Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 151 (2008) 522–530
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

PCDD/F concentrations of agricultural soil in the vicinity of fluidized bed incinerators of co-firing MSW with coal in Hangzhou, China

J.H. Yan [a], M.X. Xu [a], S.Y. Lu [a,*], X.D. Li [a], T. Chen [a], M.J. Ni [a], H.F. Dai [b], K.F. Cen [a]

[a] *State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering of Zhejiang University, Hangzhou 310027, China*
[b] *Zhejiang University School of Medicine, Hangzhou 310058, China*

Received 28 March 2007; received in revised form 1 June 2007; accepted 6 June 2007
Available online 12 June 2007

Abstract

The concentrations of 17 PCDD/F congeners as well as tetra- to octa-homologues were determined in 33 soil samples collected within a radius of 7 km from a municipal solid waste (MSW) incineration plant that is equipped with three fluidized bed incinerators (FBIs) of co-firing MSW with coal in Hangzhou, China. The total PCDD/F concentrations ranged from 0.39 to 5.04 pg I-TEQ g^{-1} (54–285 pg g^{-1}), with an average and a median value of 1.22 and 0.84 pg I-TEQ g^{-1} (105 and 86 pg g^{-1}), respectively. A systematic decrease of PCDD/F levels was observed with the increasing distances and with the decreasing downwind frequencies from the plant. The comparisons of homologue and congener patterns and multivariate analysis of soil and flue gas samples strongly indicated that most of the soil samples were influenced by the FBIs. Apart from the incineration plant, historical PCDD/F emissions of hazardous waste incinerator (HWI) and motor vehicles as well as the application of 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP) seemed to play an important role in soil samples adjacent to these potential sources.

Keywords: Polychlorinated-*p*-dioxins and dibenzofurans; Fluidized bed incinerators; Municipal solid waste incinerators; Agricultural soil; Multivariate analysis

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of most toxic and carcinogenic organic persistent contaminants that are produced unintentionally. It is well documented that their emissions and the subsequent atmospheric transport and behavior have resulted in their widespread dispersal through the environment [1]. Since the first detection of PCDD/Fs in the flue gas of municipal solid waste incinerators (MSWIs), the emissions of PCDD/Fs have become one of the most controversial issues worldwide [2].

Recent studies on the inventories of potential emissions of PCDD/Fs in a number of countries have showed that the combustion is a major contributor to the total PCDD/F concentration in the environment [3]. Given the semi-volatile and hydrophobic character, PCDD/Fs can be easily accumulated in the environment, especially in organic-rich media such as soil and sediment [4]. Therefore, the comprehensive researches have been conducted to investigate the levels of PCDD/Fs in soils in the vicinity of MSWIs over the last three decades [3–18].

Being the largest developing country, China generates annually 170 billion kg of municipal solid waste (MSW), accounting for 26.5% of the total production of the world [19]. The lack of landfill sites for the wastes has forced the local government (especially for developed regions) to choose the incineration as a substitute option. As a result, the project of constructing incineration plants in China has been booming since 2000 and 70 MSWIs were running by 2003, with a daily treatment capacity of 15 million kg [20]. Among these incineration plants, fluidized bed incinerators (FBIs) of co-firing MSW with coal have been widely applied due to its characteristics that can deal with low heat MSW value (the heat value of MSW in most Chinese cities is about 4200 kJ/kg) and keep stable burning [21].

However, till now, in China there are limited studies focused on the occurrence of PCDD/Fs in the soil near the MSWIs. Accordingly, the objectives of this study were to investigate the levels of PCDD/Fs in agricultural soil in the vicinity of a MSW incineration plant that is equipped with FBIs of co-firing MSW with coal, to compare the concentrations of PCDD/Fs with regulations currently in vigor and previous studies, and attempt to

* Corresponding author. Tel.: +86 571 8795 2628; fax: +86 571 8795 2438.
E-mail address: lushy@zju.edu.cn (S.Y. Lu).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.06.018

identify the local sources that might mean a potential elevation of PCDD/F levels in the surrounding agricultural soil.

