Benzo[a]pyrene and phenanthrene in municipal sludge from the Yangtze River Delta, China

Shen, R. Y., Luo, Y. M., Feng, S., Zhang, G. Y., Wu, L. H., Li, Z. G., ... Christie, P. (2009). Benzo[a]pyrene and phenanthrene in municipal sludge from the Yangtze River Delta, China. Pedosphere, 19(4), 523-531. DOI: 10.1016/S1002-0160(09)60145-4

Published in:
Pedosphere

Pedosphere **19**(4): 523–531, 2009
ISSN 1002-0160/CN 32-1315/P

Published by Elsevier Limited and Science Press

PEDOSPHERE

www.elsevier.com/locate/pedosphere

Benzo[a]pyrene and Phenanthrene in Municipal Sludge from the Yangtze River Delta, China*[1]

SHEN Rong-Yan[1,2,3], LUO Yong-Ming[1,3,*2], FENG Sheng[2], ZHANG Gang-Ya[1], WU Long-Hua[1], LI Zhen-Gao[1], TENG Ying[1] and P. CHRISTIE[4]

[1] *Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008 (China)*
[2] *Department of Environment and Safety Engineering, Jiangsu Polytechnic University, Changzhou 213016 (China)*
[3] *Graduate University of the Chinese Academy of Sciences, Beijing 100049 (China)*
[4] *Department of Agricultural and Environmental Science, Queen's University Belfast, Newforge Lane, Belfast BT9 5PX (UK)*

(Received October 13, 2008; revised March 11, 2009)

ABSTRACT

To evaluate the contaminated conditions of benzo[a]pyrene (B[a]P) and phenanthrene (PA) in sludge and to ascertain whether B[a]P limit for land application of sludge exists, the contents of B[a]P and PA in 46 sludge samples from 15 cities in the Yangtze River Delta area of China were determined using high performance liquid chromatography (HPLC) coupled with a fluorescence detector after ultrasonic extraction and silica gel cleanup. B[a]P contents ranged from non-detectable to 1.693 mg kg^{-1} dry weight (DW), averaged 0.402 mg kg^{-1} DW, and were < 1.0 mg kg^{-1} DW in most of the sludge samples. PA was found in all the sludge samples analyzed; its contents ranged between 0.028 and 1.355 mg kg^{-1} DW, with an average value of 0.298 mg kg^{-1} DW. Most of the sludge samples contained < 0.5 mg kg^{-1} DW PA. All 46 municipal sludge samples analyzed in this study showed B[a]P contents < 3.0 mg kg^{-1} DW, which is the limit value for sludge applied to agricultural lands in China. The contents and distributions of B[a]P and PA in municipal sludge were related to sludge types, sources and treatment technologies, along with the physical and chemical properties of these pollutants.

Key Words: benzo[a]pyrene, municipal sludge, organic pollutants, phenanthrene, Yangtze River Delta

Citation: Shen, R. Y., Luo, Y. M., Feng, S., Zhang, G. Y., Wu, L. H., Li, Z. G., Teng, Y. and Christie, P. 2009. Benzo[a]pyrene and phenanthrene in municipal sludge from the Yangtze River Delta, China. *Pedosphere*. **19**(4): 523–531.

Municipal sewage sludge is the residual material after wastewater cleanup in wastewater treatment plants (WWTPs), generally after primary and secondary treatment processes. It is an unwanted and inevitable byproduct of WWTPs. Domestic and industrial wastewater catchments receive organic pollutants from different sources: human excretion products, household disposals, fossil fuel spillages, storm water runoff from highways, cleaning compounds, lubricants, and urban runoff inputs that flush the organics deposited on the ground surface from vehicles or heating systems (Rogers, 1996). Sewage sludge is a mixture of organic (> 300 organic compounds have been identified), inorganic, and microbiological pollutants and pathogens (Pestrasek *et al.*, 1983; Jocobs *et al.*, 1987; Webber and Lesage, 1989; Wild *et al.*, 1990; Wild and Jones, 1992; Feliciano, 1993; Duarte-Davidson and Jones, 1996; Mo *et al.*, 2000, 2001; Qiao and Luo, 2001; Liao *et al.*, 2003; Sun and Luo, 2005).

It is estimated that China is now producing more than 20 billion m^3 of municipal wastewater per annum, about 7% of which, *i.e.* 1.4 billion m^3, is treated in sewage treatment plants, producing some 0.4 million ton (dry weight, DW) of sewage sludge. Furthermore, the municipal wastewater treatment rate will increase to 40%–50% by 2010 according to the national planning in China, indicating a dramatic increase in sewage sludge production in China very soon (Department of Geological Environment,

*[1]Project supported by the National Key Basic Research Support Foundation (973 Program) of China (No. 2002CB4108010) and the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KSCX2-YW-N-038).
*[2]Corresponding author. E-mail: ymluo@issas.ac.cn.

Ministry of Land and Resources, China, 2000).

