Levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in China and chemometric analysis of potential emission sources

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Abstract

Aimed to give a preliminary image of dioxin pollution in China, chemometric analysis was performed to determine background dioxin levels during the period 1994–2002 and potential emission sources. Using principal components analysis (PCA), the congener profiles of 71 sediment samples from rivers, lakes, and sea bays around China were compared with the congener profiles of various known or suspected industrial, residential, and municipal dioxin sources to determine whether the dioxin residues typically found in a broad range of potential environmental sources could explain the presence of these chemicals in China. It was found that the background dioxin levels of China were similar to those of lightly polluted samples from other countries during the period 1994–2002. Primary ferrous ore sintering and secondary lead and aluminum smelters were the major sources of dioxin emission in China. Chloranil and wastewater from chemical plants, sodium pentachlorophenate, and pulp bleaching were also important sources of dioxin emission. Open burning of e-waste as well as diesel-fueled and leaded gas-fueled vehicles were additional possible sources of dioxin. In contrast to other countries, in China, flue gases from incineration of municipal waste, hazardous waste, and medical waste might be minor sources of dioxin emission.

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1. Introduction

Persistent organic pollutants (POPs) are toxic chemicals that persist in the environment, are liable to bioaccumulation through the food web, and pose a risk of adversely affecting human health and the environment. Historically, nine of a dozen POPs have been intentionally or unintentionally produced in China. On June 25, 2004, the Chinese government ratified the Stockholm Convention on POPs. As part of this agreement, in November 2006, China will be required to submit its National Implementation Plan to the Conference of Party, together with a national inven-

tory of the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs).

In China, relatively few studies of PCDD/Fs have been carried out in comparison to the number of studies on organochlorine pesticides and polychlorinated biphenyls (Fu et al., 2003; Liu et al., 2004; Chen et al., 2005; Wong et al., 2005). However, because of China's huge size and the high cost of dioxin-monitoring, launching many large-scale dioxin-monitoring projects in China is not feasible. Moreover, PCDD/Fs are unintentionally produced in many industries throughout the country, making the issue of dioxin pollution difficult and complex to address. Therefore, identification of the major sources of dioxin emission is important for taking better countermeasures to efficiently control and reduce dioxin pollution.

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Recently, Alcock et al. (2001) and Everaert and Baeyens (2002) showed that PCDD/F emission sources have unique congener profiles and that similar industrial processes have similar emission fingerprints. Chemometric analysis is an effective and efficient tool for identifying a dioxin emission source (Okeefe et al., 1994; Buekens et al., 2000; Alcock et al., 2002; Lee et al., 2004; Schmid et al., 2005). Here, chemometric analysis was used to study dioxin pollution in China. PCDD/F levels in air, water, soil, and sediment samples collected around China over a period of about 10 years were examined and the potential emission sources were determined by principal components analysis (PCA). This study should be helpful in creating a PCDD/F inventory for China and in developing a strategy for reduction of PCDD/Fs in China.

2. Materials and method

2.1. PCDD/F samples description

PCDD/F levels in air, water, soil, and sediment samples and their congener profiles were collected around China over a period of about 10 years. More than half of the recent research on dioxins in China has focused on sediment samples. Fig. 1 shows the locations where sediment samples were collected from 1994 to 2002, and Table 1 lists their PCDD/F levels. Most of these samples were collected in the southeastern part of the country, covering a large area and several important water systems: the Yangtze

River – the largest river in China – and its catchments; the Liao He River in the Northeast; the Pearl and Liangjiang Rivers in the South; the Nanpaiwu River in Tianjin; Poyang Lake; Dongting Lake; Ya-Er Lake; Bohai Bay; and Hong Kong Bay.

The sediment and soil samples were extracted by Soxhlet method and cleaned by several liquid chromatographic purification steps, including: alumina, multilayer silica and florisil columns (Wu et al., 1997). Multilayer silica column purification was commonly adopted, but the composition and structure of the column varied between different researchers (Luksemburg et al., 1996; Zheng et al., 1997; Wu et al., 2001a; Chen et al., 2003b; Hu et al., 2005). Water samples were enriched by XAD (Suplco Company), then freeze-dried and extracted by Soxhlet-apparatus (Wu et al., 2001b). Air sampling of PCDD/Fs was conducted by semi-volatile samplers (Model GPS-1, Graseby Andersen, USA) and a precleaned PUF plug (6 cm diameter, 7.5 cm length). Sample clean-up included liquid–liquid partition with 20% w/v potassium hydroxide solution and concentrated sulphuric acid, and column chromatography using mixed silica and alumina (Louie and Sin, 2003). The PCDD/F samples were analyzed according to US EPA Method 1613A or Japanese Industry Standard Method K0311. The identification of PCDD/Fs was accomplished with high resolution gas chromatography–mass spectrometry. Quantization of PCDD/Fs was performed in selected-ion monitoring mode (Luksemburg et al., 1996; Chen et al., 2003a; Hu et al., 2005).

