

PCDD/F, PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China

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Received 6 December 2005; received in revised form 13 April 2006; accepted 25 April 2006

Available online 13 June 2006

Abstract

In order to better understand land application of sewage sludge, the characterization of heavy metals, PCDD/F and PAHs in sewage sludge was investigated from six different wastewater treatment plants (WWTP) in Beijing City, China. It was found that the total concentrations of Zn in Wujiacun (WJC) sewage sludge, and Cd and Hg in sewage sludge generated from all of the six different places are higher than Chinese regulation limit of pollutants for sludge to be used for agriculture (GB18918-2002). The levels of 16 PAHs that have been categorized as priority pollutants by US EPA in the sewage sludge samples varied from 2467 to 25923 µg/kg (dry weight), the highest values of 25923 µg/kg being found in WJC WWTP. The concentrations of Benzo[a]pyrene were as high as 6.1 mg/kg dry weight in WJC sewage sludge, exceeding the maximum permitted content by GB18918-2002. Individual PAH content varies considerably with sewage samples. The ratios of anthracene to anthracene plus phenanthrene (An/178), benz[a]anthracene to benz[a]anthracene plus chrysene (BaA/228), indene[1,2,3-cd]pyrene to indene[1,2,3-cd]pyrene plus benzo[g,h,i]perylene (In/In + BP), and fluoranthene to fluoranthene plus pyrene (Fl/Fl + Py) suggest that petroleum and combustion of fossil fuel were the dominant contributions for the PAHs in sewage sludge. The concentrations of total PCDD/F in the sewage sludge ranged from 330 to 4245 pg/g d.w. The toxicity equivalent concentrations is between 3.47–88.24 pg I-TEQ according to NATO/CCMS, which is below Chinese legislation limit value proposed for land application. The PCDD/F congener/homologue profiles found in the Beijing samples indicated that the high chlorinated PCDD/F contamination might originate mainly from PCP-related source and depositional sources while the low chlorinated PCDD/F homologues could be originating from incineration or coal combustion. The major source of PCDD/Fs in Beijing sludge is still unclear.

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Keywords: Sewage sludge; Heavy metals; PCDD/F; PAHs; Homologue profile

1. Introduction

The increasing amounts of sewage sludge produced in developing countries have been one of a prime environmental issue in China. Approximately more than four million tons (dry weight) of municipal sewage sludge are produced annually in China. At the moment, most of the municipalities in China are trying to adopt co-disposal of it with solid waste at landfill sites and to use it for land

application as main alternatives for the final disposal of sewage sludge. The land application technique is one of the methods being considered and is thought to be very effective and efficient. Sludge may be applied to agricultural land, forest, disturbed land or dedicated disposal sites (Planquart et al., 1999; Murphy et al., 2000; Scancar et al., 2000; Alvarez et al., 2003; Bhogal et al., 2003; During et al., 2003; Walker et al., 2003). However, any form of disposal need to be controlled in order to protect human health and the environment, considering that sewage sludge potentially carries chemical pollutants such as heavy metals and persistent organic pollutants (POPs) (Jones and

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Alcock, 1996; Schnaak et al., 1997; Berti and Jacobs, 1998; Bright and Healey, 2003). Many wastewater treatment plants receive discharges not only from residential area but also from industry. Sludge generated in industry contains heavy metals and organic compounds at relatively high concentrations, which may vary considerably with time and mostly depend on industrial activities (Alloway and Jackson, 1991; Baveye et al., 1999). In China, up to 2002, there was no specific legislation regarding the maximum equivalent concentration levels of organochlorine compounds, especially polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polyaromatic hydrocarbons (PAHs) in sewage sludge for land application. Trace amounts of PCDD/Fs in the pg-ng TEQ/g dry weight range have been detected in most sewage sludge reported in the literature (Koch et al., 2001; Stevens et al., 2001; Pereira and Kuch, 2005; Molina et al., 2000). There are a number of potential sources of PCDD/Fs in sewage sludge: domestic wastewater, trade effluent, deposition and run-off into storm drains or formation from precursors in the wastewater (Stevens et al., 2001). Due to their low solubility in water and their lipophilic nature, these compounds are concentrated in the sewage sludge during wastewater treatment. Possible transfer pathways of these compounds into the human food chain would be food crops or grazing livestock that eat contaminated feed grown on sludge-amended soil or ingest contaminated soil directly while grazing (Prinz et al., 1993; McLachlan et al., 1996). The WHO/EURO tolerable daily intake (TDI) guideline value of 1–4 pg WHO-TEQ/kg bw/day PCDD/Fs could be exceeded if a person diet derived solely from sources originating from the products growing on land application of sewage sludge containing high concentrations of PCDD/Fs (Wild et al., 1994).