The organic contaminants present in the sewage sludge have been studied in several countries for many years (Jacobs *et al.*, 1987; Crathorne *et al.*, 1989; Webber and Lesage, 1989; Wang and Jones, 1994; Jones, 1996; Mo *et al.*, 2000, 2001; Cai *et al.*, 2003, 2004). Among the most frequent contaminants found are aromatic hydrocarbons, organochloronated compounds, aliphatic hydrocarbons, amines, nitrosamines, phenols, esters, and phthalates. The origins of these pollutants are very diverse, ranging from industrial processes (Junk and Ford, 1980; Gil, 1982; Kirton and Crisp, 1990) to urban activities (Takada and Ishiwatari, 1990). However, little work has been done on this subject in China and only few organic contaminants have been studied (Mo *et al.*, 2000, 2001; Cai *et al.*, 2003, 2004). It is therefore necessary to characterize organic contaminants in sludge in China to assess their potential threat to the environment.

Polycyclic aromatic hydrocarbons (PAHs) are a well-known group of toxic compounds. Due to their carcinogenic activity, they have been included in the European Union (EU) and the Environmental Protection Agency (EPA) priority pollutant lists. Benzo[a]pyrene (B[a]P), which is regarded as a carcinogenic representative of PAHs, as well as other PAH compounds such as phenanthrene (PA), which has acute human toxicity, is released into the environment and accumulated in sludge mainly by the combustion of coal, petroleum, wood and wastewater treatment (Hites *et al.*, 1980; Grimer *et al.*, 1983, 1985; Prhal *et al.*, 1984). These compounds are known to be present in the atmosphere, water, sediments, tobacco smoke, food and sewage sludge. The presence of PAHs in environmental samples such as water, sediments, and particulate air has been extensively studied but sewage sludge has received less attention (Koester and Clement, 1993; Eisert and Levsen, 1996).

The management and the disposal of sewage sludge is an important issue in the Yangtze River Delta area, the most industrialized region of China. Large amounts of industrial and domestic wastewater containing high contents of various chemical pollutants will be treated and a great mass of contaminated sludge should be generated in this region. Unjustified management of sludge with considerable organic micropollutant contamination may lead to secondary contamination of the environment. The objective of the present study was to determine the contents of the two typical representatives of PAHs (B[a]P and PA) in 46 sewage sludge samples from WWTPs in 15 cities in the Yangtze River Delta area by high performance liquid chromatography (HPLC).

MATERIALS AND METHODS

Reagents and samples

A mixed standard solution of B[a]P and PA at 2 μg mL^{-1} in dichloromethane purchased from Supelco (Bellefonte, Pennsylvania, USA) as methylene chloride solutions was diluted with dichloromethane to prepare a series of standard solutions at 5, 10, 20, 50, and 100 ng mL^{-1} of B[a]P and PA. HPLC grade hexane, dichloromethane, acetonitrile, and cyclohexane were supplied by the Tedia Company Inc. (Fairfield, OH 45014, USA). Silica gel (100–200 mesh) was purchased from the Chinese Chemical Reagent Company (Shanghai, China) and anhydrous sodium sulfate (AR grade) from the Nanjing Chemical Reagent No. 1 Factory (Nanjing, China).

Sewage sludge samples (Table I) were collected from 46 sewage treatment plants purifying river sewage, municipal sewage, or mixtures of industrial and domestic sewage in 15 cities (Zhejiang, Jiangsu, and Shanghai) of the Yangtze River Delta area. They were stored in glass vessels at −20 °C, freeze-dried, and homogenized prior to extraction. The glass vessels containing the sewage sludge samples were stored in the dark and were firmly closed to avoid contamination or losses.

Sample pretreatment and analysis

The samples were pretreated by ultrasonic extraction and silica gel cleanup. Aliquots of homogenized 5 g sludge samples were ultrasonically extracted with 20 mL of dichloromethane for 2 h. The extracts were concentrated to 1–3 mL in a rotary evaporator and reduced to near dryness under a nitrogen flow.

TABLE I

Sewage sludge sampling sites, sample types, and sampling dates as well as the influent sewage types and wastewater treatment technologies of the wastewater treatment plants (WWTP)