2. Materials and methods

2.1. Sampling sites

Hangzhou, located 180 km southwest of Shanghai, is a famous scenic city in China. The study area belongs to a satellite town, in the northeast part of this city, where industrial and residential area co-exist (Fig. 1). The town has about 37,000 inhabitants, and covers an area of 30 km^2, of which 57% is agricultural land. The regional agricultural soil in this area is made up of two types, with the prevailing Fluvo-aquic type and paddy soil only in the eastern part of the stack.

The MSW incineration plant referred in this study is located in an industrial zone in the center of the town, adjacent to two motorways with heavy traffic in the west and north sides. In addition, a small-scale hazardous waste incinerator (HWI), about 800 m northward to the MSW incineration plant, had once been occasionally in operation during 2002 and 2004. However, the capacity and PCDD/F emission data from this HWI were not available due to secrecy.

The MSW incineration plant is equipped with three FBIs and began its operation of first two lines in 2002, and has been in full operation with a total daily capacity of 0.8 million kg since 2003, the ratio of MSW to coal of each incinerator is 80:20. All of flue gases are purified by the air pollution control device consists of a semi-dry scrubber and a bag-house filter. Consequently, the emission level measured during its fully operational in 2003 varied from 0.0054 to 0.1961 ng I-TEQ N m^{-3}, which was quite below the national legal limit of 1 ng I-TEQ N m^{-3} [21].

The sampling points were selected according to the atmospheric dispersion modeling based on the wind rose resulting from pluriannual (2002–2005) observations [22]. Meteorological data were obtained from the Meteorological Bureau of Hangzhou and used to make a wind frequency distribution diagram depicted in Fig. 1. Thirty-three soil samples were collected from agricultural land in a two-day period, in September 2006. The exact sampling points were determined and recorded within ~10 m of accuracy by a handheld GPS device (*Meridian Color*, Thales Navigation, USA). Thirty samples were collected within a radius of 3 km from the stack mainly in the historical prevailing downwind directions (W, S, SE, SSE, SW and NE) (Fig. 1). The other three samples collected in the least downwind frequency direction of east, 6–7 km from the stack were served as background controls. The location of the MSW incineration plant, HWI and the sampling sites within a radius of 2 km from the stack were depicted in Fig. 1 by transforming the coordinate of each point into the Geographic Information System (GIS) software packages of Google Earth (2006).

2.2. Sample preparation and analysis

The soil samples were collected by mixing five different aliquots (each in four main directions of 5 m to the center) within a 25 m^2 area. As the agricultural soil is often being farmed, the sampling was carried out by inserting a cylindrical steel

