Environ Monit Assess (2010) 169:89–100
DOI 10.1007/s10661-009-1153-9

Occurrence and distribution of polycyclic aromatic carbons in sludges from wastewater treatment plants in Guangdong, China

**Xiangying Zeng · Zheng Lin · Hongyan Gui ·
Wenlan Shao · Guoying Sheng ·
Jiamo Fu · Zhiqiang Yu**

Received: 30 December 2008 / Accepted: 18 August 2009 / Published online: 16 September 2009

Abstract In this study, the occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) were investigated in six sludge samples collected from Guangdong Province, China. Concentrations of PAHs varying from 2,534.1 to 6,926.6 μg kg^{-1} (dry sludge) were observed in three municipal wastewater treatment plants with phenanthrene (Phe), fluoranthene, and pyrene being the main compounds. In addition, 682.6 μg kg^{-1} PAHs were detected in one sludge sample from a food processing plant, with fluorene, Phe, and chrysene being the main components. No PAHs were detected in sludge samples obtained from two cosmetic plants. The levels and distributional characteristics of PAHs, polychlorinated biphenyls (PCBs), and polycyclic musks (PMs) from the samples were also compared. The results of this comparison indicated that petrochemical refineries and road traffic played important roles in the PAH loads in sludge, while PMs primarily originated from domestic wastewater and industrial wastewater from cosmetic plants. Finally, the presence of 98.8 μg kg^{-1} PCBs in sludge suggested diffusional emission sources from electrical components containing PCBs.

Keywords PAHs · PCBs · PMs ·
Domestic wastewater · Industrial wastewater

Introduction

The Pearl River Delta (PRD) located in southern China has become one of the most rapidly developing regions in China. Due to the rapid devel opment of industrial and agricultural activities as well as the high level of urbanization, the pollution status in this region has become serious. Extensive studies have revealed serious contamination of the air, water sediment, soil, and biota of this region PAHs, polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), organochlorinated pesticides (OCPs), and polychlorinated biphenyls (PCBs; Zhang et al. 2007). However, to the best of our knowledge, little is known about the levels and distributions about these pollutants in sewage sludge collected from the PRD (Cai et al. 2007).

X. Zeng · Z. Lin · W. Shao · G. Sheng ·
J. Fu · Z. Yu (✉)
State Key Laboratory of Organic Geochemistry,
Guangzhou Institute of Geochemistry, Chinese
Academy of Sciences, Guangzhou, China
e-mail: zhiqiang@gig.ac.cn

H. Gui
The Wastewater Treatment Plant of Guangzhou
Economic and Technological Development District,
Guangzhou, China

It is well known that PAHs originate from the incomplete combustion of organic materials, particularly fossil fuels. After being emitted from vehicles, domestic heaters, and power plants, PAHs may enter wastewater treatment plants (WWTPs) through industrial wastewater, domestic sewage, urban runoff, or atmospheric deposition. Due to their low solubility in water and high hydrophobicity, PAHs tend to be adsorbed onto particles during wastewater treatment, which results in their being concentrated in sewage sludge (Chang et al. 2003; Manoli and Samara 2008). Because sludge contains many nutrients for plants, such as N, P, and K, the most effective and economical method of sewage sludge disposal is application to soil as fertilizer. However, when sludge is used as fertilizer or disposed of in landfills, pollutants concentrated in the sludge such as PAHs, OCPs, PCBs, and inorganics (e.g. heavy metals) are introduced into soil. These pollutants may have adverse effects in soil or accumulate in crops or vegetables (Donato et al. 2006; Oleszczuk 2006; Mannino and Orecchio 2008). Therefore sludge should be monitored for the occurrence and levels of these compounds because it is one of the primary pathways through which these pollutants enter the environment and human bodies. Indeed, it has been demonstrated that PAHs primarily impact humans through food (Oleszczuk and Baran 2004).

Previously, we reported the occurrence and distribution of one group of emerging contaminants, polycyclic musks (PMs), in six sludge samples collected from different WWTPs in Guangdong Province (Zeng et al. 2005). In the present study, we evaluated the levels and the distributions of PAHs in these sludges. In addition, we distinguished the levels and different origins of PAHs, PCBs, and PMs from these sludges.

Experimental

Standards and reagents

The following 16 PAHs, which are the priority pollutants specified by EPA Method 610, were evaluated in this study: 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), benzo(a)pyrene (Bap), indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthrancene (Dib), and benzo(ghi)perylene (BghiP). These standards and five perdeuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were obtained from Supelco (Bellefonte, PA, USA). The internal standard, hexamethylbenzene (HMB), was obtained from laboratories of Ehrenstofer-Schäfer Bgm-Schlosser (Augsburg, Germany).