It is, therefore, important to know the PCDD/F levels in China sludge and to be able to reliably quantify and assess the transfers of TEF rated compounds into the human food chain. Within China, however, so far only limited published information exists on POPs in sewage sludge. In this study, we investigated the concentration levels of PCDD/Fs and PAHs, as well as the heavy metals in sewage sludge from six Beijing wastewater treatment plants. The potential toxicity and probable sources of these contaminants in Beijing sewage sludge were also discussed. The results from this study can be very useful for the proper application of sewage sludge into agriculture soils.

2. Material and methods

2.1. Plant description and sampling

Samples of sewage sludge were collected from six wastewater treatment plants (WWTPs) within Beijing City. They were Gaobeidian (GBD), Beixiaohe (BXH), Fangzhuang (FZH), Jiuxianqiao (JXQ), Qinghe (QH) and Wujiacun (WJC) Plants. The WWTP locations are given in Fig. 1. A summary of different wastewater from these factories is

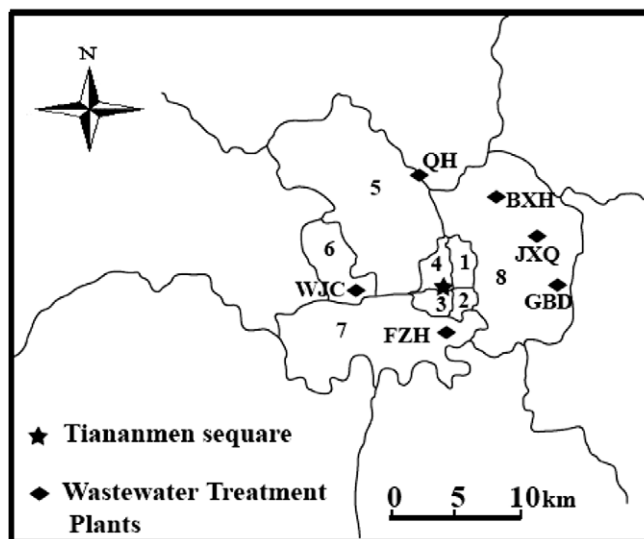


Fig. 1. Location of wastewater treatment plants in Beijing (1. Dongcheng District; 2. Chongwen District; 3. Xuanwu district; Xicheng District; 5. Haidian District; 6. Shijingshan District; 7. Fengtai District; 8. Chaoyang District).

shown in Table 1. Five kilograms of the sewage sludge from each site at two points were collected immediately after dewatering by the belt filter press over a 12-month period (February 2004–May 2005). The samples (500 g) were lyophilized for 48 h, grounded to sieve through 100 mesh, and stored at 4 °C for further analysis. PCDD/F analyses were performed at the Laboratory of Dioxin in Center for Modern Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China. PAHs analyses were conducted at the laboratory of National Research Center for Environmental Analysis and Measurement, Beijing, China.

2.2. Determination of the total concentration of heavy metal

Five grams of dried samples were subjected to the total extraction procedure. The total concentration of heavy metals in sludge samples was determined by ICP-AES (Thermo Jarrell Ash) following HNO₃ + HClO₄ (70%) + HF acidic digestion (Scancar et al., 2000). The detection limit of Cd, Cr, Cu, and Zn was 0.001, Hg 0.0001, As 0.0002, Ni 0.005, Pb 0.03 mg/l, respectively. Mercury was determined using F732-S Dual Beam Mercury Analyzer. Values were expressed as mg metal/kilogram of dry sludge. During the sample analysis, metal standard solution was checked every ten samples for quality control. For each sample, analysis was made in triplicate and differences between replications were kept <3%.

2.3. PCDD/F analysis

Ten grams of each freeze-dried sample were spiked with ¹³C-labeled surrogate standards according to the EPA method 1613B and soxhlet extracted for 24 h with tol-

Table 1
Characterization of the overall influents generated from wastewater treatment plants in Beijing in 2004–2005

Wastewater treatment plant	Capacity ($\times 10^4$ m ³ /day)	Secondary treatment	Digestion treatment	COD _{Cr} (mg/l)	BOD ₅ (mg/l)	% input of trade effluent
GBD	100	AS	Anaerobic	110–557	73–327	50
BXH	4	AS	Anaerobic	299–593	127–430	10
FZH	4	AS	Aerobic	218–1020	107–578	0
JXQ	20	OD	None	243–1070	137–570	20
QH	20	AS	A ² O	300–900	150–400	15
WJC	8	SBR	CASS	400–800	200–400	30

AS—activated sludge; OD—oxidation ditch; SBR—sequencing batch reactor; CASS—cyclic activated sludge system. BOD₅: 5 d Biochemical oxygen demand; COD_{Cr}: Chemical oxygen demand (dichromate method).

uene. The extracts were concentrated to about 1 ml by rotary evaporator and sequentially subjected to multilayered silica gel, acid alumina and florisil chromatographic columns for cleanup (described by Zhang and Jiang, 2005). After cleanup, the samples were spiked with ¹³C-labeled injection standard, evaporated down to 15 μ l for analysis. Samples were quantified by HRGC/HRMS (HP 6890/Micromass Autospec Ultima) using a HP5-ms capillary column (60 m \times 0.25 mm i.d. \times 0.25 μ m film thickness). The oven temperature programs was set as following: starting at 80 °C for 2 min; increasing the temperature from 80 to 180 °C at a rate of 15 °C/min and from 180 to 280 °C at a rate of 7.5 °C/min. The recovery rates of the standards after extraction and cleanup procedures were between 65% and 80%. The quality control measurement was described previously (Ni et al., 2005).