Fig. 1. Surficial sediment sampling locations.

Table 1
Sampling locations and PCDD/F levels of the sediment samples

Sample	Water system	Position in Fig. 1	Number of samples	PCDD/F concn range (pg g ⁻¹)	Year	Reference
1–4	Ya–Er Lake	D	4	61–33837	1994	Wu et al. (1997)
5–9	Ya–Er Lake	D	5	2100–6620	1997	Wu et al. (2001a)
10–17	Dongting Lake	J	8	52617–233304	1995	Zheng et al. (1997)
18–24	Dongting Lake	J	7	641–1881	1999	Zheng et al. (2003)
25–31	Liangjiang River	Q	7	56–743180	2002	Luksemburg et al. (2002)
32–38	Dagu	B	7	425–1456170	2001	Luksemburg et al. (2001)
39	Bengbu Harbor	F	1	129	1995	Luksemburg et al. (1996)
40	Hongze Lake	G	1	62.09	1995	Luksemburg et al. (1996)
41	Grand Canal	F	1	58.5	1995	Luksemburg et al. (1996)
42	Fu River	I	1	103.9	1995	Luksemburg et al. (1996)
43	Nanfei River	L	1	3944.5	1995	Luksemburg et al. (1996)
44	Dongting Lake	J	1	267.86	1995	Luksemburg et al. (1996)
45	Han River	H	1	13.52	1995	Luksemburg et al. (1996)
46	Poyang Lake	M	1	900.49	1995	Luksemburg et al. (1996)
47–50	Yangtze River	N	4	162.4–462.0	1995	Luksemburg et al. (1996)
51–52	Huangpu River	O	2	65.29–178.29	1995	Luksemburg et al. (1996)
53	Huaihe River	E	1	515.4	1995	Luksemburg et al. (1996)
54–60	Hong Kong Bay	R	7	314–10997	2001	Muller et al. (2002)
61–68	Pearl River	P	8	498–2590	1997	Zheng et al. (2001)
69–70	Nanpaiwu River	B	2	121302–3289600	2002	Hu et al. (2005)
71	Bohai Bay	C	1	447.8	2002	Hu et al. (2005)
– ^a	Yangtze River	N	2	751–1024	1998	Martens et al. (2000)
– ^a	Yangtze River	K	1	23197	1999	Martens et al. (2000)
– ^a	Liao He River	A	1	18.3	1999	Martens et al. (2000)

^a Only the TEQ level was reported; no information about the congener profile was provided.

2.2. Congener profiles of the suspected emission sources

Fig. 2 shows congener profiles of the suspected sources of dioxin emission. The congener profiles for sodium pentachlorophenate, chloranil, wastewater from chemical plants, pulp bleaching, diesel-fueled vehicles, and open burning of e-waste were derived from studies pertaining to China (Schechter et al., 1994; Bao et al., 1995; Jiang et al., 1995; Luksemburg et al., 1996; Zhang et al., 2000a,b, 2002; Luksemburg et al., 2002; Lee et al., 2004). The other profiles (profiles for emissions from municipal solid waste incineration (MSWI), hazardous waste incineration (HWI), medical waste incineration (MeWI), crematoria, leaded gas-fueled vehicles, unleaded gas-fueled vehicles, utilities and industrial boilers, cement kilns not burning hazardous waste, primary ferrous ore sintering, secondary aluminum smelters, secondary copper refining, and secondary lead smelters) were derived from the dioxin database compiled by the US Environmental Protection Agency (US-EPA) ((US-EPA), 2001). Paralleling the results for the sediment samples, OCDD was the dominant compound in most of the emission sources.

2.3. Principal components analysis

SPSS 13 (Apache Software Foundation) was adopted for the principal components analysis of the 71 surficial sediment samples listed in Table 1. The congener profiles of these samples were compared with the congener profiles

of suspected industrial, residential, and municipal sources of dioxin to determine whether the PCDD/F residues typically found in a broad range of potential environmental sources could explain the presence of these chemicals in China.