Analytical grade dichloromethane (DCM), *n*-hexane and acetone were re-distilled using a glass system prior to use. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet extracted by DCM for 72 h, dried at room temperature, baked for 12 h at 180°C and 250°C, respectively, deactivated with 3% re-distilled water, and then stored in *n*-hexane until use. Anhydrous sodium sulfate was dried at 450°C for 6 h prior to use.

Three waste sludge samples, GD_1, GD_2, and GD_3, were collected from three different municipal WWTPs in Guangdong Province. In addition, two samples (A and B) were collected from WWTPs attached to cosmetics plants and one sample (C) was collected from a food manufacturing factory. One duplicate sample from each plant was also collected and analyzed. All samples were stored −20°C until analysis. The detailed information regarding these samples has been reported in our previous study (Zeng et al. 2005).

Extraction and separation

Prior to extraction, the sludge samples were freeze-dried and then ground finely to pass through a 30-mesh sieve. For PAH analyses of these samples, the extraction and separation procedures were conducted according to Luo et al. (2004). Briefly, approximately 1 g of each sample was spiked with a known amount of perdeuterated PAHs and then Soxhlet extracted for 72 h with DCM. Activated copper was then added to the flask to remove the sulfur from the extract. Next, the extract was concentrated by rotary evaporation to approximately 1 ml, after which the solvent was exchanged with *n*-hexane and reduced to 0.5 ml under a gentle N_2 stream. The concentrated extract was then loaded onto a combined column of silica gel/alumina (2:1), and subsequently eluted with *n*-hexane and a mixture of *n*-hexane/DCM (7:3). The PAHs were collected in the second fraction, which was concentrated to 0.5 ml, exchanged with *n*-hexane, concentrated again to 0.5 ml and adjusted to 0.2 ml under a gentle stream of nitrogen. A known aliquot of the internal standard, HMB, was added prior to gas chromatography (GC) and GC-mass spectrometer (MS) analysis.

Instrumental analysis

Identification and quantification of PAHs were conducted using a Platform II Gas Chromatography–Mass Spectrometer with a 30 m × 0.25 mm I.D × 0.25 μm film (Agilent Technology) fused silica capillary column (DB-5). The temperature program was set as follows: 80°C for 1 min, followed by an increase to 295°C at 3°C min^{-1}, where it was held for 15 min. The mass spectrometer was operated in selective ion monitoring mode and EI-mode with a source temperature of 180°C. Data acquisition and processing were conducted using Masslynx v 2.3, and 15 PAHs (all of the aforementioned except for Nap) were quantified using the internal calibration method based on five-point curves for each compound.

To evaluate the loss of the analytes during the treatment and analysis procedures, a blank sample (solvent), a spiked blank (spiked standards into solvent), a spiked matrix (pre-extracted sludge spiked with standards), and a duplicate sample were analyzed with each batch of actual samples. In addition, to monitor the procedural performance and matrix effects, perdeuterated PAHs were added to every sample as surrogate standards. The recoveries of the perdeuterated PAHs were 63.9 ± 2.3% for acenaphthene-d_{10}, 91.9 ± 3.0% for phenanthrene-d_{10}, 83.3 ± 9.7% for chrysene-d_{12}, and 71.4 ± 13.7% for perylene-d_{12}, while the recoveries for naphthalene-d_8 were low and not reported in this study. No PAHs were detected in the blank samples.

Results and discussion

Levels of PAHs in sludge samples

The concentrations of PAHs in the sludge samples are listed in Table 1. Because the recoveries of Nap from blank-spiked samples and matrix-spiked samples were low, the concentrations of Nap in sludge samples were not reported in this

Table 1 Concentrations of PAHs in six sludge samples μg kg^{-1}

Compounds	Samples					
	GD1	GD2	GD3	A	B	C
Ace	6.7	25.1	0.8	ND	ND	LOD
Dih	40.4	33.7	90.6	ND	ND	17.9
Flu	139.6	43.9	693.3	ND	ND	65.8
Phe	542.6	1,209.7	2,247.5	ND	ND	249.0
Ant	56.8	156.5	459.1	ND	ND	LOD
Flua	301.5	571.0	1,304.5	ND	ND	21.1
Pyr	572.4	677.4	1,192.0	ND	ND	59.9
BaA	130.9	176.0	LOD	ND	ND	LOD
Chr	214.5	298.0	10.8	ND	ND	194.9
BbF	229.5	312.7	55.8	ND	ND	50.5
BkF	45.0	64.9	205.3	ND	ND	21.1
BaP	14.8	10.2	LOD	ND	ND	2.4
Ind	61.5	139.1	310.5	ND	ND	LOD
Dib	3.4	5.9	326.1	ND	ND	LOD
BghiP	174.5	LOD	30.3	ND	ND	LOD
∑PAHs	2,534.1	3,724.1	6,926.6	ND	ND	682.6

study. As shown in Table 1, no PAHs were observed in sample A or B, which were collected from cosmetic manufacturing plants. In these plants, the primary products are detergents and personal care products. The manufacturing procedures used at these plants do not involve heat or the combustion of organic matter; therefore, it is reasonable to assume that no PAHs are produced in these two plants.