Sludge sample No.	Sludge sampling site	Sludge sample type	WWTP influent sewage type	WWTP wastewater treatment technology	Sludge sampling date in 2003	Sludge sample No.	Sludge sampling site	Sludge sample type	WWTP influent sewage type	WWTP wastewater treatment technology	Sludge sampling date in 2003
1	Hangzhou, Zhejiang	Dehydrated	Mixed-flow	A^2/O treatment[a)]	Sep. 23	24	Shanghai	Pond	Domestic	Activated sludge	Dec. 1
2	Hangzhou, Zhejiang	Dehydrated	Domestic	Activated sludge	Sep. 24	25	Shanghai	Pond	Domestic	A^2/O treatment	Dec. 5
3	Hangzhou, Zhejiang	Dehydrated	Domestic	Activated sludge	Sep. 25	26	Shanghai	Pond	Domestic	Activated sludge	Dec. 5
4	Hangzhou, Zhejiang	Dehydrated	Domestic	Activated sludge	Sep. 25	27	Nanjing, Jiangsu	Pond	Domestic	Activated sludge	Dec. 5
5	Ningbo, Zhejiang	Dehydrated	Domestic	A^2/O treatment	Sep. 25	28	Suzhou, Jiangsu	Dehydrated	Mixed-flow	Oxidation ditch	Dec. 30
6	Ningbo, Zhejiang	Dehydrated	Mixed-flow	Oxidation ditch	Sep. 24	29	Suzhou, Jiangsu	Dehydrated	Mixed-flow	Oxidation ditch	Dec. 30
7	Ningbo, Zhejiang	Pond	Industrial	Activated sludge	Sep. 24	30	Suzhou, Jiangsu	Dehydrated	Domestic	Activated sludge	Dec. 5
8	Shaoxing, Zhejiang	Dehydrated	Industrial	Activated sludge	Sep. 27	31	Suzhou, Jiangsu	Pond	Domestic	Activated sludge	Dec. 29
9	Jiaxing, Zhejiang	Dehydrated	Industrial	A^2/O treatment	Sep. 27	32	Suzhou, Jiangsu	Dehydrated	Domestic	AB technology	Dec. 29
10	Jinhua, Zhejiang	Dehydrated	Mixed-flow	A^2/O treatment	Sep. 25	33	Wuxi, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Jun. 17
11	Jinhua, Zhejiang	Dehydrated	Domestic	A^2/O treatment	Sep. 29	34	Wuxi, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Dec. 14
12	Huzhou, Zhejiang	Dehydrated	Mixed-flow	A^2/O treatment	Dec. 24	35	Changzhou, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Dec. 14
13	Huzhou, Zhejiang	Dehydrated	Mixed-flow	A^2/O treatment	Dec. 24	36	Changzhou, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Oct. 21
14	Taizhou, Zhejiang	Dehydrated	Domestic	Oxidation ditch	Dec. 25	37	Changzhou, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Oct. 21
15	Taizhou, Zhejiang	Dehydrated	Industrial	A^2/O treatment	Dec. 24	38	Yangzhou, Jiangsu	Dehydrated	Domestic	A^2/O treatment	Oct. 21
16	Shanghai	Dehydrated	Domestic	Activated sludge	Dec. 24	39	Taizhou, Jiangsu	Dehydrated	Industrial	A^2/O treatment	Oct. 22
17	Shanghai	Dehydrated	Domestic	Activated sludge	Dec. 24	40	Nantong, Jiangsu	Dehydrated	Mixed-flow	Activated sludge	Oct. 22
18	Shanghai	Dehydrated	Domestic	Activated sludge	Nov. 19	41	Shanghai	River	River	Activated sludge	Oct. 22
19	Shanghai	Dehydrated	Domestic	Activated sludge	Nov. 19	42	Shanghai	Dehydrated	Domestic	Activated sludge	Oct. 22
20	Shanghai	Dehydrated	Domestic	Activated sludge	Nov. 20	43	Shanghai	Dehydrated	Domestic	Activated sludge	Oct. 22
21	Shanghai	Dehydrated	Industrial	Activated sludge	Nov. 20	44	Shanghai	Enterprise[b)]	Industrial	Activated sludge	Oct. 23
22	Shanghai	Dehydrated	Domestic	A^2/O treatment	Nov. 20	45	Nanjing, Jiangsu	Enterprise	Industrial	Activated sludge	Oct. 23
23	Shanghai	Dehydrated	Mixed-flow	Activated sludge	Dec. 4	46	Nanjing, Jiangsu	Enterprise	Industrial	Activated sludge	Oct. 22

[a)] Anaerobic-anoxic-aerobic treatment; [b)] Brew house sludge or paper mill sludge.

Cyclohexane (2 mL) was then added to the raw extracts.

A glass column was packed with 1 g of silica gel and a top layer of anhydrous sodium sulphate. The stationary phase was soaked with 20 mL of hexane for 15 min before use. A 0.5 mL raw extract of cyclohexane solution phase was pipetted into the top of the silica gel column. The column was then eluted using 5 mL of a mixture of hexane and dichloromethane (50:50, v/v). The first 1 mL of eluted liquid was discarded and then the following 2 mL was collected in a 5-mL tube and further concentrated under a gentle stream of nitrogen to dryness. Finally the extracts were introduced into 5 mL of acetonitrile in the tube and then the tube was stored at −20 °C. Prior to analysis the tube was allowed to equilibrate at ambient temperature.

A high performance liquid chromatography (HPLC, Shimadzu Corporation, Japan) was equipped with an LC-10AT$_{VP}$ isocratic pump, a VP-ODS PAH column (Serial No. 9122504, 150 mm long × 4.6 mm inner diameter), and an FL2000 fluorescence detector. Water circulation through a thermostatically controlled water bath was used to maintain the column temperature at 30 °C. An aliquot (40 μL) of the acetonitrile solution phase was injected into the HPLC system and eluted with acetonitrile and water (90:10, v/v) at a constant flow rate of 0.5 mL min^{-1}. For detection and quantification, two excitation (Ex) and emission (Em) wavelengths were used: Ex = 296 nm and Em = 404 nm for B[a]P and Ex = 270 nm and Em = 350 nm for PA. Quantitative analyses of B[a]P and PA were performed using external standard calibrations with a reference standard solution prepared by appropriate dilution. The analytical method and condition of B[a]P and PA had been validated to have adequate exactness (15%–30%), limit of detection (7–87 pg g^{-1} of all sludge samples) and recovery yields (from 60.42% for B[a]P to 85.74% for PA).