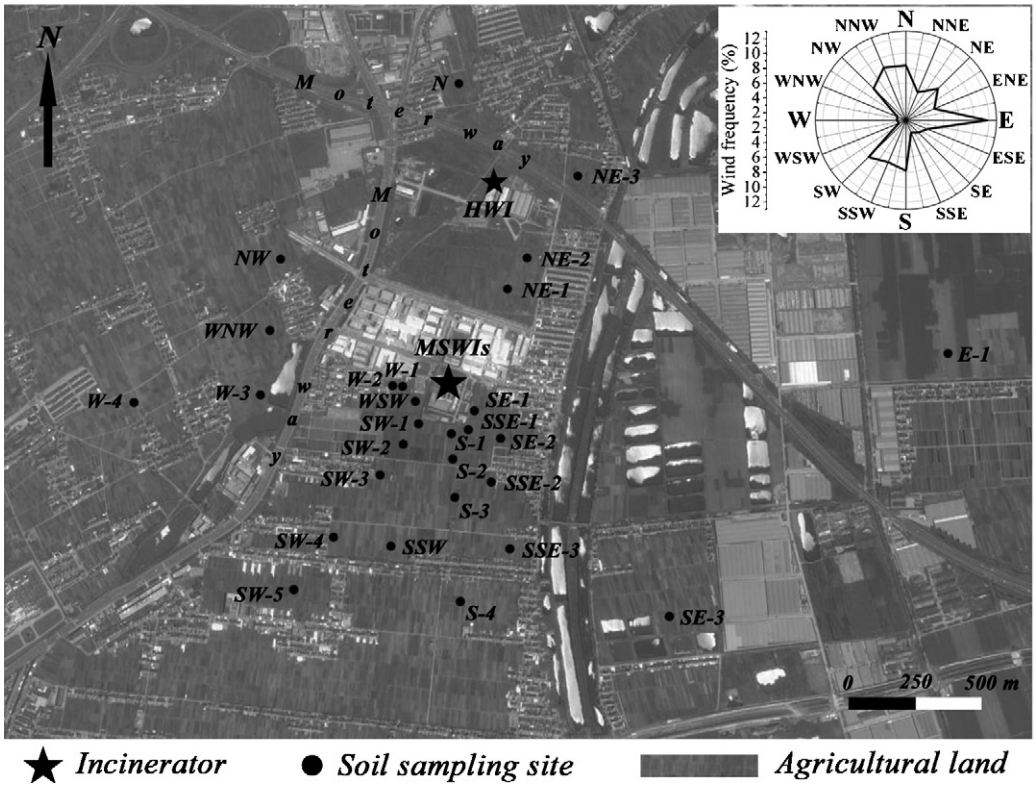

Fig. 1. Schematic of wind frequency diagram and the distribution of soil samples around the MSWIs.

corer (24 cm × 4 cm, length × internal diameter, Eijkelkamp, Holland) down to a 20-cm depth and then extracting an earth core specimen so defined [5]. Approximately 2 kg of soil was taken at each site. The soils were subsequently dried in a ventilated room until constant weight. Then, they were ground and passed through a 2-mm sieve. About 500 g soil of each sample was finally homogenized through a 60-mesh sieve, and was refrigerated until analysis.

About 10 g (dry matter) of soil sample (60-mesh) were used for PCDD/F analysis. A selective pressured liquid extraction (SPLE) method was used for sample extraction by using a fully automated ASE 300 system (Dionex, Sunnyvale, CA, USA). The extraction condition and procedure was referred to the SPLE method with a slight modification [23]. Briefly, a 100-ml extraction cell was used and the ratio of the sample:alumina:copper was 5:5:1. Each sample was spiked with a mixture of $^{13}C_{12}$-labelled PCDD/F compound stock solution (5 μl) and clean-up standard (5 μl) before extraction. The extracts from the ASE were subsequently followed by rotary evaporation and multilayer silica gel column clean-up procedure following the Method of USEPA 1613 [24]. The extracts were blow-down to 20 μl under a gentle stream of nitrogen (N_2), and 5 μl of $^{13}C_{12}$-labelled PCDD/Fs internal standard solution were added before sample were subjected to analysis by high-resolution gas chromatography coupled with a high-resolution mass spectrometry (HRGC/HRMS) (JEOL JMS-800D) with a DB-5MS column (60 m × 0.25 mm × 0.25 μm). The temperature program of the capillary column was as follows: (1) 150 °C hold for 1 min; (2) increased at 25 °C min^{-1} to 190 °C; (3) increased at 3 °C min^{-1} to 280 °C, hold for 20 min. The injection volume was 1 μl by automatic splitless injection. The MS was operated at a resolution of 10,000 under positive EI conditions (38 eV electron energy), and the data were obtained in the selective ion monitoring mode.

The toxic 2,3,7,8-substituted PCDD/Fs (referred to as congeners) as well as tetra- to octa-chlorinated homologues were identified based on isotope ratios within ±15% of the theoretical values and signal to noise ratios of equal or greater than 2.5. Quantification of PCDD/Fs was performed by an isotope dilution method using relative response factors previously obtained from the five calibration standard solutions. A blank sample was analyzed for every batch of six samples, and a duplicate sample was analyzed for every two batches. Recoveries of internal standards, as determined against external standard, generally varied between 70 and 110%, and were all satisfied with the Method of USEPA 1613. Besides, the average limits of detection (LOD) varied between 0.040 and 0.223 pg g^{-1} from tetra- to octa-chloro PCDD/Fs, respectively.