As shown in Table 1, the concentration of the total 15 PAHs (ΣPAHs) was 682.6 μg kg^{-1} for sample C. As mentioned in our previous report (Zeng et al. 2005), the wastewater treated by this WWTP primarily originates from food processing facilities, although it also includes a small amount of domestic sewage produced by workers living in the workshop. The foods produced in this plant include baked biscuits, milk, and related products and beverages. Therefore, the PAHs produced in this study were formed and released from the incomplete combustion or thermal processing of organic materials during food processing (Djinovic et al. 2008). These results were also consistent with those of a study conducted by Poster et al. (2006), who found that the thermal processing of biomass was the primary source of PAHs in the environment.

The concentrations of ΣPAHs in GD$_1$, GD$_2$, and GD$_3$ were 2,534.1, 3,724.1, and 6,926.6 μg kg^{-1}, respectively. These levels of PAHs are similar to those of municipal sludges evaluated in other studies (Perez et al. 2001a; Stevens et al. 2003; Blanchard et al. 2004; Busetti et al. 2006; Harrison et al. 2006; Villar et al. 2006; Dai et al. 2007). For example, Perez et al. (2001a) found 3,940 and 5,520 μg kg^{-1} PAHs in sludge from a WWTP in Spain that received domestic sewage water exclusively. In addition, Dai et al. (2007) detected 2,467.31∼2,5923.79 μg kg^{-1} ΣPAHs in six sewage sludges collected in Beijing in 2004 to 2005, with the highest concentration being observed in a WWTP that received wastewater from the steel and dyeing industry. However, Cai et al. (2007) found 1.4∼30 mg kg^{-1} ΣPAHs in four sewage sludge samples collected from Guangdong Province in 1998 to 1999, which was much higher (except for Shenzhen WWTP) than the results observed in the present study.

The European Union has released a draft directive suggesting that the sum of PAHs (Σ10 PAHs), including Ace, Phe, Flu, Flua, Pyr, BkF, BbF, BaP, BghiP, and Ind, should not exceed 6,000 μg kg^{-1} in sewage sludge to be applied to agriculture (Perez et al. 2001a; Cai et al. 2007). In our study, the Σ10 PAHs varied from 469.8 to 6,040 μg kg^{-1}, with the highest value (6,040 μg kg^{-1}) being found in GD$_3$. This value was close to the limit proposed by the EU and suggests that there is a potential risk of contamination associated with the application of this sludge to land. The results of the present study are similar to the results of previously conducted studies (Blanchard et al. 2004; Harrison et al. 2006; Cai et al. 2007; Dai et al. 2007).

Of the 16 PAHs evaluated here, seven (BaA, Chr, BbF, BkF, BaP, Ind, and Dib) are carcinogenic. In this study, the total concentrations of these PAHs (Σ7 PAHs) ranged from 268.9 to 1,006.8 μg kg^{-1} in three municipal sludge samples and one food waste sample. It should be noted that the Σ7 PAHs of the sample that originated from the food processing was 268.9 μg kg^{-1}. Perez et al. (2001b) also reported that meat charbroiling was the major source of Ant, Flua, Pyr, and Phe in the household. These results suggest that the PAHs contamination observed in these samples were derived from food processing.

Distributions and compositions of PAHs in sludges

The sources of PAHs have been traced in many studies using various diagnostic ratios such as determination of the Phe/Phe+Ant and Pyr/Pyr+Flua ratios (Blanchard et al. 2004; Dai et al. 2007; Shen et al. 2007). However, the authors of the present study agreed with the suggestion by Katsoyiannis et al. (2007) that these ratios were not appropriate for source discrimination. This is because a WWTP may receive various types of wastewater, including municipal, domestic, and industrial wastewater, as well as street runoff and dry/wet deposition from the atmosphere. Each of these sources may contain different concentrations of PAHs and different diagnostic molecular ratios. However, when these wastewaters reach the WWTP, they will be mixed and homogenized; therefore, the diagnostic ratios in the mixed wastewater will be shifted from their original ratios. Furthermore, after reaching the WWTP, the wastewater will undergo several treatment steps such as primary sedimentation, activated sludge treatment and secondary settling, after which the distinctive fate (i.e., sorption, volatilization, biotransformation) of each PAH will depend on its physical–chemical properties such as the log *K*ow, the Henry's Law constant, and the water solubility. Accordingly, the ratios of these compounds will be shifted by the treatment processes. For these reasons, the sources of PAHs were not evaluated using these diagnostic ratios in the present study.