RESULTS AND DISCUSSION

Benzo[a]pyrene

The B[a]P contents differed substantially among the sludge samples, ranging from non-detectable to 1.693 mg kg^{-1} DW and averaging 0.402 mg kg^{-1} DW (Fig. 1). Most of the sludge samples investigated showed B[a]P contents < 1.0 mg kg^{-1} DW (Fig. 2) and all of them contained B[a]P < 3.0 mg kg^{-1} DW, which is the limit value for sludge application to agricultural lands in China (Mo *et al.*, 2001).

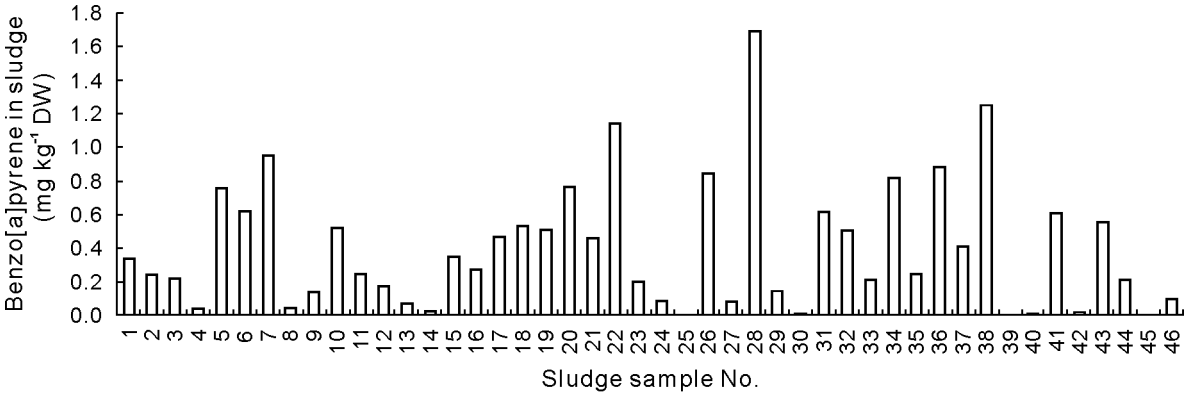

Fig. 1 Benzo[a]pyrene contents in 46 sludge samples studied.

According to the locations of the WWTPs, the sludge samples in this study were classified (Tables I and II) into three groups: 1) Zhejiang sludge, 2) Jiangsu sludge, and 3) Shanghai sludge. B[a]P contents in different groups also varied (Table II). Jiangsu sludge had the highest content of B[a]P but there were no significant differences in average contents among the three geographical groups ($P < 0.05$).

B[a]P contents varied in the sludge samples from different WWTP influent sewage types (Table III).

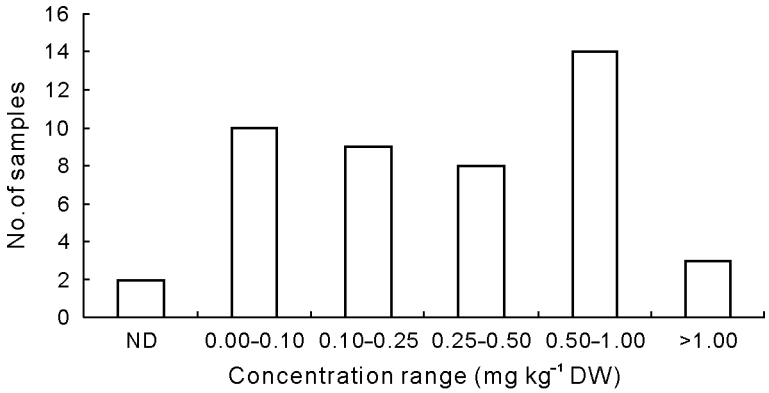

Fig. 2 Frequency distribution of benzo[a]pyrene contents in 46 sludge samples studied. ND = non-detectable.

TABLE II

Contents of benzo[a]pyrene (B[a]P) and phenanthrene (PA) in 46 sludge samples from different locations

Location	No. of Samples	Minimum content		Maximum content		Average content	
		B[a]P	PA	B[a]P	PA	B[a]P	PA
		mg kg^{-1} DW					
Zhejiang	16	0.02	0.10	0.95	0.86	0.32a[b)]	0.28a
Jiangsu	16	< LOD[a)]	0.03	1.69	1.35	0.53a	0.38a
Shanghai	14	< LOD	0.04	1.15	0.90	0.48a	0.32a

[a)]Limit of detection; [b)]Average contents followed by the same letter within a column are not significantly different ($P < 0.05$).