To reduce the effect of concentration differences among the sediment samples, the data were normalized before calculation. The foregoing analysis showed that OCDD is preponderant in both the sediment samples and the dioxin emission sources, so OCDD could overwhelm the influence of less dominant congeners during normalization by relative concentration. Therefore, the congener profiles for the 17 possible 2,3,7,8-substituted congeners were generated as follows: For the sixteen 2,3,7,8-substituted congeners exclusive of OCDD, normalization was implemented by dividing the concentration of each congener by the sum of the concentrations of all 16 congeners. OCDD was normalized by dividing its concentration by the sum of the concentrations of all 17 possible 2,3,7,8-substituted congeners. Concentrations that were below the detection limit were treated as the half of the detection limit.

3. Results and discussion

3.1. PCDD/F levels in environmental samples

The PCDD/F concentrations of the sediment samples vary from 14 to 3,289,600 pg g⁻¹ (Table 1). The OCDD mass fraction was about 80%. The minor pollutant sample

Fig. 2. PCDD/F congener profiles of some emission sources.

was collected at Han River and Liao He River, while the major pollutant samples were collected at Nanpawu River and Dagou Bay in Tianjin, where many large chemical plants were located. The PCDD/F concentrations of most of the samples were lower than $100 \text{ pg I-TEQ g}^{-1}$, which is

quite close to values for lightly polluted rivers and bays in other countries, e.g., the Tama River, Tokyo Bay, and Osaka Bay in Japan (Onodera et al., 1999; Hosomi et al., 2003; Takigami et al., 2005); the Lower Great Lakes, North America (Marvin et al., 2002); and the Po River

and Venice Lagoon, Italy (Frignani et al., 2001; Fattore et al., 2002).

Wu et al. (2001b) showed that PCDD/Fs, other than hexachlorocyclohexane (HCH), were prominent pollutants in some areas of the Yangtze River after production of HCH was banned in the late 1990s. Ya-Er Lake, located along the middle-lower reaches of the Yangtze River, had PCDD/F levels in the range 0.11–0.43 pg I-TEQ l⁻¹. Moreover, all water samples analyzed by Wu had the same congener profile, and OCDD was the dominant congener. The concentrations of most of the 2,3,7,8-substituted congeners decreased with increasing distance from the wastewater discharge of a pesticide plant.

In 1994, soil samples from rice and cotton fields in Hubei Province, southern China, were collected for analysis of pollutants. The fields were suspected of being polluted by pesticides and contaminated irrigation water. The mean PCDD/F concentrations in the samples were about 26.21 pg g⁻¹ (0.11 pg I-TEQ g⁻¹) for samples from the cotton field and 95.55 pg g⁻¹ (1.30 pg WHO-TEQ g⁻¹) for samples from the rice field (Wu et al., 1998; Wu et al., 2002). The congener profiles of the samples showed high proportions of OCDD, OCDF, and 1234678-HpCDD. Later, in September 2002, Chen studied 42 surface soil samples collected around Beijing in northern China and found that the background dioxin level of the samples was about 0.88 pg WHO-TEQ g⁻¹ (Chen et al., 2003b). This value is comparable to that for lightly polluted urban and industrial soil of other countries [e.g., 0.7–1.5 pg I-TEQ g⁻¹ in Italy (Caserini et al., 2004), 1.1–11 pg I-TEQ g⁻¹ in Switzerland (Schmid et al., 2005) and 0.13–24.20 pg I-TEQ g⁻¹ in Spain (Schuhmacher et al., 2002)], lower than the background level for soil in Tokyo (42.8 pg I-TEQ g⁻¹), and higher than the background level for unpolluted areas [e.g., 0.16 pg I-TEQ g⁻¹ in Spain and 0.4–4.27 pg I-TEQ kg⁻¹ in Japan (Sakurai et al., 2000)].