The occurrence and distribution of the 15 PAHs detected in the three municipal WWTPs sludges are shown in Fig. 1. Among these 15 PAHs, Phe, Flua, and Pyr were generally the most abundant components, which reflect the extensive traffic in the regions (Blanchard et al. 2004). Phe, Chr, and Flu were the primary components detected in sample C.

The most abundant compounds detected in GD_1 were Pyr (23%), followed by Phe (21%) and Flua (12%), which are primarily derived from intensive road traffic and industrial activities in which coal is burned in steel and coke industrial plants. These results were in accordance with those of a study conducted by Mai et al. (2001), who used indicators such as the alkyl homologue distributions of Nap, Phe/Ant, and Flua/Pyr, as well as the parent compound distributions (PCDs) in sediments in this region to identify the main sources of PAHs as industrial activities that involved the burning of large amounts of coal.

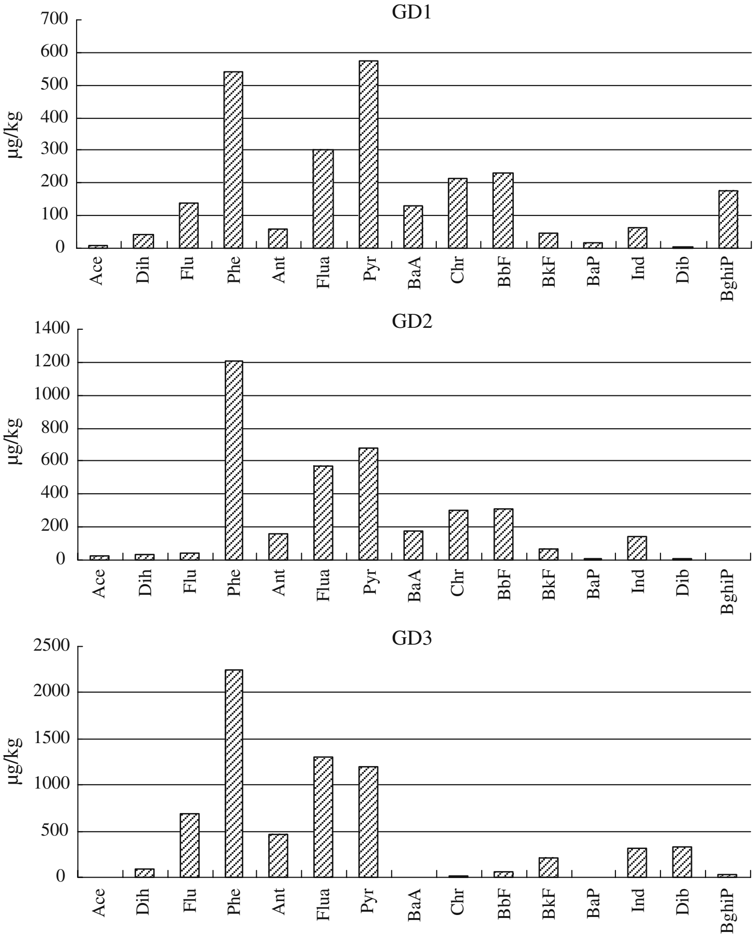


Fig. 1 Occurrence and distribution of PAHs in three municipal sludge samples

The primary components of PAHs in GD_2 were Phe (32%), Pyr (18%), and Flua (15%). Phe generally originates from petroleum products, whereas heavier PAHs such as Pyr and Flua originate from pyrolysis. These findings indicate that the primary sources of PAHs were traffic emission and household activities in the region. These results are in agreement with those of studies conducted by Blanchard et al. (2004) and by Bi et al. (2003), who reported that the primary origins of PAHs were the combustion of fossil fuels by automobiles and unburnt petroleum residues present in the air.

The GD_3 WWTP is located in an Economy & Development Zone in Guangdong Province, where a petroleum-chemical refinery has been built. Phe was found to be the primary PAH in the sludge (32%), followed by Flua (19%) and Pyr (17%). High loads of PAHs, especial Phe, have been attributed to extensive traffic and industrial activities, with emissions from the petroleum-chemical refinery being a primary source of such emissions (Shen et al. 2007).

Comparison of the levels of PAHs, PCBs, and PMs in sludges

The concentrations, distributions and sources of polycyclic musks in these six sludges have previously been reported (Zeng et al. 2005), and the levels and distributions of 41 PCBs have been investigated in a related study that will be published elsewhere. It is interesting to note that there were markedly different distributional patterns for these three groups of organic pollutants (PAHs, PCBs, and PMs) in the sludges due to their different origins and the composition of the wastewater they were obtained from (see Fig. 2).