TABLE III

Contents of benzo[a]pyrene (B[a]P) and phenanthrene (PA) in 46 sludge samples from different wastewater treatment plant (WWTP) influent sewage types

WWTP influent sewage type	No. of samples	Minimum content		Maximum content		Average content	
		B[a]P	PA	B[a]P	PA	B[a]P	PA
		mg kg^{-1} DW					
Domestic sewage	27	< LOD[a)]	0.040	1.250	1.350	0.450c[b)]	0.320b
Mixed-flow sewage	9	0.010	0.070	1.690	0.480	0.420c	0.240a
Industrial sewage	9	< LOD	0.030	0.950	0.860	0.320b	0.280a
River sewage	1	–	–	–	–	0.610d	0.340b

[a)]Limit of detection; [b)]Average contents followed by the same letter within a column are not significantly different ($P < 0.05$).

The highest content of B[a]P was found in those from the mixed-flow sewage and the average contents in those from the domestic and mixed-flow sewage were higher than those from the industrial sewage (Table III). B[a]P contents in the sludge samples from a uniform type of sewage were also different. For example, a minimum of 0.01 mg kg^{-1} DW and a maximum of 1.69 mg kg^{-1} DW of B[a]P were detected in two sludge samples from the mixed-flow sewage.

Owing to the hydrophobic properties (fairly low water solubility and fairly high octanol-water partition coefficients), B[a]P was exclusively bound to the organic fraction and concentrated onto the organic-rich particles during wastewater treatment (Nowell and Capel, 2003). In general, sludge samples from the industrial sewage contained higher contents of B[a]P than those from the domestic sewage. For example, the Ningbo pond sludge derived from $\geq$ 95% industrial wastewater (No. 7) and the Ningbo dehydrated sludge (No. 6) and the Suzhou dehydrated sludge (No. 28) from 50% industrial wastewater

all contained high detectable contents of B[a]P (0.6230–1.6925 mg kg^{-1} DW). However, contrasting examples were also present as a result of many complex factors. For instance, B[a]P contents found in the samples from the WWTPs with higher domestic sewage influent loadings such as Nos. 5, 18, 19, 20, and 36 were higher than those of Nos. 8, 9, and 39 from the plants where the industrial sewage inputs were at least as important as the domestic sewage sources. It therefore sometimes seemed that industrial sources were not the main contributory sources of B[a]P to sludge. The most important factor was the ratio of B[a]P in industrial and domestic wastewater in sludge. Many other factors such as sludge treatment processes also affected the B[a]P content in sludge. In this study, the sludge samples from the plants using the treatment technology of an oxidation ditch such as Nos. 6, 28, and 29 contained high contents of B[a]P and some sludge samples from the plants using the technologies of activated sludge and A^2/O also contained higher contents of B[a]P (Fig. 1, Table I). However, reverse examples also occurred, with B[a]P content in sludge affected by many synthetic and complex factors. Single factors could not all-round explain the patterns of B[a]P in sludge.

Phenanthrene

The PA contents in the 46 sludge samples analyzed ranged from 0.028 to 1.355 mg kg^{-1} DW with an average value of 0.298 mg kg^{-1} DW (Fig. 3). Most were lower than 0.5 mg kg^{-1} DW (Fig. 4). PA contents in sludge from different locations and different sewage types are shown in Tables II and III. The highest PA content tended to be in the Jiangsu sludge group but there were no significant differences among the three sewage groups (Table II, $P < 0.05$). PA contents in sludge samples from different sewage types were significantly different (Table III, $P < 0.05$), with the highest content in those from the domestic sewage. However, there were no clear differences among the other sewage types.

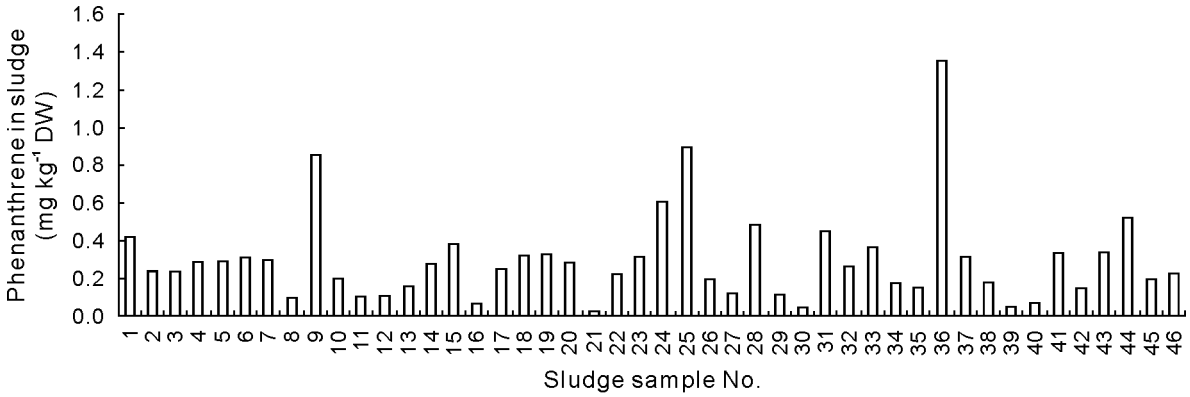

Fig. 3 Phenanthrene contents in 46 sludge samples studied.