2.4. PAHs

Each sample (~15 g) was spiked with surrogate standards (naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂), then Soxhlet-extracted for 48 h with dichloromethane (DCM). Activated copper was added for desulphurization. The obtained extract was concentrated and solvent-exchanged to hexane, then was subjected to a 1:2 alumina/silica gel glass column for cleanup. The analytes of interest were eluted with 70 ml of a mixture of

DCM and hexane (V:V 30:70), the collected extract was concentrated to 0.2 ml under a gentle nitrogen stream. Known quantity of internal standard hexamethylbenzene was added to the samples prior to the instrumental analysis in order to quantify the PAHs concentrations.

PAHs were analyzed using a Hewlett–Packard (HP) 5890 GC equipped with a 30 m \times 0.25 mm i.d. DB-5 capillary column (0.25 μ m membrane thickness) coupled with a HP-5972 mass selective detector operated in the electron impact mode (70 eV). The injection temperature was 260 °C, the column temperature increased from 45 to 200 °C at 3 °C/min followed by an increase to 285 °C at 5 °C/min and a hold for 30 min at 285 °C. The carrier gas was helium at a constant flow rate of 1.5 ml/min. The average recoveries were 52% for Na-*d*₈, 90% for Ph-*d*₁₀, 80% for Ace-*d*₁₀, 95% for chr-*d*₁₂.

3. Results and discussion

3.1. Heavy metal in sewage sludge

The concentrations of heavy metals expressed on a dry mass basis in sludge are given in Table 2. Chinese legislation law (GB18918-2002) prohibits the use of sewage sludge as fertilizer in agriculture that exceeds the maximum values allowed for total concentrations of heavy metals (Table 2). The total concentrations of Hg in all of the

Table 2
The Concentration of heavy metals in sewage sludge sampling from different WWTP and their comparisons with maximum permitted content used for soil (GB18918-2002) (mg/kg dry matter)

Heavy metals	GBD	BXH	FZH	JXQ	QH	WJC	Maximum permitted content used for soil pH in China	
							PH < 6.5	pH \geq 6.5
Cd	7.0 \pm 1.2	7.3 \pm 3.4	5.9 \pm 1.4	13.0 \pm 4.4	12.7 \pm 1.8	9.3 \pm 1.3	5	20
As	16.7 \pm 4.0	23.7 \pm 6.5	23.5 \pm 5.4	21.2 \pm 1.5	25.2 \pm 4.8	26.0 \pm 7.7	75	75
Cr	57.8 \pm 22.3	45.8 \pm 19.6	45.8 \pm 7.5	59.2 \pm 12.4	78.4 \pm 19.1	54.8 \pm 11.1	600	1000
Hg	21.8 \pm 2.9	19.3 \pm 2.7	23.4 \pm 3.4	18.8 \pm 2.2	17.0 \pm 2.4	24.0 \pm 6.0	5	15
Ni	49.9 \pm 12.8	49.3 \pm 17.1	51.8 \pm 21.2	95.5 \pm 10.1	56.8 \pm 10.2	60.0 \pm 15.1	100	200
Pb	57.5 \pm 10.4	57.5 \pm 18.3	70.4 \pm 21.6	109.3 \pm 33.5	81.3 \pm 7.4	95 \pm 22.6	300	1000
Cu	229.0 \pm 70.4	218.0 \pm 97.5	131.2 \pm 27.8	272.2 \pm 66.7	253.6 \pm 84.2	394.5 \pm 204.9	800	1500
Zn	1431.4 \pm 395.1	1088.2 \pm 259.6	783.4 \pm 118.1	1182.8 \pm 172.2	1376.8 \pm 267.9	3096.3 \pm 1303.5	2000	3000

The concentration of heavy metal is the mean concentration \pm SE (SE: standard error; *N* = 5, Sampling date is as following: 9 February 2004; 31 May 2004, 14 September 2004; 1 November 2004; 17 May, 2005).

sewage sludge and that of Zn in WJC sewage sludge obviously exceed the limit values for basic soil, while the total concentrations of Cd in all of the sewage sludge exceed the limit values for acidic soil according to the law. Based on our results in Table 2, all of the sewage sludge should not be recommended for use in agriculture, particularly due to the high total concentration of Hg and Zn in WJC sewage sludge. The high Hg concentration in sewage sludge can be originated from sterilization in hospital and household used in Beijing. The high Zn concentration in WJC sewage sludge may result from industrial source (Wang, 1997). The possible final deposition according to German legislation law would be used for landfilling.