Occurrence of PAHs, PCBs, and PMs in industrial sludges

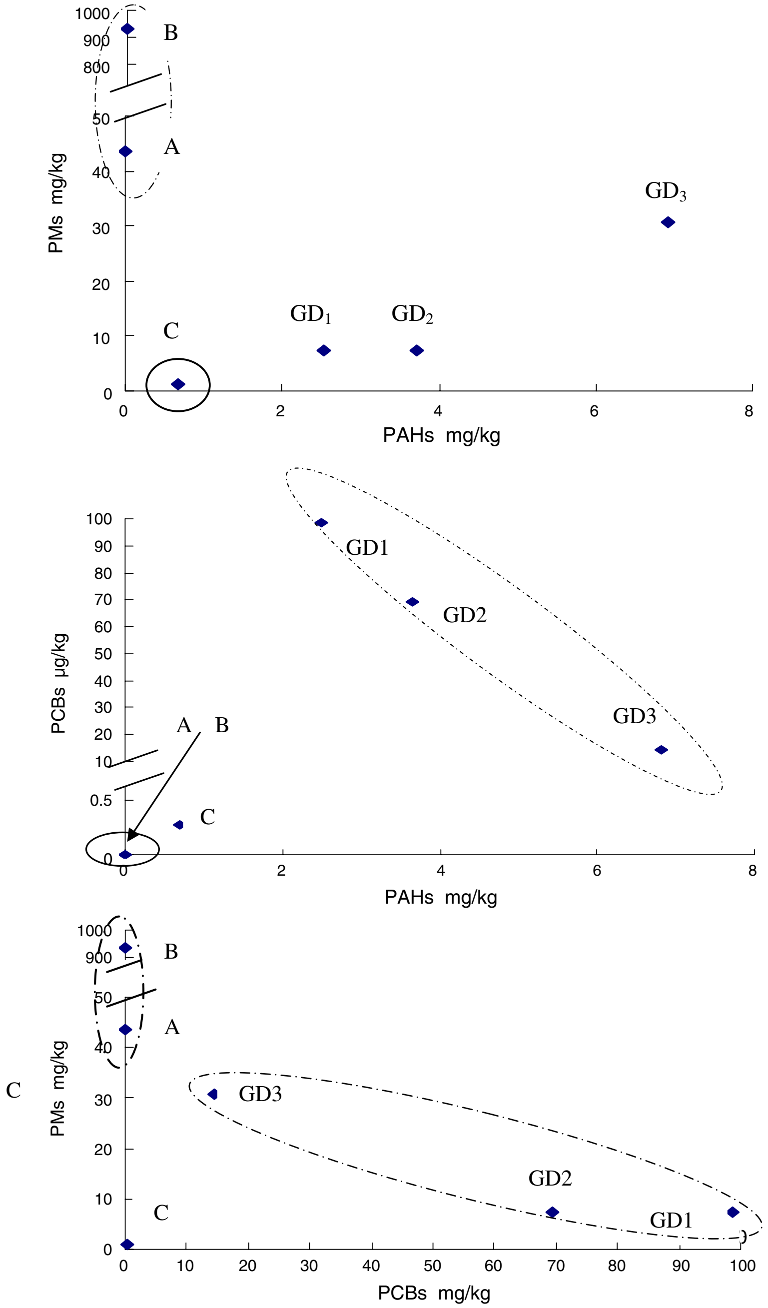
Samples A and B were collected from two cosmetic plants that produce household products such as detergents, air fresher, and personal care products. Polycyclic musks are one class of fragrant chemicals added into personal care products (Reiner and Kannan 2006); therefore, it was not surprising that high concentrations (43,625 and 933,732 $\mu g\ kg^{-1}$ for A and B, respectively) of PMs were found in these industrial sludges even though no PAHs and PCBs were present. The food plant sludge (Sample C) showed generally lower levels of PAHs (682.6 $\mu g\ kg^{-1}$), PCBs (0.27 $\mu g\ kg^{-1}$), and PMs (1,108 $\mu g\ kg^{-1}$) than municipal sludges that might be formed during food processing (Mai et al. 2005; Rey-Salgueiro et al. 2008).