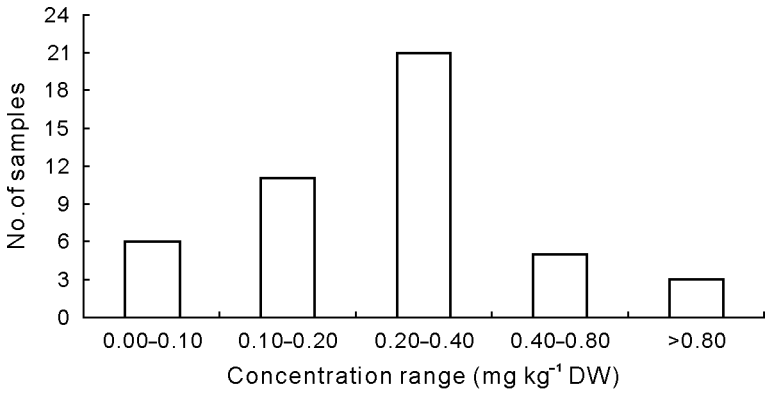

Fig. 4 Frequency distribution of phenanthrene contents in 46 sludge samples studied.

As with B[a]P, PA also had fairly high octanol/water coefficient and was exclusively bound to the organic fraction derived from sludge. In general, sludge samples from industrial sewage contained higher contents of PA than those from domestic sewage. The Ningbo pond sludge derived from $\geq 95\%$ industrial wastewater (No. 7) and the Ningbo dehydrated sludge (No. 6) and Suzhou dehydrated sludge (No. 28) from 50% industrial wastewater were all found to contain high detectable contents of PA (0.283, 0.295, and 0.484 mg kg^{-1} DW). However, opposite trends were also found. For example, PA contents found in the samples from the WWTPs with higher domestic sewage influent loadings, such as Nos. 5, 18, 19, 20, and 36, were higher than those of Nos. 8, 21, and 39 from the plants where the industrial sewage inputs were at least as important as domestic sewage inputs. Therefore, industrial sources were not always the main contributors of PA to sludge. The most important factor was the ratio of PA in industrial and domestic wastewater in sludge. Many other factors such as sludge treatment processes also affected the PA content in sludge.

Most sludge samples from the plants using the technology of A^2/O, such as Nos. 1, 5, 9, 15, 25, 33, 36, and 37, tended to contain higher contents of PA (Table I, Fig. 3). The PA contents in the sludge samples from the plants using the technology of oxidation ditch, such as Nos. 6, 14, and 28, were high, but those in sludge from the plants using the same treatment such as Plant 29 were low. Some sludge samples from the plants using the technology of activated sludge, such as Nos. 16, 21, 30, and 40, contained lower contents of PA (Table I, Fig. 3). However, opposite trends were also found, with PA contents in sludge affected by many synthetic and complex factors. Single factors could not correctly explain the contents of PA in sludge.

Comparison of B[a]P and PA in sludge of this study with those detected elsewhere

From the results above, it can be seen that B[a]P and PA were found to be common micro-contaminants in Chinese sewage sludge. Although information pertaining to contents of organic pollutants in sewage sludge is limited both in terms of the number of surveys conducted and number of samples analyzed, it is of value here to compare the results of the present survey with those of previous studies carried out in China and elsewhere. In general, B[a]P contents in the sludge samples from the Yangtze River Delta area were lower than those in the sludge samples in Canada (4.0–7.6 mg kg^{-1}, Webber and Lesage, 1989), Germany (0.1–15.0 mg kg^{-1}, Jones *et al.*, 1989), the USA (0.7–25.0 mg kg^{-1}, Naylor and Loehr, 1982), and Britain (0.2–2.0 mg kg^{-1}, Wild and Jones, 1992), and similar to those in Switzerland (non-detectable–1.4 mg kg^{-1}, Frost *et al.*, 1993). In most of the sludge samples from this study, B[a]P contents were lower than those in sludge samples from the other Chinese cities except Shenzhen (0.050 mg kg^{-1}), Xi'an (0.063 mg kg^{-1}), Lanzhou (0.049 mg kg^{-1}), Dapu (0.007 mg kg^{-1}), and Shatian (0.033 mg kg^{-1}) (Mo *et al.*, 2001). PA contents in this study were lower than those in sludge samples from other Chinese cities (0.040–6.592 mg kg^{-1}, Mo *et al.*, 2001) and other countries ($>$ 1.500 mg kg^{-1}, Ahmad *et al.*, 2004). The results of all these surveys appeared to be broadly comparable.

In a number of cases, the occurrence of some elevated contents of PAHs in sludge may be related to known industrial users of certain compounds such as the timber industry, coal gas production and tar plants in particular areas. Furthermore, there were a limited number of cases in which elevated content of determinands occurred in sewage sludge sampled from sewage treatment works receiving principally domestic sewage. It is possible that household disposals may have been responsible. No clear indications of a relationship between industrial effluent discharges to sewage treatment works and contents of B[a]P or PA in the resultant sewage sludge were obtained from the correlation analyses carried out. It appears, therefore, that a significant proportion of persistent organic PAH residues in raw sewage and subsequently sewage sludge, may arise from domestic disposals and human excretion. Although no statistically significant differences were found between the contents of B[a]P and PA in sludge which had undergone different types of treatment; *i.e.* sludge treatment was demonstrated to have no effect upon persistent organic pollutant residues. It should be emphasized that the samples were grab samples of

sludge and any potential differences in contents arising from treatment almost certainly would have been obscured by confounding variables such as the spatial variation in residue contents. However, this may be an important area of interest since it has been postulated recently that anaerobic processes may be significant in the preliminary biotransformation of organic molecules prior to biodegradation (Kobayashi and Rittmann, 1982). The possibility therefore exists for the potential amelioration of organic PAH residues in sewage sludge prior to disposal by means of anaerobic sludge digestion.