3.2. PAHs in the sewage sludge

The total contents of 16 PAHs, categorized as priority pollutants by US EPA, range from 2467 to 25923 $\mu\text{g}/\text{kg}$ (dry weight) (Table 3). The highest values of 25923.79 $\mu\text{g}/\text{kg}$ were found in WJC WWTP where the sewage sludge was collected from complicated wastewater discharged from steel industry and dyeing industry. Individual PAH content varied significantly with sewage samples (Fig. 2). PAHs with less than 4 rings represented 6%, 10%, 11%, 11%, 16%, and 17% of the total PAHs from WJC, JXQ, GBD, QH, BXH, and FZH, respectively. The 4–6 ring PAHs accounted for 88% of the total PAHs for GBD, whereas those PAHs rose up to 93% of the total PAHs for WJC. The higher molecular weight PAHs, indene[1,2,3-*cd*]pyrene and benzo[*g,h,i*]perylene, were detected in every sites except for QH WWTP. Their presence in sludge from

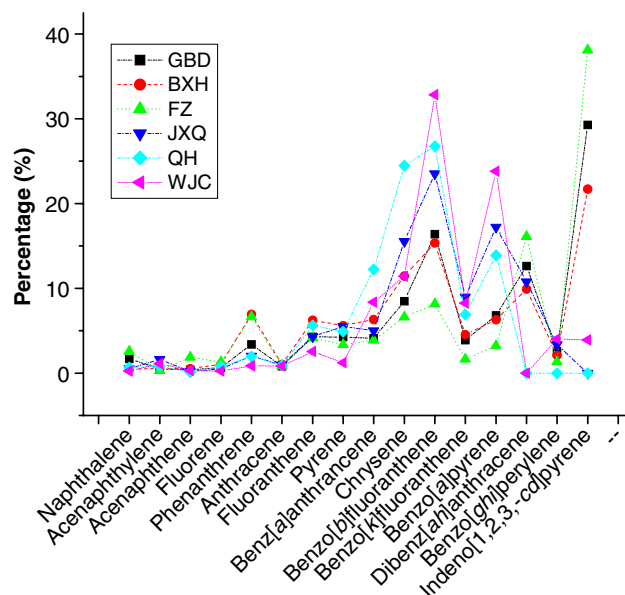


Fig. 2. Different distribution patterns of PAHs in sewage sludge in Beijing.

the five WWTPs could be attributed to discharge from fuel industry because those WWTPs treat wastewater that come from the domestic and industrial area in Beijing. The concentrations of Benzo[*a*]pyrene were as high as 6.1 mg/kg dry weight in WJC sewage sludge, exceeding the maximum content permitted by 'Discharge standards of pollutant for municipal wastewater treatment plant' (GB18918-2002). Therefore, WJC sewage sludge should not be recommended

Table 3

Summary of PAH concentrations and relative ratios of PAHs in the sewage sludge from different wastewater treatment plants in Beijing ($\mu\text{g}/\text{kg}$ dry weight)

Compound	GBD	BXH	FZH	JXQ	QH	WJC
Naphthalene	97.91	23.89	180.95	17.73	16.23	64.21
Acenaphthylene	29.30	29.26	21.55	54.90	20.08	289.86
Acenaphthene	21.32	26.88	131.14	6.47	3.11	75.35
Fluorene	37.61	54.08	91.77	17.37	19.65	65.27
Phenanthrene	196.92	360.15	466.41	68.39	48.37	226.72
Anthracene	46.13	52.91	58.69	32.73	22.46	214.44
Fluoranthene	249.48	323.86	293.47	146.31	138.40	658.33
Pyrene	247.73	290.93	236.31	187.01	120.47	317.31
Benz[<i>a</i>]anthracene	238.90	328.30	274.19	170.58	302.05	2171.24
Chrysene	493.89	595.74	463.96	528.46	603.85	2958.66
Benzo[<i>b</i>]fluoranthene	955.09	797.86	572.71	800.49	659.91	8514.09
Benzo[<i>k</i>]fluoranthene	226.65	235.60	115.07	305.18	170.15	2138.07
Benzo[<i>a</i>]pyrene	395.90	327.18	226.73	585.48	342.58	6174.17
Dibenz[<i>ah</i>]anthracene	735.87	514.56	1134.62	366.82	N.D.	N.D.
Benzo[<i>g,h,i</i>]perylene	150.44	108.98	93.14	113.68	N.D.	1038.67
Indeno[1,2,3- <i>cd</i>]pyrene	1705.99	1128.21	2682.70	N.D.	N.D.	1017.40
Σ PAHs	5829.13	5198.39	7043.41	3401.6	2467.31	25923.79
An/178	0.19	0.13	0.11	0.32	0.32	0.49
BaA/228	0.33	0.36	0.37	0.24	0.33	0.42
In/(In + BP)	0.92	0.91	0.97	–	–	0.49
Flua/pyrene + Flua	0.50	0.53	0.55	0.44	0.53	0.67
Pyrene/fluoranthene	0.99	0.90	0.81	1.28	0.87	0.48
Phen/anthr	4.27	6.81	7.95	2.09	2.15	1.06
Benzo[<i>a</i>]pyrene/anthr	8.58	6.18	3.86	17.89	15.25	28.79

N.D.: not detectable.

for agriculture use. The highest permissible concentrations of PAHs (sum of six PAHs, namely fluoranthene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene and indeno[1,2,3-*cd*]pyrene) in sludge used for soil amendment in Sweden since 1996 is 3.0 mg/kg of dry sludge. According to this limit, sewage sludge from GBD, BXH, and FZH also should not be recommended for use in land application. However, the contaminant levels of the sludge were lower than those proposed by EPA and Dutch guidelines.