Occurrence of PAHs, PCBs, and PMs from municipal sludges

Of the three municipal WWTPs evaluated in this study, GD_1 collected mixed wastewater in an aged industrial and densely populated area. Specifically, the plant treats water composed of approximately 60% domestic sewage from about 700,000 inhabitants and 40% industrial discharges from steel, coke, plastics, and dyeing facilities. The catchment for GD_2 is approximately 66.5 km^2 and the daily capacity was 220,000 tons of domestic wastewater. The catchment of GD_2 is densely populated with 1,200,000 citizens and intensive road traffic. Similar levels of PMs (7,215 and 7,454 $\mu g\ kg^{-1}$ for GD_1 and GD_2, respectively) were found in these two sludge samples, which demonstrated they had similar origins. However, a higher concentration of PAHs (3,724.1 $\mu g\ kg^{-1}$) was detected in GD_2 than in GD_1 (2,534.1 $\mu g\ kg^{-1}$), which suggests that intensive road traffic contributed to this sample. The GD_3 WWTP is located in an Economy & Development Zone in Guangdong Province, in which many industrial enterprises have been built, including a petroleum-chemical refinery and several cosmetic plants (i.e., A and B). Because the wastewater treated at this WWTP primarily originates from industrial enterprises (about 70%) and domestic sewage from 60,000 inhabitants, the loads of PAHs (6,926.6) and PMs (30,716 $\mu g\ kg^{-1}$) were considerably higher than those found in GD_1 or GD_2, even though its daily capacity is 30,000 tons. This may be ascribed to the industrial discharges from the petroleum-chemical refinery and cosmetic plants (Chen et al. 2007).

In a related study, low levels of PCBs were also detected in these samples, with 98.76 $\mu g\ kg^{-1}$ and 69.27 $\mu g\ kg^{-1}$ PCBs being found in GD_1 and GD_2, respectively. This may suggest some

Fig. 2 Different levels and distribution characteristic of PAHs, PCBs, and PMs in six sludge samples



diffusive emission sources in the regions and can be attributed to the application of old transformers and capacitors or leakage from buried transformers. A considerably lower concentration (14.54 μg kg^{-1}) of PCBs was found in GD$_3$ sludge. Indeed, the concentration of PCBs in GD$_3$ sludge was about 1/7~1/6 that of the PCBs detected in GD$_1$ and GD$_2$, which suggests no obvious emissions in this district. These results were in good accordance with the levels of PCBs detected in the atmosphere in the study area. Specifically, 1,961 pg m^{-3} PCBs were found in the atmosphere in the region that GD$_1$ was collected from, and it was suggested that these PCBs were emitted from PCB-containing electrical installations such as transformers and capacitors still in use

Table 2 Correlation coefficients of POPs concentrations in three municipal sludge samples

	Dih	Flu	Phe	Ant	Flua	Pry	BaA	Chr	BbF	BkF	BaP	Ind	Dib	PCB52	PCB101	PCB138	DPMI	HHCB	AHTN
GD 3																			
Dih	1																		
Flu	1.000	1																	
Phe			1																
Ant				1															
Flua				1.000	1														
Pry						1													
BaA							1												
Chr							0.999	1											
BbF							0.997	0.999	1										
BkF						0.999				1									
BaP				−0.998	−0.999						1								
Ind				0.998	0.999						−1.000	1							
Dib													1						
PCB52			−0.999								0.999	−0.999		1					
PCB101													1.000		1				
PCB138													1.000		1.000	1			
DPMI				0.998		1.000				0.998							1		
HHCB													1.000		1.000	1.000		1	
AHTN															1.000	1.000		1.000	1
GD1																			
Dih	1																		
Flu	1.000	1																	
Phe			1																
Ant				1															
Flua				1.000	1														
Pry						1													
BaA							1												
Chr							0.999	1											
BbF							0.997	0.999	1										
BkF						0.999				1									

BaP				−0.998	−0.999						1								
Ind				0.998	0.999						−1.000	1							
Dib													1						
PCB52			−0.999								0.999	−0.999		1					
PCB101													1.000		1				
PCB138													1.000		1.000	1			
DPMI				0.998		1.000				0.998							1		
HHCB													1.000		1.000	1.000		1	
AHTN													1.000		1.000	1.000		1.000	1
GD2																			
Dih	1																		
Flu	1.000	1																	
Phe			1																
Ant				1															
Flua				1.000	1														
Pry						1													
BaA							1												
Chr							0.999	1											
BbF							0.997	0.999	1										
BkF						0.999				1									
BaP				−0.998	−0.999						1								
Ind				0.998	0.999						−1.000	1							
Dib													1						
PCB52			−0.999								0.999	−0.999		1					
PCB101													1.000		1				
PCB138													1.000		1.000	1			
DPMI			0.977	0.998	0.997	1.000				0.998							1		
HHCB													1.000		1.000	1.000		1	
AHTN													1.000		1.000	1.000		1.000	1

or stored at landfills or from volatilization from contaminated soils (unpublished data, Laiguo Chen, Zhencheng Xu, Xiaochun Peng, Jiaren Sun, Bixian Mai, Guoying Sheng, Jiamo Fu. Concentrations, profiles and sources of PCBs in the atmosphere of Guangzhou, China). PCBs were produced commercially since 1929, although their production and usage have been banned worldwide. However, even though the Chinese Government issued the "Relevant Regulations for Stopping the Production of PCBs" in 1974 and the "Circular on Preventing the Pollution of Hazardous Substances of PCBs" in 1979, some transformers, capacitors, and paints that contained PCBs remained in use for several years. Furthermore, in Guangdong Province, these apparatuses have been sealed/stored for more than 20 years, during which time they have served as potential emission sources of PCBs to the environment (Zhang et al. 2007).