Given our results, it is apparent that contents of B[a]P and PA residues in Chinese sewage sludge were generally lower than those detected elsewhere. The significance of these results, particularly the mean values, is difficult to place in true perspective, owing to the lack of legislation or guidelines and the paucity of toxicological information. However, where elevated contents of organic contaminants are known to occur on a sporadic or regular basis in certain sewage sludge, it would be advantageous to employ disposal mechanisms which limit both the availability of residues to food chains and the potential for further environmental contamination.

CONCLUSIONS

The contents of B[a]P and PA in 46 sludge samples derived from 15 cities in the Yangtze River Delta area were as follows. B[a]P in the sludge tested ranged from < LOD to 1.693 mg kg^{-1} DW and averaged 0.402 mg kg^{-1} DW. Most of the sludge samples studied had B[a]P < 1.0 mg kg^{-1} DW. PA was found in all sludge samples in this study and contents varied between 0.028 and 1.355 mg kg^{-1} DW, with an average of 0.298 mg kg^{-1} DW. Most of the sludge samples had PA < 0.5 mg kg^{-1} DW. The contents and distribution of B[a]P and PA in the municipal sludge were related to the wastewater sources and treatment processes, sewage types and the physico-chemical properties of B[a]P and PA. The contents of B[a]P and PA in sludge were affected by many synthetic and complex factors. Single factors could not correctly, on an all-round basis, explain the contents of B[a]P and PA in sludge. The content of B[a]P in all municipal sludge was < 3.0 mg kg^{-1}, the limit value for sludge applied to agricultural land in China. Thus, there is no B[a]P limit in sludge land application in China for the moment, but because of the complexity and instability of sludge composition, their potential threat to the environment should be taken into account in the near future.

REFERENCES

Ahmad, U. K., Ujang, Z., Woon, C. H., Indran, S. and Mia, M. N. 2004. Development of extraction procedures for the analysis of polycyclic aromatic hydrocarbons and organochlorine pesticides in municipal sewage sludge. *Water Sci. Technol.* **50**(9): 137–144.

Cai, Q. Y., Mo, C. H., Lai, K. R., Zeng, Q. Y., Wu, Q. T., Wang, B. G. and Li, H. Q. 2004. Preliminary study of nitro organic pollutants in selected municipal sludges of China. *Chinese J. Appl. Ecol.* (in Chinese). **23**(3): 76–80.

Cai, Q. Y., Mo, C. H., Zhu, X. Z., Wu, Q. T., Wang, B. G. and Li, G. R. 2003. PAEs in composts of municipal sludge and rice straw. *Chinese J. Appl. Ecol.* (in Chinese). **14**(11): 1 993–1 996.

Crathorne, B., Donaldson, H., James, H. A. and Rogers, R. 1989. The determination of organic contaminants in UK sewage sludges. *In* Quaghebeur, D., Temmerman, Y. and Angeetti, G. (eds.) Organic Contaminants in Waste Water, Sludge and Sediment: Occurrence, Fate and Disposal. Elsevier Applied Science, London. pp. 46–65.

Department of Geological Environment, Ministry of Land and Resources, China. 2000. Strategy for the sustainable development of water industry, China. *Water Wastewater Eng.* (in Chinese). **5**: 31–35.

Duarte-Davidson, R. and Jones, K. C. 1996. Screening the environmental fate of organic contaminants in sewage sludge applied to agricultural soils: II. The potential for transfers to plants and grazing animals. *Sci. Total Environ.* **185**: 59–70.

Eisert, R. and Levsen, K. 1996. Development of a prototype system for quasi-continuous analysis of organic contaminants in surface or sewage water based on in-line coupling of solid-phase microextraction to gas chromatography. *J. Chromatogr.* **733**(1–2): 143–157.

Feliciano, D. V. 1993. Sludge on land—but where are going? *J. Water Pollut. Con. F.* **9**: 1 259–1 266.

Frost, P., Camenzind, R., Mäger, A., Bonjour, R. and Karlaganis, G. 1993. Organic micro-pollutants in Swiss sewage sludge. *Chromatography.* **643**: 379–388.

Gil, A. 1982. The persistent PCB problem. *Environ. Sci. Technol.* **16**: 98A–99A.

Grimmer, G., Jacob, J. and Naujack, K. W. 1983. Profile of the polycyclic aromatic compounds from crude oils. *Fresen. J. Anal. Chem.* **314**: 29–36.

Grimer, G., Jacob, J., Dettbarn, C. and Naujack, W. 1985. Determination of polycyclic aromatic hydrocarbons azaarenes and thiaarenes emitted from coal-fined residential furnaces by gas chromatography/mass spectrometry. *Fresen. J. Anal. Chem.* **322**: 595–602.