3.3. PAHs source

Generally, sludge from a petrogenic-source has lower molecular weight (LMW) PAHs with depletion of higher molecular weight (HMW), while sludge from pyrogenic sources is abundant with HMW PAHs. Although the sewage sludge in Beijing contained a considerable amount of HMW PAHs, it was also abundant in LMW PAHs. This result indicates the sludge comes from both petrogenic and pyrogenic origins.

Concentration ratios of various PAHs are often used to distinguish between combustion and petroleum sources (Soclo et al., 2000). Using molecular mass of 178 as a measure, anthracene to anthracene plus phenanthrene (An/178) ratio lower than 0.10 is usually taken as an indication of petroleum sources while the ratio higher than 0.10 usually is considered as an indication of combustion sources (Budzinski et al., 1997; Schauer et al., 1999a,b). For the sewage sludge in Beijing, the ratios of all samples were higher than 0.10, suggesting that the contamination source resulted from combustion activities. Using molecular mass of 228 as a measure, benz[*a*]anthracene to benz[*a*]anthracene plus chrysene (BaA/228) ratio lower than 0.20 implies a petroleum source for sludge; the ratio from 0.20 to 0.35 is considered as either petroleum or combustion sources; and the ratio higher than 0.35 should originate from combustion sources (Yunker et al., 2002). From Table 3, we can find that BaA/228 ratios in sludge samples from JXQ, QH, and GBD were between 0.20 and 0.35, while those from BXH, FZH, and WJC were higher than 0.35. These data suggest that combustion also is a main pollution source in addition to petroleum. Indene[1,2,3-*cd*]pyrene to indene[1,2,3-*cd*]pyrene plus benzo[*g,h,i*]perylene (In/In + BP) ratio lower than 0.20 indicates a petroleum source; the ratio between 0.20 and 0.50 indicates a source from liquid fossil fuel (vehicle and crude oil) combustion; and the ratio higher than 0.50 suggests the PAHs mainly originate from grass, wood and coal combustion (Yunker et al., 2002). In this study, In/In + BP ratios for GBD, BXH, FZH samples were higher than 0.50, implying a combustion character of liquid fossil fuel or coal. Fluoranthene to fluoranthene plus pyrene (Fl/Fl + Py) ratio of 0.50 is usually defined as the petroleum/combustion transition point (Budzinski et al., 1997). If the Fl/Fl + Py ratio is below 0.50 the PAHs in sludge most likely result from petroleum combustion (gasoline, diesel, fuel oil and

crude oil combustion and emissions from cars and diesel trucks). If the ratio is above 0.50, the PAH contamination could result from kerosene, grass, coal and wood combustion, and creosote. In this study, Fl/Fl + Py ratio for all of sample except JXQ are higher than 0.50, implying the PAHs in the sludge resulted from grass, wood or coal combustion. In 2002, there were 2 100 000 motor vehicles in Beijing (Zhou et al., 2005). The pyrene/fluoranthene ratio for JXQ sewage sludge was 1.28, showing the PAHs resulted from motor-driven vehicle exhaust. Our result is consistent with data measured in other situations, such as 1.2 for dusts collected in a parking lot in the center of Paris (Ollivon et al., 1999) and 1.4 in motor car exhaust (Giger and Schaffner, 1978). For the samples from GBD, BXH, FZH, QH, and WJC, the ratio values ranged from 0.48 to 0.99 suggest the PAH contamination did not mainly resulted from car exhaust. In addition, there are a number of steel works and power plants in Beijing urban area that use coal as their energy sources. Those PAHs may enter the WWTP by direct discharge or/and deposition from air in road-runoff/stormwater drain.