Dioxin-monitoring data for ambient air samples were available only for Hong Kong. There is still no regular dioxin-monitoring net in mainland China. The PCDD/F concentration in Hong Kong varies from 40 to 180 fg I-TEQ m⁻³, depending on the season (Louie and Sin, 2003). In this paper, the soil–air partition coefficient (K_{SA}) and plant–air partition coefficient (K_{PA}) (Chen et al., 2003a) were employed to assess the level of PCDD/Fs in the ambient air of Beijing and Dalian. Assuming gas-phase equilibrium (i.e., assuming atmospheric burdens were mainly due to a mixture of primary sources and did not involve revolatilization from the soil), a PCDD/F concentration of about 35.6 fg I-TEQ m⁻³ was calculated for Beijing. This value is comparable to the values for the urban air of Spain (10–357 fg I-TEQ m⁻³), Brazil (47–751 pg I-TEQ m⁻³), and Athens (166.6–701.5 fg I-TEQ m⁻³) (Abad et al., 2002; Assuncao et al., 2005; Moon et al., 2005). The ambient air of Dalian, which is a tourism city in northeastern China, had a PCDD/F level of 2.72 fg I-TEQ m⁻³, a value that is much lower than that for Beijing.

3.2. PCA of the sediment samples

Five principal components (PC1–PC5) with latent roots or eigenvalues above 1.0 were extracted by SPSS for the normalized 71 sediment samples. These five components represent about 68.47% of the total components. Fig. 3a–c show plots of PC1 vs PC2, PC3 vs PC4, and PC4 vs PC5 for the 2,3,7,8-substituted compounds. These plots graphically tell us the mass fraction of each 2,3,7,8-substituted compound in each component: the higher the value for a compound, the greater its mass fraction in the principal component.

In Fig. 3a (a plot of the first two principal components), the Y coordinate is the first principal component (PC1), which explains 21.76% of the variance, and the X coordinate is PC2, which explains 13.92% of the variance. PC1 mainly represents 23478-PeCDF, 2378-TCDF, 123789-HxCDF, 12378-PeCDF, 123678-HxCDF, and 123478-HxCDF. It reveals that the following sources are responsible for these compounds: primary ferrous ore smelting, secondary lead smelters, open burning of e-waste, and secondary aluminum smelters. The second principal component (PC2) mainly represents OCDF, 123678-HxCDD, 123789-HxCDD, and 1234678-HpCDD, whose potential sources are chloranil and wastewater from chemical plants.

Fig. 3b shows a plot of the third principal component (PC3) vs the fourth principal component (PC4). PC3 mainly represents 1234789-HpCDF, 1234678-HpCDF, 123478-HxCDF, 123678-HxCDF, OCDD, and 1234678-HpCDD. Potential sources of these compounds are sodium pentachlorophenate, chloranil, wastewater from chemical plants, diesel-fueled vehicles, pulp bleaching, hazardous waste incineration, and leaded gas-fueled vehicles. PC4 has abundant OCDF, 2378-TCDD, 12378-PeCDD, and 123789-HxCDF, and PC5 mainly represents OCDF and 123478-HxCDD (Fig. 3c). Table 2 summarizes the results for the principal components analysis and potential sources of the compounds.

In Fig. 4a–c, the factor scores of the 71 sediment samples are plotted with respect to the first five principal components. The scatterplots allow us to view the positions of the samples on the first five principal components and tell us the relationship of the samples to the principal components.

Fig. 4a shows that samples 31, 27, 28, 41, 51, 23, 53, 19, 6, 7, 65, 25, 40, 52, 39, 40, and 20 have high factor scores on PC1. Therefore, primary ferrous ore sintering, secondary lead smelters, open burning of e-waste, and secondary aluminum smelters are potential sources of dioxins in these samples (Table 2). The fact that these samples were collected from geographically diverse locations covering a very large area, including Ya-Er Lake (6, 7), Dongting Lake (19, 20, 23), Liangjiang River (25, 27, 28, 31), Bengbu Harbor (39), Hongze Lake (40), Grand Canal (41), Huangpu River (51, 52), Huaihe River (53), and Hong Kong Bay (65), suggests that many rivers and lakes in China might be polluted by dioxins emitted from both the ferrous and non-ferrous metal industries.

Fig. 4. Factor scores of the 71 sediment samples plotted with respect to the first five principal component: (a) PC1 vs PC2; (b) PC3 vs PC4; (c) PC4 vs PC5.

sion factors (1996 values) recommended by the UNEP toolkit for plants with normal air pollution control were $80 \mu\text{g I-TEQ t}^{-1}$ of lead and $35 \mu\text{g I-TEQ t}^{-1}$ of aluminum. Thus, in 1996, the dioxin emissions from secondary lead and secondary aluminum were about 14.4 and 6.7 g I-TEQ. Therefore, the aforementioned result is simply a consequence of the huge scale of the metal refining industry in China. Regarding emission of dioxins from open burning of e-waste, Luksemburg et al. (2002) analyzed the ash from e-waste burned at Guiyu, Guangdong Province, and found a dioxin level as high as $5.7 \text{ ng I-TEQ g}^{-1}$ in the ash. Although the extent of open burning of e-waste is difficult to estimate, such burning might be a source of dioxin emission in some cities in southeastern China.