Hites, R. A., Laflamme, R. E. and Windsor, J. G. 1980. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt river (Rhode Island, USA). *Geochim. Cosmochim. Acta.* **44**: 873–878.

Jacobs, L. W., O'Connor, G. A., Overcash, M. A., Zabik, M. J. and Rygiewicz, P. 1987. Effects of trace organics in sewage sludges on soil-plant systems and assessing their risk to humans. *In* Page, A. L., Logan, T. J. and Ryan, J. A. (eds.) Land Application of Sludge Food Chain Implications. Lewis, Chelsea, MI. pp. 101–143.

Jones, K. C. 1996. Introduction. *Sci. Total Environ.* **185**: 1.

Jones, K. C., Stratford, J. A., Tidridge, P., Waterhouse, K. S. and Johnston, A. E. 1989. Polynuclear aromatic hydrocarbons in an agricultural soil: long-term changes in profile distribution. *Environ. Pollut.* **56**: 337–351.

Junk, G. A. and Ford, C. S. 1980. A review of organic emissions from selected combustion processes. *Chemosphere.* **9**: 187–230.

Kirton, P. J. and Crisp, P. T. 1990. The sampling of coke oven emissions for polycyclic aromatic hydrocarbons: a critical review. *Fuel.* **69**: 633–638.

Kobayashi, J. and Rittmann, B. E. 1982. Microbial removal of hazardous organic compounds. *Environ. Sci. Technol.* **16**: 170A–183A.

Koester, C. J. and Clement, R. E. 1993. Analysis of drinking water for trace organics. *Crit. Rev. Anal. Chem.* **24**(4): 263–316.

Liao, J. P., Lin, X. G. and Cao, Z. H. 2003. Effect of arbuscular mycorrhizal fungi on bioavailability of copper in sewage sludge amended red soil. *Acta Pedol. Sin.* (in Chinese). **40**(6): 929–936.

Mo, C. H., Cai, Q. Y., Wu, Q. T., Wang, B. G., Li, T. and Tian, K. 2001. A study of polycyclic aromatic hydrocarbons (PAHs) in municipal sludge of China. *Acta Scientiae Circumstantiae* (in Chinese). **21**(5): 613–618.

Mo, C. H., Wu, Q. T., Cai, Q. Y., Li, G. R. and Jiang, C. A. 2000. Utilization of municipal sludge in agriculture and sustainable development. *Chinese J. Appl. Ecol.* (in Chinese). **11**(1): 157–160.

Naylor, L. M. and Loehr, R. C. 1982. Priority pollutants in municipal sewage sludge. Part I. A perspective on the potential health risks of land application. *BioCycle.* **21**: 18–22.

Nowell, L. and Capel, P. 2003. Semivolatile Organic Compounds (SVOC) in Bed Sediment from United States Rivers and Streams: Summary Statistics. Preliminary Results from Cycle I of the National Water Quality Assessment Program (NAWQA), 1992–2001. Available online at: http://ca.water.usgs.gov/pnsp/svoc/SVOC-SED_2001_Text.html. (verified on August 25, 2004).

Pestrasek, A. C., Kugelman, I. J. and Austem, B. M. 1983. Fate of toxic organic compounds in waste water treatment plants. *J. Water. Pollut. Con. F.* **55**(10): 1 286–1 296.

Prhal, F. G., Crecellus, E. and Carpenter, R. 1984. Polycyclic aromatic hydrocarbons in Washington coastal sediments: an evaluation of atmospheric and riverine routes of introduction. *Environ. Sci. Technol.* **18**: 687–693.

Qiao, X. L. and Luo, Y. M. 2001. A preliminary probing of chemical constitute and its agricultural application of China municipal sludges. *Soils* (in Chinese). **33**(4): 205–209.

Rogers, H. R. 1996. Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Sci. Total Environ.* **185**(1–3): 3–26.

Sun, Y. H. and Luo, Y. M. 2005. Environmental and health risks of pathogens in sewage sludge and their abating approaches. *Soils* (in Chinese). **37**(5): 474–481.

Takada, H. and Ishiwatari, R. 1990. Biodegradation experiments of linear alkylbenzenes (LABs): Isomeric composition of C12 LABs as an indicator of the degree of LAB degradation in the aquatic environment. *Environ. Sci. Technol.* **24**: 86–91.

Wang, M. J. and Jones, K. C. 1994. Behavior and fate of chlorobenzenes (CBs) introduced into soil-plant systems by sewage sludge application: a review. *Chemosphere.* **28**: 1 325–1 360.

Webber, M. D. and Lesage, S. 1989. Organic contaminants in Canadian municipal sludges. *Waste Manage. Res.* **7**: 63–82.

Wild, S. R. and Jones, K. C. 1992. Polynuclear aromatic hydrocarbons uptake by carrots grown in sludge-amended soil. *J. Environ. Qual.* **21**: 217–225.

Wild, S. R., McGrath, S. P. and Jones, K. C. 1990. The polynuclear aromatic hydrocarbon (PAH) content of archived sewage sludge. *Chemosphere.* **20**: 703–716.