As shown in Fig. 2, there was a greater level of PMs than PAHs and PCBs in these three municipal sludge samples, which indicates that greater attention must be paid to these emerging pollutants and the risk they pose to the environment and humans.

Correlation analysis of PAHs, PCBs, and PMs concentrations

The Pearson correlation coefficients for the concentrations of PAHs, PCBs, and PMs in sludge from the three municipal WWTPs are shown in Table 2. Only coefficients that were significant above the 95% confidence level are presented. Because neither PAHs nor PCBs were detected in the two cosmetic sludge samples, and lower levels of PAHs and PCBs were found in food sludge sample, correlation coefficient analysis was not conducted for these three samples. As shown in Table 2, the concentrations of Flu and Dih, Flua and Ant, Ind and Ant, and Ind and Flua were well correlated in the three samples, suggesting similar origins of petrochemical facilities and heavily road traffic. In addition, BbF and Chr, Chr and BaA, and BkF and Pyr were well correlated, which suggests that they originated from the pyrolysis of organic materials. Moreover, HHCB and AHTN were especially well correlated, which indicates that they both originated from domestic wastewater. It should be noted that strong correlations were also found between HHCB and PCB101, HHCB and PCB138, AHTN and PCB101, and AHTN and PCB138. Additionally, DPMI and Phe, and DPMI and Flua were well correlated in GD_2, which might indicate their similar removal during wastewater treatment procedure (Katsoyiannis and Samara 2004).

Conclusion

Because PMs were the main components of the contaminants observed in the samples evaluated in this study, additional research should be conducted to evaluate the occurrence, transformation and ultimate fate of these emerging pollutants in the environment, as well as their risk to the environment and humans. Due to the contribution of pollutants by petrochemical refineries and intensive road traffic, PAHs were consistently observed among sludges. The presence of PAHs detected in food-origin sludge indicates that there is a risk of human exposure to these substances through food. Although the production and use of PCBs have been prohibited, these materials are still persistent in the environment, and their risk should not be ignored. Sludge was an important medium for the transfer of organic pollutants into the environment; therefore, greater attention should be paid to the occurrence, levels, and distribution of other pollutants such as PBDEs, PCDD/Fs, and pesticides in sludge.

Acknowledgements The authors are grateful for the financial support from the Chinese National Basic Research Program, "Water environmental quality evolution and water quality criteria in lakes" (2008CB418200), the National Natural Science Foundation of China (40872204) and the Chinese Academy of Sciences (GIGCX-07–02). This is contribution No. IS-1104 from GIGCAS. The authors also thank Mr. Tongshou Xiang for his help with the GC-MS analysis.

References

Bi, X. H., Sheng, G. Y., Peng, P. A., Chen, Y. J., Zhang, Z. Q., & Fu, J. M. (2003). Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmospheric Environment, 37*, 289–298.

Blanchard, M., Teil, M. J., Ollivon, D., Legenti, L., & Chevreuil, M. (2004). Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environmental Research, 95*, 184–197.

Busetti, F., Heitz, A., Cuomo, M., Badoer, S., & Traverso, P. (2006). Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant. *Journal of Chromatography A, 1102*, 104–115.

Cai, Q. Y., Mo, C. H., Wu, Q. T., Zeng, Q. Y., & Katsoyiannis, A. (2007). Occurrence of organic contaminants in sewage sludges from eleven wastewater treatment plants, China. *Chemosphere, 68*, 1751–1762.

Chang, B. V., Chang, S. W., & Yuan, S. Y. (2003). Anaerobic degradation of polycyclic aromatic hydrocarbons in sludge. *Advances in Environmental Research, 7*, 623–628.

Chen, D., Zeng, X., Sheng, Y., Bi, X., Gui, H., Sheng, G., et al. (2007). The concentrations and distribution of polycyclic musks in a typical cosmetic plant. *Chemosphere, 66*, 252–258.

Dai, J. Y., Xu, M. Q., Chen, J. P., Yang, X. P., & Ke, Z. S. (2007). PCDD/F, PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere, 66*, 353–361.

Djinovic, J., Popovic, A., & Jira, W. (2008). Polycyclic aromatic hydrocarbons (PAHs) in different types of smoked meat products from Serbia. *Meat Science, 80*(2), 449–456.

