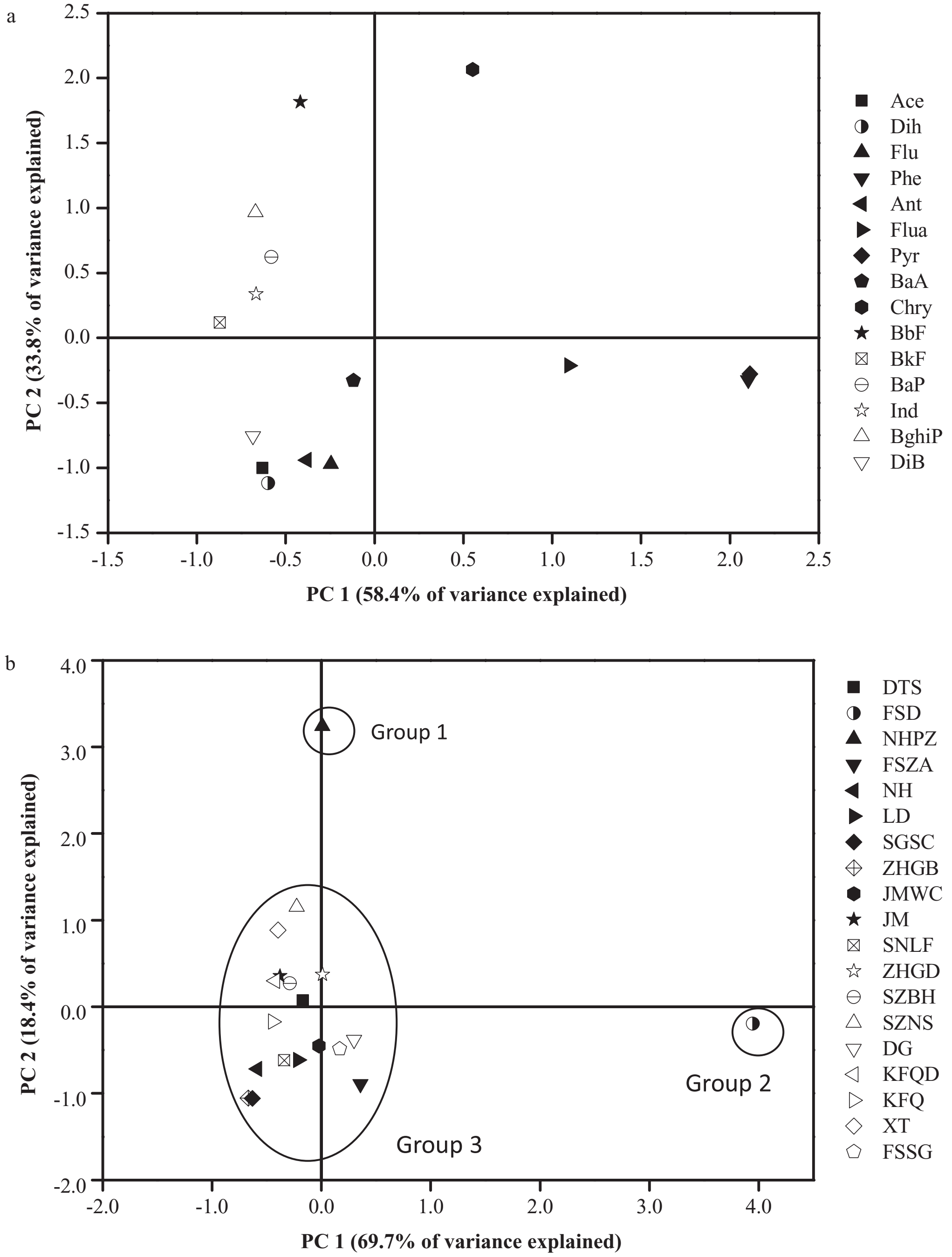

Fig. 2. Principal component analyses for the distribution of PAHs (a) 15 PAHs; and (b) 19 WWTPs.

Conclusions

In summary, the levels, distributions and preliminary sources of PAHs, polycyclic musks and nitromusks were analyzed in 19 sludge samples of six cities collected in the GD. PAHs were found in all sludges at concentrations ranging from 177.2 to 4421.8 μg/kg dw, with two primary sources, road traffic and pyrogenic processes. Four polycyclic musks were found in most of these samples, with HHCB and AHTN being the main components, which were mainly derived from domestic wastewater. Evaluation of the nitromusks revealed that MK and MX were identified in most of these samples, suggested that MK and MX are still used in the GD. Further studies should be carried out to investigate their occurrence, transformation, degradation and removal in soil to which sludge was applied.

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