3.4. PCDD/Fs in the sewage sludge

The concentrations of PCDD/F in the sewage sludge and the toxicity equivalent concentration calculated according to NATO/CCMS are shown in Table 4. The sludge samples contained low contamination of PCDD/Fs since the total PCDD/Fs ranged from 330 to 4245 pg/g d.w. The sludge from GBD had the highest concentration of total PCDD/Fs that was 13 times more than the lowest from BXH. These values are within the normal range for sewage sludge reported by others (Rappe et al., 1994; Stevens et al., 2001). The toxicity equivalent concentrations were situated between 3.4 and 88.2 pg/g I-TEQ according to NATO/CCMS. The highest I-TEQ was found in the samples from GBD (88.2 pg/g d.w.), followed by that from JXQ (32.8 pg/g d.w.), WJC (7.0 pg/g d.w.), QH (5.3 pg/g d.w.), FZH (4.1 pg/g d.w.), and BXH (3.4 pg/g d.w.). The PCDD/F equivalent concentrations found in Beijing sewage sludge were below the upper limit concentration for land application according to GB18918-2002, the Chinese legislation law for agricultural use. The maximum PCDD/F level for sludge considered for disposal in soils is 100 pg I-TEQ/g (dry weight).

GBD plant with a 50% input of trade effluent has the highest concentration of total PCDD/Fs concentration. This indicates that point sources (trade effluent discharges) are the most important contributors of PCDD/F to the sludge. This is not in agreement with the data reported by Stevens et al. (2001), indicating no positive or negative correlation of PCDD/F concentration with the size and degree of a known industrial input to the plants. The second and third highest total PCDD/F concentrations came from samples from JXQ and WJC. However, plant JXQ and QH have different total PCDD/F concentrations although both of them have similar size and receive similar

Table 4
Concentration of PCDD/F (pg/g d.w.) in different wastewater treatment plants in Beijing

PCDD/F	Concentration of PCDD/F (pg/g d.w.)					
	GBD	BXH	FZH	JXQ	QH	WJC
2,3,7,8-TCDD	7.61	<0.17	<0.18	<0.10	<0.14	<0.08
1,2,3,7,8-PeCDD	20.96	<0.35	<0.24	5.58	1.18	0.60
1,2,3,4,7,8-HxCDD	19.86	<0.18	<0.17	6.54	2.68	1.60
1,2,3,6,7,8-HxCDD	33.10	1.34	<0.20	16.83	1.56	2.80
1,2,3,7,8,9-HxCDD	24.19	0.59	<0.09	10.50	1.39	2.20
1,2,3,4,6,7,8-HpCDD	226.18	10.75	12.64	118.63	13.15	16.30
OCDD	503.76	106.41	210.59	316.36	262.55	34.90
2,3,7,8-TCDF	97.03	3.19	3.00	14.31	3.35	4.40
1,2,3,7,8-PeCDF	23.31	2.89	3.81	24.58	4.61	4.70
2,3,4,7,8-PxCDF	62.76	2.59	2.32	14.91	2.62	5.70
1,2,3,4,7,8-HxCDF	44.85	4.66	7.80	65.08	6.32	6.40
1,2,3,6,7,8-HxCDF	46.12	3.89	3.90	38.69	4.58	5.30
1,2,3,7,8,9-HxCDF	46.82	<0.21	.20	2.40	<0.14	2.50
2,3,4,6,7,8-HxCDF	5.90	2.17	2.57	20.51	3.33	6.60
1,2,3,4,6,7,8-HpCDF	195.46	21.17	37.02	180.80	27.47	25.70
1,2,3,4,7,8,9-HpCDF	26.41	<0.20	23.83	41.01	6.86	3.40
OCDF	828.78	24.95	110.67	114.80	106.84	11.60
Total TCDD	162.68	18.17	17.42	54.30	23.17	29.70
Total PeCDD	103.23	4.76	2.87	28.27	14.72	43.40
Total HxCDD	438.29	1.93	<LOQ	52.87	6.64	57.90
Total HpCDD	448.33	20.95	23.95	233.04	24.33	50.10
Total PCDD, Tetra to Octa	1656.29	152.20	254.83	684.83	331.41	216.00
Total TCDF	438.35	84.98	59.63	159.04	80.12	163.30
Total PeCDF	683.79	30.01	24.02	89.95	35.16	173.80
Total HxCDF	322.39	16.70	19.90	181.41	23.81	92.90
Total HpCDF	315.40	21.17	85.84	323.91	45.50	55.20
Total PCDF, Tetra to Octa	2588.72	177.80	300.06	869.10	291.42	496.80
Total PCDD/F	4245.01	330.00	554.89	1553.93	622.83	712.80
I-TEQ dioxins	28.57	0.41	0.34	7.68	1.55	1.16
I-TEQ furans	59.67	3.06	3.79	25.12	3.75	5.91
$R_{TEQ\ PCDD/TEQ\ PCDF}$	0.48	0.13	0.09	0.31	0.41	0.20
I-TEQ	88.24	3.47	4.13	32.80	5.30	7.07

amounts of trade effluent. Interestingly, plant JXQ uses oxidation ditch for secondary treatment of wastewater whereas plant QH employs activated sludge tanks for the treatment. Therefore, the types of the treatment of wastewater seem to be more important in defining the amount of PCDD/Fs than trade effluent for sludge.