Donato, F., Magoni, M., Bergonzi, R., Scarcella, C., Indelicato, A., Carasi, S., et al. (2006). Exposure to polychlorinated biphenyls in residents near a chemical factory in Italy: The food chain as main source of contamination. *Chemosphere, 64*, 1562–1572.

Harrison, E. Z., Oakes, S. R., Hysell, M., & Hay, A. (2006). Organic chemicals in sewage sludges. *Science of the Total Environment, 367*, 481–497.

Katsoyiannis, A., & Samara, C. (2004). Persistent organic pollutants (POPs) in the sewage plant of Thessaloniki, north Greece: Occurrence and removal. *Water Research, 38*, 2685–2698.

Katsoyiannis, A., Terzi, E., & Cai, Q. Y. (2007). On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere, 69*, 1337–1339.

Luo, X. J., Mai, B. X., Yang, Q. S., Fu, J. M., Sheng, G. Y., & Wang, Z. S. (2004). Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. *Marine Pollution Bulletin, 48*, 1102–1115.

Mai, B. X., Fu, J. M., Zhang, G., Lin, Z., Min, Y. S., Sheng, G. Y., et al. (2001). Polycyclic aromatic hydrocarbons in sediments from the Pearl River and estuary, China: Spatial and temporal distribution and sources. *Applied Geochemistry, 16*, 1429–1445.

Mai, B. X., Zeng, E. Y., Luo, X. J., Yang, Q. S., Zhang, G., Li, X. D., et al. (2005). Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. *Environmental Science & Technology, 39*, 49–56.

Mannino, M. R., & Orecchio, S. (2008). Polycyclic aromatic hydrocarbons (PAHs) in indoor dust matter of Palermo (Italy) area: Extraction, GC-MS analysis, distribution and sources. *Atmospheric Environment, 42*, 1801–1817.

Manoli, E., & Samara, C. (2008). The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: Experimental calculations and model predictions. *Environmental Pollution, 151*, 477–485.

Oleszczuk, P. (2006). Persistence of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge-amended soil. *Chemosphere, 65*, 1616–1626.

Oleszczuk, P., & Baran, S. (2004). Application of solid-phase extraction to determination of polycyclic aromatic hydrocarbons in sewage sludge extracts. *Journal of Hazardous Materials, 113*, 237–245.

Perez, S., Farre, M. L., Garcia, M. J., & Barcelo, D. (2001a). Occurrence of polycyclic aromatic hydrocarbons in sewage sludge and their contribution to its toxicity in the ToxAlert(R) 100 bioassay. *Chemosphere, 45*, 705–712.

Perez, S., Guillamon, M., & Barcelo, D. (2001b). Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants. *Journal of Chromatography A, 938*, 57–65.

Poster, D. L., Schantz, M. M., Sander, L. C., & Wise, S. A. (2006). Analysis of polycyclic aromatic hydrocarbons (PAHs) in the environmental samples: A critical review of gas chromatographic (GC) methods. *Analytical and Bioanalytical Chemistry, 386*, 859–881.

Reiner, J. L., & Kannan, K. (2006). A survey of polycyclic musks in selected household commodities from the United States. *Chemosphere, 62*, 867–873.

Rey-Salgueiro, L., Garcia-Falcon, M. S., Martinez-Carballo, E., & Simal-Gandara, J. (2008). Effects of toasting procedures on the levels of polycyclic aromatic hydrocarbons in toasted bread. *Food Chemistry, 108*, 607–615.

Shen, R. Y., Luo, Y. M., Zhang, G. Y., Teng, Y., Li, Z. G., & Wu, L. H. (2007). Contamination of PAHs in sludge samples from the Yangtze river delta area. *Pedosphere, 17*, 373–382.

Stevens, J. L., Northcott, G. L., Stern, G. A., Tomy, G. T., & Jones, K. C. (2003). PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in UK sewage sludge: Survey results and implications. *Environmental Science & Technology, 37*, 462–467.

Villar, P., Callejon, M., Alonso, E., Jimenez, J. C., & Guiraum, A. (2006). Temporal evolution of polycyclic aromatic hydrocarbons (PAHs) in sludge from wastewater treatment plants: Comparison between PAHs and heavy metals. *Chemosphere, 64*, 535–541.

Zeng, X. Y., Sheng, G. Y., Xiong, Y., & Fu, J. M. (2005). Determination of polycyclic musks in sewage sludge from Guangdong, China using GC-EI-MS. *Chemosphere, 60*, 817–823.

Zhang, G., Li, X. D., Mai, B. X., Peng, P. A., Ran, Y., Wang, X. M., et al. (2007). Sources and occurrence of persistent organic pollutants in the Pearl River Delta, South China. *Developments in Environmental Science, 7*, 289–311.