Fig. 4a also shows that samples 28, 30, 32, 37, 36, 39, 35, 59, 60, 69, 34, 71, 33, 1, 3, 4, and 36 have high factor scores on PC2. Thus, chloranil and wastewater from chemical plants are potential sources of dioxins in these samples (Table 2). The samples were collected from Ya-Er Lake (1,3,4), the Liangjiang River (28,29,30), Dagou (32–37), Hong Kong Bay (59,60), the Nanpawu River (69), and

Bohai Bay (71). Dagou, the Nanpawu River, and Bohai Bay are just in Tianjin, where there are many large chemical and pesticide plants. In China, the chemical industry produces a large amount of wastewater, about 17.5% of the total. Some chemical processes involving organochlorines may produce PCDD/F byproducts. For example, high concentrations of PCDD/Fs were found in chloranil products (Zhang et al., 2000a; Zhang et al., 2000b) and the wastewater discharged from a pesticide plant (Luksemburg et al., 2001). Thus, because of the large-scale of the chemical industry in China, dioxin emission from related products and wastewater must be seriously considered.

Fig. 4b indicates that the dioxins in samples 18, 25, 5, 27, 41–43, and 35–39 might come from sodium pentachlorophenate, chloranil, wastewater from chemical plants, pulp bleaching, hazardous waste incineration, or diesel-fueled and leaded gas-fueled vehicles. In the 1990s sodium pentachlorophenate was widely used to control snail-borne schistosomiasis in southern China, and high concentrations of OCDD, OCDF, and 1234678-HpCDD were found in pentachlorophenol (PCP) and sodium pentachlorophenate

samples (Schechter et al., 1994; Jiang et al., 1995; Zheng et al., 1999; Hong et al., 2005). Thus, the former use of sodium pentachlorophenate to control snail-borne schistosomiasis might be the source of the PCDD/Fs in samples collected in southern China. The concentration of PCDD/Fs in Na-PCP products was reported to be about 29.9–163.7 ng I-TEQ g⁻¹ (Bao et al., 1995; Zheng et al., 1997; Chi and Huang, 2002). Also, pulp bleaching with chlorine will produce PCDD/Fs. Zhang et al. (2000b) reported a PCDD/F concentration of 10.11 pg I⁻¹ in wastewater from Chinese pulp and paper processing plants.

Unlike developed countries, landfill was still the leading municipal waste disposal method in China, and the incineration ratio was only 4.90%. Most Chinese MSWI facilities are located in eastern and southern provinces, for example, in Shanghai, Zhejiang, and Guangdong. Recent studies have shown that the dominant 2378-substituted congeners detected were OCDD and 1234678-HpCDD, followed by 1234678-HpCDF and OCDF in the flue gases and fly ash of Chinese MSWI facilities. Research has shown that most of the large incinerators in China can meet the national standard for dioxin emissions (1 ng TEQ Nm⁻³) (Li et al., 2001; Zhang et al., 2004). Comparing with ferrous and non-ferrous industry, the total estimated PCDD/F emissions from Chinese municipal, hazardous, and medical waste incineration combined will be minor. However, municipal solid waste, hazardous and medical waste incineration should not be neglected in the future owing to the rapidly increasing use of incineration anticipated.

Diesel-fueled and gas-fueled vehicles are also important potential sources of dioxin emission. However, some uncertainty exists because only a few samples are available for diesel-fueled vehicles. Moreover, in Japan, where automobiles are more commonly used than in China, dioxins emitted from vehicles amounted to less than 1% of the total dioxin inventory. Therefore, more data are needed to evaluate whether emissions from vehicles are an important source of dioxins.