3.5. PCDD/Fs homologue pattern and possible sources

All the samples contained very high concentrations of OCDD and OCDF, and relatively high concentrations of HpCDDs and HpCDFs. Fig. 3 shows the 2,3,7,8-PCDD/F congener pattern without OCDD and OCDF because they were dominating the profile. The ratio $R_{TEQ\ PCDD/TEQ\ PCDF}$ was calculated, and the values ranged from 0.09 to 0.48 with a mean value of 0.27 (Table 4). Generally, sewage sludge samples are characterized by a $R_{TEQ\ PCDD/TEQ\ PCDF} > 1$ (Eljarrat et al., 1997, 1999). However, all of samples analyzed in our study presented a $R_{TEQ\ PCDD/TEQ\ PCDF} < 1$; and concentration of the total PCDD was lower than that of the total PCDF except for QH samples. Fig. 4 displays a comparison among the profiles of homologues found in the sludge samples. Table 5 shows the ratios between the total sums of PCDD and PCDF as well as the dioxin/furan ratios of the

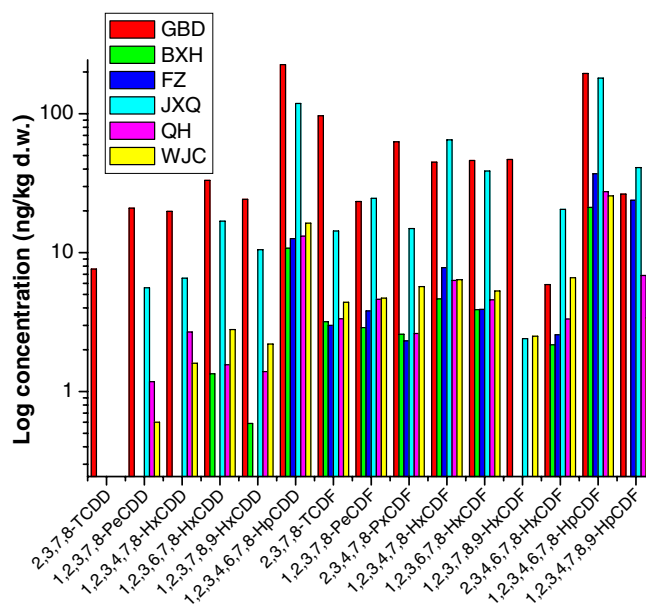


Fig. 3. PCDD/F congener profile excluding OCDD and OCDF.

hepta- and octa-groups, as an indicator of different sources of contamination according to previous reports (Hagenma-

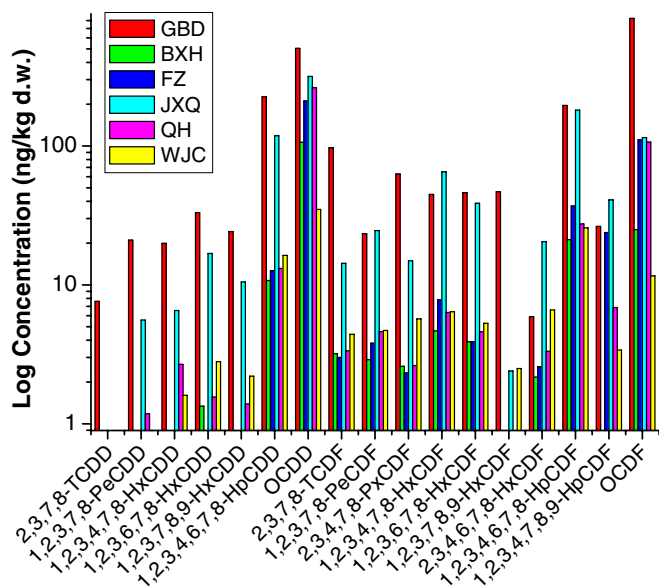


Fig. 4. Homologue profile of the sludge samples.

ier et al., 1990; Huntzinger and Fiedler, 1993; Horstmann and McLachlan, 1994). The homologue profiles in the sludge samples indicate a characteristic predominance of the highly chlorinated congeners HxCDD/F-OCDD/F except for WJC samples. They contributed for 58–81% of the total PCDD/F in the sludge samples, indicating that thermal processes were not the primary source of the contamination. These contamination profiles bear some resemblance to the typical PCDD/F contamination reported by Rappe et al. (1989). This is confirmed by the ratios of OCDD/OCDF and $\sum\text{HpCDD}/\sum\text{HpCDF}$ observed for these samples. The OCDD/OCDF ratios range from 0.61 (GBD) to 4.27 (BXH), while the $\sum\text{HpCDD}/\sum\text{HpCDF}$ ratios are from 0.34 (FZH) to 1.16 (GBD). Those ratios are within the values described by Huntzinger and Fiedler (1993) for contaminations from PCP, and the values observed by Horstmann and McLachlan (1994) for chloroaniline precursors. Eljarrat et al. (1999) suggest that the ratio