It should be mentioned that all internal standard solutions used in this study were purchased from the Cambridge Isotope Laboratories, Inc (USA).

2.3. Statistical analysis

All the experimental results were expressed on a dry weight basis. The 2,3,7,8-TCDD toxic equivalents (I-TEQ) were calculated using the NATO/CCMS factors. In the case of values below the detection limit, I-TEQ calculations were carried out, by using the half of the LOD. The geometric average of three soil control samples and three flue gas samples were served as the background soils and flue gas sample in this study, respectively [21]. Data were normalized before comparison of homologue and congener patterns and the multivariate analysis [25]. Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used to evaluate the similarities and differences of PCDD/F homologue patterns between background soil, soil samples and the stack gas sample. Each sample was assigned a score after PCA analysis, allowing the summarized data to be further plotted and analyzed. All statistical analyses were performed using the SPSS 13.0 statistical software package.

3. Results and discussion

3.1. PCDD/F concentration

Table 1 summarizes the concentrations of PCDD/Fs in soils. The TEQ values (sum concentration of tetra- to octa-PCDD/Fs homologues, i.e., $\Sigma_{PCDD/Fs}$) ranged from 0.39 to 5.04 pg I-TEQ g^{-1} (54–285 pg g^{-1}), with an average and a median value of 1.22 and 0.84 pg I-TEQ g^{-1} (105 and 86 pg g^{-1}), respectively. The occurrence of PCDD/Fs in soils in the vicinity of MSWIs has been investigated since 1980s in other places such as Italy, Spain, Korea and Taiwan. Oh et al. [17] had given a summarized report about recent investigations of PCDD/F concentrations in soils collected near the incinerators. The I-TEQ values observed in the present study are generally higher than those found in soil samples collected near MSWIs in Adige Valley (Italy) [16], lower than those in Barcelona (Spain) [3,8], Buchon (Korea) [17], and are consistent with those found in Catalonia (Spain) [6,7,13] and Hsinchu (Taiwan) [15]. Although background data prior to the construction of the MSW incineration plant were not available, the TEQ values and $\Sigma_{PCDD/Fs}$ of most soil samples in this study were generally below 1.20 pg I-TEQ g^{-1} and 120 pg g^{-1} (Table 1), respectively. This concentration was at the lower average values for rural areas (1–5 pg I-TEQ g^{-1} and 120–300 pg g^{-1}, respectively), indicating a low contamination of the soil around the MSW incineration plant of Hangzhou [26–28].

It should be noted that the unusually high values of both TEQ and $\Sigma_{PCDD/Fs}$ were only found in three soil samples (i.e., WSW, NW and N), with concentrations in sequence of 5.04 pg I-TEQ g^{-1} (285 pg g^{-1}), 4.03 pg I-TEQ g^{-1} (269 pg g^{-1}) and 3.56 pg I-TEQ g^{-1} (244 pg g^{-1}), respectively. The sample of WSW was collected just outside the property of the incinerator and the other two (NW and N) were adjacent to motorways with heavy traffic and downwind the HWI (Fig. 1). The high PCDD/F concentrations of these three samples might be attributed to uncontrolled dispersion of fly ash and fugitive emission sources such as motor vehicles and HWI, respectively. This assumption was later confirmed by the multivariate analysis of homologue patterns.