4. Conclusion

Chemometric analysis of environmental samples collected throughout China from 1994 through 2002 indicated that the background dioxin levels in air, water, soil, and sediment samples from China were similar to those in lightly polluted samples from developed countries. Principal components analysis revealed that primary ferrous ore sintering, secondary lead smelting, and secondary aluminum smelting were the major recent sources of dioxin emission in China. Chemical products, such as chloranil and sodium pentachlorophenate, and wastewater discharge from chemical plants and pulp bleaching operations were also important sources of dioxin emission in China. Open burning of e-waste and diesel-fueled and gas-fueled vehicles were suspected potential sources of dioxin emission. Because China still has a relatively low incineration ratio, incineration of municipal waste, hazardous waste, and medical waste

might contribute only slightly to the current total dioxin inventory. In contrast, the recent rapid growth in the ferrous and non-ferrous metal industries might result in a greatly increased emission of PCDD/Fs from those industries.

References

- Abad, E., Caixach, J., Rivera, J., Gustems, L., Massague, G., Puig, O., 2002. Surveillance programme on dioxin levels in ambient air sites in Catalonia (Spain). *Chemosphere* 49, 697–702.
- Alcock, R.E., Sweetman, A.J., Anderson, D.R., Fisher, R., Jennings, R.A., Jones, K.C., 2002. Using PCDD/F congener patterns to determine the source of elevated TEQ concentrations in cows milk, a case study. *Chemosphere* 46, 383–391.
- Alcock, R.E., Sweetman, A.J., Jones, K.C., 2001. A congener-specific PCDD/F emissions inventory for the UK, do current estimates account for the measured atmospheric burden? *Chemosphere* 43, 183–194.
- Assuncao, J.V., Pesquero, U.R., Bruns, R.E., Carvalho, L., 2005. Dioxins and furans in the atmosphere of Sao Paulo City, Brazil. *Chemosphere* 58, 1391–1398.
- Bao, Z.C., Wang, K., Kang, J.X., Zhao, L.W., 1995. Analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in pentachlorophenol and sodium pentachlorophenate. *Environ. Chem.* 14, 317–321 (in Chinese).
- Buekens, A., Cornelis, E., Huang, H., Dewettinck, T., 2000. Fingerprints of dioxin from thermal industrial processes. *Chemosphere* 40, 1021–1024.
- Caserini, S., Cernuschi, S., Giugliano, M., Grosso, M., Lonati, G., Mattaini, P., 2004. Air and soil dioxin levels at three sites in Italy in proximity to MSW incineration plants. *Chemosphere* 54, 1279–1287.
- Chen, J.W., Zhao, H.M., Gao, L., Quan, X., Henkelmann, B., Schramm, K.W., 2003a. PCDD/F levels in pine needles sampled from Dalian, China. *Organohal. Compd.* 51, 494–497.
- Chen, Y., Wang, C.X., Wang, Z.J., 2005. Residues and source identification of persistent organic pollutants in farmland soils irrigated by effluents from biological treatment plants. *Environ. Int.* 31, 778–783.
- Chen, Z.S., Li, W., Li, C.Q., Huang, P., Liu, G.Y., Zhou, Z., 2003b. Background levels of PCDD/Fs in soil of Beijing area, China. *Organohal. Compd.* 62, 495–498.
- Chi, J., Huang, G.L., 2002. A multimedia fugacity river model of pentachlorophenol in South Drainage Canal, China. *J. Environ. Sci. Health Part A – Toxic/Hazard. Subst. Environ. Eng.* 37, 113–125.
- Everaert, K., Baeyens, J., 2002. The formation and emission of dioxins in large scale thermal processes. *Chemosphere* 46, 439–448.
- Fattore, E., Vigano, L., Mariani, G., Guzzi, A., Benfenati, E., Fanelli, R., 2002. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in River Po sediments. *Chemosphere* 49, 749–754.
- Frignani, M., Bellucci, L.G., Carraro, C., Raccanelli, S., 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon. *Chemosphere* 43, 567–575.
- Fu, J.M., Mai, B.X., Sheng, G.Y., Zhang, G., Wang, X.M., Peng, P.A., Xiao, X.M., Ran, R., Cheng, F.Z., Peng, X.Z., Wang, Z.S., Tang, U.W., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China, an overview. *Chemosphere* 52, 1411–1422.
- Hong, H.C., Zhou, H.Y., Luan, T.G., Lan, C.Y., 2005. Residue of pentachlorophenol in freshwater sediments and human breast milk collected from the Pearl River Delta, China. *Environ. Int.* 31, 643–649.
- Hosomi, M., Matsuo, T., Dobashi, S., Katou, S., Abe, H., 2003. Survey of dioxins in Tokyo Bay bottom sediment. *Mar. Pollut. Bull.* 47, 68–73.
- Hu, J.Y., Wan, Y., Shao, B., Jin, X., An, W., Jin, F., Yang, M., Wang, X.J., Sugisaki, M., 2005. Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpau River, North China. *Mar. Chem.* 95, 1–13.