of 1,2,3,6,7,8-HxCDD/1,2,3,4,7,8-HxCDD is a useful indicator for technical mixture of PCP (>100). But in this study, the ratios of these two HxCDD congeners were from 0.58 to 2.57. This suggests that PCP is not a major source of PCDD/Fs in our samples. Horstmann and McLachlan (1995a) found the PCDD/PCDF in the synthetic textiles and in the cotton products originated from dyes derived from chloranil. Furthermore, Alcock and Jones (1997) found that the PCP-based textile preservatives, and chloranil-based dyes and pigments contain large amount of PCDD/PCDF and can be significant source of the higher chlorinated congeners of PCDD/PCDF, particularly octaCDD in sewage sludge. Rappe et al. (1999) postulated that there was natural formation of higher chlorinated PCDDs in sediments. As an alternative explanation to PCP contamination, the formation was also responsible for the homologue pattern of sludge in which the higher chlorinated PCDDs were dominant. According to these reports we hypothesize that the household water including effluent from textile washing are the main source of higher chlorinated congeners in Beijing sludge samples. In the other hand, the congener profile dominated by octaCDD was also found in storm sewer water (urban runoff) (Naf et al., 1990) and in urban street runoff and sediments from storm water (Horstmann and McLachlan, 1995b). Therefore, the urban runoff could be another important source of PCDD/PCDF in WWTP plant.

Meanwhile, the Beijing sludge samples contained a large portion of lower chlorinated TCDD/F-PeCDD/F congeners (ranging from 18.7% to 57.2%) in a typical “burning profile” (Table 5). Such pattern suggests that Beijing might require domestic use of combustible material in severe weather condition. Rappe et al. (1987) reported that the congeners pattern of pentaCDF with 1,2,3,7,8-CDF and 2,3,4,7,8-CDF as the predominated congeners were similar with that of samples from car exhaust and emission from incinerator plant. The emission of PCDD/PCDF from Guohua power plant in the vicinity of GBD could be contributor of lower chlorinated congeners of PCDD/F. However, quite large car traffic in GBD area can be considered as another contributor of lower chlorinated congeners of

Table 5

Sums of PCDD and PCDF and the dioxin/furan ratios of the hepta- and octa-group, as indicator of different of contamination according to several other publications

	GBD	BXH	FZH	JXQ	QH	WJC	Incinerator ^a	Fossil fuel burning ^b	PCP ^c	Chloroaniline ^d
$\sum\text{HxCDD}/\text{F-OCDD}/\text{F}\%$	67.30	58.21	81.27	78.66	75.41	42.45	33.4	27.8	100	100
$R_{\text{PCDD:PCDF}}$	0.64	0.86	0.85	0.79	1.14	0.43	3.8	3.5	0.2	1.8
$R_{\text{OCDD:OCDF}}$	0.61	4.27	1.90	2.76	2.46	3.01	1.1	19.6	6.5–10	0.5
$R_{\text{HpCDD:HpCDF}}$	1.16	0.51	0.34	0.66	0.48	0.63	3.9	6.5	2	0
1,2,3,6,7,8-HxCDD/1,2,3,4,7,8-HxCDD	1.67	–	–	2.57	0.58	1.75				
$\sum\text{TCDD}/\text{F-PeCDD}/\text{F}\%$	32.70	41.79	18.73	21.34	24.59	57.55				
2,3,7,8-TCDF/Total TCDF%	22.13	3.75	5.03	9.00	4.18	2.69				
1,2,3,4,6,7,8-HpCDF/ $\sum\text{HpCDF}$	61.97	100.00	43.12	55.82	60.37	46.56				

^a Hagenmaier (1987).

^b Hagenmaier (1990).

^c Huntzinger and Fiedler (1993).

^d Horstmann and McLachlan (1994).

PCDD/PCDF in GBD WWTP due to atmospheric deposition from the traffic in the surrounding of the WWTPs (Oleszek-Kudlak et al., 2005). The number of data obtained in this study, however, is rather not enough to indicate precisely the main sources of PCDD/PCDF in samples from WWTP.

4. Conclusions

The total concentrations of Zn in WJC sewage sludge, and of Hg and Cd in all of sludge exceed regulatory limits for sludge to be used in agriculture in China (GB18918-2002). Therefore, the sludge from those wastewater treatment plants should not be permitted for agricultural use. For PCDD/F, the WHO-TEQ values in the sludge are below those recommended by Chinese regulatory law for agricultural use. Homologue profiles of the samples indicated that higher chlorinated PCDD/F contamination seems to originate mainly from PCP-related source, while lower chlorinated homologues contamination may be originating from incineration or coal combustion. The major sources of PCDD/Fs to Beijing sludge are still unclear. Regarding PAHs, the value of Benzo[*a*]pyrene in WJC sewage sludge exceeded much the maximum content permitted by 'Discharge standards of pollutant for municipal wastewater treatment plant'. Individual PAH content varies considerably with sewage samples. The PAHs in sewage sludge originated from mixed source including combustion of petroleum and fossil fuel.

Acknowledgement

This work was funded by the Innovation Project of the Chinese Academy of Sciences (No: KSCX2-SW-128 to Dai).

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