Concerning the different congeners, among all soil samples, OCDD was the predominant congener, accounting for around 70 and 87% of the total concentration of 17 congeners for

Table 1
PCDD/F concentrations in soil samples in the vicinity of the MSWIs (pg g^{-1})[a]

	W-1	W-2	W-3	W-4	W-5	WNW	NW	N	NE-1	NE-2	NE-3	E	SE-1	SE-2	SE-3	Back[2]
2,3,7,8-TCDD	0.10	0.16	0.03	0.05	0.04	0.03	0.15	0.17	0.07	0.03	0.06	0.05	0.08	0.10	0.03	0.06
1,2,3,7,8-PeCDD	0.30	0.20	0.22	0.26	0.20	0.52	1.18	1.11	0.33	0.13	0.11	0.23	0.08	0.13	0.04	0.08
1,2,3,4,7,8-HxCDD	0.20	0.16	0.15	0.07	0.22	0.17	0.99	0.84	0.06	0.19	0.05	0.03	0.22	0.20	0.09	0.21
1,2,3,6,7,8-HxCDD	0.40	0.39	0.29	0.41	0.32	0.67	2.84	2.34	0.27	0.04	0.38	0.53	0.34	0.07	0.16	0.25
1,2,3,7,8,9-HxCDD	0.07	0.43	0.34	0.49	0.43	0.77	3.16	2.59	0.32	0.33	0.37	0.50	0.39	0.07	0.19	0.36
1,2,3,4,6,7,8-HpCDD	3.25	3.33	2.82	4.10	3.63	5.81	24.6	19.4	3.64	3.02	5.79	3.68	3.88	3.19	1.81	3.68
OCDD	31.0	32.1	26.3	27.2	35.5	30.4	62.2	61.2	40.2	45.8	68.3	44.1	47.3	36.6	30.9	62.7
2,3,7,8-TCDF	0.50	0.65	0.38	0.36	0.45	0.69	0.88	1.09	0.51	0.24	0.37	0.21	0.57	0.35	0.19	0.27
1,2,3,7,8-PeCDF	0.06	0.82	0.62	0.90	0.58	1.07	2.94	3.19	0.22	0.36	0.46	0.34	0.71	0.52	0.13	0.29
2,3,4,7,8-PeCDF	0.65	1.36	0.80	0.48	0.56	0.69	0.49	0.53	0.46	0.31	0.36	0.29	0.79	0.57	0.25	0.21
1,2,3,4,7,8-HxCDF	0.46	0.93	0.79	1.56	0.62	1.94	10.1	7.40	0.64	0.45	0.68	0.57	0.87	0.62	0.26	0.44
1,2,3,6,7,8-HxCDF	0.75	0.95	0.75	0.77	0.56	1.04	3.29	3.36	0.54	0.45	0.72	0.49	0.82	0.62	0.27	0.39
2,3,4,6,7,8-HxCDF	0.72	0.98	0.80	0.87	0.57	0.76	1.28	1.19	0.48	0.38	0.35	0.58	0.73	0.62	0.29	0.30
1,2,3,7,8,9-HxCDF	0.35	0.30	0.27	0.37	0.20	0.15	0.54	0.46	0.19	0.13	0.14	0.04	0.34	0.11	0.06	0.05
1,2,3,4,6,7,8-HpCDF	2.33	2.52	2.28	3.67	2.43	4.69	25.8	20.6	1.87	1.39	2.27	2.04	2.47	1.99	0.86	1.35
1,2,3,4,7,8,9-HpCDF	0.12	0.19	0.36	0.42	0.14	0.46	1.30	1.15	0.15	0.06	0.07	0.22	0.26	0.41	0.13	0.18
OCDF	1.66	1.52	1.50	2.34	1.66	2.57	14.5	10.7	2.44	1.20	1.99	1.21	1.92	2.39	0.69	1.22
Sum of 17 congeners	42.9	47.0	38.7	44.3	48.1	52.4	156	137	52.4	54.5	82.5	55.1	61.8	48.6	36.4	72.0
TCDD	5.12	6.21	3.57	4.17	3.02	6.75	8.80	11.7	4.09	2.60	3.55	15.8	5.57	4.80	2.52	4.89
PeCDD	6.83	5.97	3.54	5.63	3.80	8.93	21.3	20.5	4.23	2.05	4.22	6.78	5.02	3.34	2.21	2.77
HxCDD	6.49	7.38	5.32	8.29	6.21	11.8	40.1	32.2	5.40	3.96	5.63	7.75	7.25	5.19	2.78	4.55
HpCDD	7.37	7.59	6.29	8.13	8.08	10.7	38.8	30.7	8.14	7.12	10.7	8.43	8.68	7.53	4.70	8.96
OCDD	31.0	32.1	26.3	27.2	35.5	30.4	62.2	61.2	40.2	45.8	68.3	44.1	47.3	36.6	30.9	62.7
TCDF	14.6	22.2	10.6	10.5	8.71	15.2	12.4	14.8	9.08	6.10	8.88	53.8	14.1	8.27	4.44	11.1
PeCDF	8.59	14.3	8.13	7.99	6.07	10.1	14.6	15.4	5.21	3.62	6.02	6.53	9.28	7.30	3.52	3.47
HxCDF	7.77	9.57	7.69	8.97	5.91	9.44	26.3	23.9	4.86	3.86	5.48	5.10	8.09	4.35	3.11	3.47
HpCDF	2.85	3.92	3.57	4.55	3.01	6.23	29.6	22.5	2.49	1.54	2.85	2.63	3.29	3.05	1.21	1.80
OCDF	1.66	1.52	1.50	2.34	1.66	2.57	14.5	10.7	2.44	1.20	1.99	1.21	1.92	2.39	0.69	1.22
$\Sigma_{PCDD/Fs}$	92.3	111	76.5	87.8	82.0	112	269	244	86.1	77.9	118	152	111	82.8	56.1	105
I-TEQ	1.01	1.56	1.03	1.07	0.89	1.45	4.03	3.56	0.88	0.58	0.78	0.73	1.10	0.84	0.39	0.56