- Jiang, K., Li, L.J., Chen, Y.D., Li, S.B., Gong, Y.F., 1995. Residual dioxins in Chinese schistosomiasis region and its eco-environmental risk. *Chin. Sci. Bull.* 40, 1740–1747.
- Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J., Wu, K.Y., Lin, C., 2004. Source identification of PCDD/Fs for various atmospheric environments in a highly industrialized city. *Environ. Sci. Technol.* 38, 4937–4944.
- Li, X.D., Gu, Y.L., Ni, M.J., Cen, K.F., 2001. Study of PCDD/F emissions from an MSW fluidized bed incinerator. *J. Eng. Thermophys.* 22, 526–528 (in Chinese).
- Liu, M., Yang, Y., Xu, S., Hou, L., Liu, Q., Ou, D., Jiang, H., 2004. Persistent organic pollutants (POPs) in intertidal surface sediments from the Yangtze estuarine and coastal areas, China. *J. Coast. Res.* 43 (special issue), 162–170.
- Louie, P., Sin, D., 2003. A preliminary investigation of persistent organic pollutants in ambient air in Hong Kong. *Chemosphere* 52, 1397–1403.
- Luksemburg, W., Wong, A., Maier, M., Spas, R., Zhou, H., 2001. A follow-up study of polychlorinated dibenzodioxin and dibenzofuran near a pesticide plant in Dagou, China. *Organohal. Compd.* 51, 223–225.
- Luksemburg, W.J., Mittel, R.S., Peterson, R.G., Hedin, J.M., Maier, M., Schuld, M., Zhou, H., Wong, A.S., 2002. Polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs) levels in environmental and human hair samples around an electronic waste processing site in Guiyu, Guangdong Province, China. *Organohal. Compd.* 55, 347–349.
- Luksemburg, W.J., Mittel, R.S., Zhou, H., Hedin, J.M., Silverbush, B.B., Wong, A.S., 1996. Polychlorinated dioxins and dibenzofurans in environmental samples from China. *Organohal. Compd.* 28, 262–266.
- Martens, D., Zhang, A., Jiang, X., Chen, J., Gawlik, B.M., Henkelmann, B., Schramm, K.W., Kettrup, A., 2000. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans, pentachlorophenol, pentachloroanisole and hexachlorobenzene in sediments of the Yangtze River and the Liao-He River in China. *Organohal. Compd.* 46, 431–434.
- Marvin, C., Alae, M., Painter, S., Charlton, M., Kaus, P., Kolic, T., MacPherson, K., Takeuchi, D., Reiner, E., 2002. Persistent organic pollutants in Detroit River suspended sediments, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls and polychlorinated naphthalenes. *Chemosphere* 49, 111–120.
- Moon, H.B., Lee, S.J., Choi, H.G., Ok, G., 2005. Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in urban and suburban areas of Korea. *Chemosphere* 58, 1525–1534.
- Muller, J.F., Gaus, C., Prange, J.A., Papke, O., Poon, K.F., Lam, M.H., Lam, P.K., 2002. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in sediments from Hong Kong. *Mar. Pollut. Bull.* 45, 372–378.
- Okeefe, P., Smith, R., Conner, S., Aldous, K., Valente, H., Donnelly, R., 1994. Principal components analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in sediments from Lake Champlain and Lake George, New York, USA. *Arch. Environ. Contam. Toxicol.* 27, 357–366.
- Onodera, S., Sugimoto, M., Takagi, T., Tanaka, K., 1999. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans, their concentrations and profiles in sediments in the Tama River, Japan. *Jpn. J. Toxicol. Environ. Health* 45, 1–7.
- Sakurai, T., Kim, J.G., Suzuki, N., Matsuo, T., Li, D.Q., Yao, Y.A., Masunaga, S., Nakanishi, J., 2000. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment, soil, fish, shellfish and crab samples from Tokyo Bay area, Japan. *Chemosphere* 40, 627–640.
- Schecter, A., Jiang, K., Papke, O., Furst, P., 1994. Comparison of dibenzodioxin levels in blood and milk in agricultural workers and others following pentachlorophenol exposure in China. *Chemosphere* 29, 2371–2380.
- Schmid, P., Gujer, E., Zennegg, M., Bucheli, T.D., Desaulles, A., 2005. Correlation of PCDD/F and PCB concentrations in soil samples from the Swiss soil monitoring network (NABO) to specific parameters of the observation sites. *Chemosphere* 58, 227–234.
- Schuhmacher, M., Agramunt, M.C., Rodriguez-Larena, M.C., Diaz-Ferrero, J., Domingo, J.L., 2002. Baseline levels of PCDD/Fs in soil and herbage samples collected in the vicinity of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 46, 1343–1350.
- Tagigami, H., Sakai, S., Brouwer, A., 2005. Bio/chemical analysis of dioxin-like compounds in sediment samples from Osaka Bay, Japan. *Environ. Technol.* 26, 459–469.
- United States Environmental Protection Agency (US-EPA), 2001. Database of Sources of Environmental Releases of Dioxin-like Compounds in the United States (Version 3.0). <http://www.epa.gov/ncea/Dioxin_Database/dioxindb.zip>.
- Wong, M.H., Leung, A., Chan, J., Choi, M., 2005. A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk. *Chemosphere* 60, 740–752.
- Wu, W.Z., Schramm, K.W., Henkelmann, B., Xu, Y., Yediler, A., Kettrup, A., 1997. PCDD/F-s, PCBs, HCHs and HCB in sediments and soils of Ya-Er Lake area in China, results on residual levels and correlation to the organic carbon and particle size. *Chemosphere* 34, 191–202.
- Wu, W.Z., Schramm, K.W., Henkelmann, B., Xu, Y., Zhang, Y.Y., Kettrup, A., 1998. Survey on PCDDs and PCDFs in sediments and soils in Ya-Er Lake area, China. *Chin. J. Oceanol. Limnol.* 16, 45–53.
- Wu, W.Z., Schramm, K.W., Xu, Y., Kettrup, A., 2001a. Mobility and profiles of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment of Ya-Er Lake, China. *Water Res.* 35, 3025–3033.
- Wu, W.Z., Schramm, K.-W., Xu, Y., Kettrup, A., 2002. Contamination and distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in agriculture fields in Ya-Er Lake area, China. *Ecotoxicol. Environ. Safety* 53, 141–147.
- Wu, W.Z., Xu, Y., Schramm, K.W., Kettrup, A., 2001b. Persistence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in Ya-Er Lake area, China. *Environ. Int.* 26, 323–326.
- Zhang, H., He, P.J., Li, G.J., Takeda, N., 2004. Dioxins measurement of municipal solid waste incineration ash. *J. Tongji Univ. (Natural Science)* 32, 1655–1659.
- Zhang, Q.H., Wu, W., Zhan, W., Xu, Y., 2000a. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in C.I. Violet 23 dyes and chloranil. *Chin. J. Chromatogr.* 18, 22–25.
- Zhang, Q.H., Xu, Y., Wu, W.Z., Schramm, K.W., Kettrup, A., 2002. Reduction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans levels in chloranil from China. *Bull. Environ. Contam. Toxicol.* 69, 459–462.
- Zhang, Q.H., Xu, Y., Wu, W.Z., Xiao, R.M., Feng, L., Schramm, K.W., Kettrup, A., 2000b. PCDDs and PCDFs in the wastewater from Chinese pulp and paper industry. *Bull. Environ. Contam. Toxicol.* 64, 368–371.
- Zheng, M., Zhang, B., Bao, Z.C., Yang, H., 2003. Analysis of PCDD/Fs from sediments of Dongting Lake in China. *Organohal. Compd.* 62, 190–192.
- Zheng, M.H., Bao, Z.C., Wang, K.O., Yang, H., Xu, X.B., 1997. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in lake sediments from Chinese schistosomiasis areas. *Bull. Environ. Contam. Toxicol.* 59, 653–656.
- Zheng, M.H., Bao, Z.C., Xu, X.B., 1999. Formation mechanisms of dioxins during hypochlorite bleaching or chlorination of non-wood plant fibers pulp. *Environ. Chem.* 18, 526–531 (in Chinese).
- Zheng, M.H., Chu, S.G., Sheng, G.Y., Min, Y.S., Bao, Z.C., Xu, X.B., 2001. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surface sediments from Pearl River Delta in China. *Bull. Environ. Contam. Toxicol.* 66, 504–507.