	SSE-1	SSE-2	SSE-3	S-1	S-2	S-3	S-4	S-5	SSW	SW-1	SW-2	SW-3	SW-4	SW-5	WSW	Back[b]
2,3,7,8-TCDD	0.02	0.10	0.08	0.03	0.02	0.14	0.01	0.07	0.03	0.03	0.05	0.03	0.08	0.04	0.10	0.06
1,2,3,7,8-PeCDD	0.22	0.31	0.27	0.10	0.16	0.23	0.10	0.14	0.11	0.16	0.14	0.02	0.03	0.02	1.03	0.08
1,2,3,4,7,8-HxCDD	0.13	0.29	0.20	0.05	0.15	0.22	0.05	0.17	0.06	0.06	0.26	0.05	0.22	0.20	1.27	0.21
1,2,3,6,7,8-HxCDD	0.16	0.61	0.39	0.05	0.30	0.21	0.22	0.26	0.25	0.36	0.33	0.19	0.36	0.39	1.69	0.25
1,2,3,7,8,9-HxCDD	0.19	0.62	0.42	0.22	0.40	0.22	0.33	0.33	0.25	0.51	0.50	0.17	0.33	0.35	1.86	0.36
1,2,3,4,6,7,8-HpCDD	3.02	6.54	3.41	2.50	3.21	2.32	3.13	2.55	2.60	4.28	3.26	1.90	2.78	3.34	11.8	3.68
OCDD	31.3	41.4	37.0	27.1	37.1	28.5	31.0	28.3	26.2	31.7	29.4	17.0	31.5	32.1	40.9	62.7
2,3,7,8-TCDF	0.37	0.32	0.42	0.37	0.39	0.53	0.31	0.29	0.31	0.52	0.39	0.38	0.41	0.45	1.83	0.27
1,2,3,7,8-PeCDF	0.55	0.65	0.34	0.46	0.51	0.50	0.56	0.46	0.41	0.69	0.26	0.46	0.46	0.51	2.41	0.29
2,3,4,7,8-PeCDF	0.62	1.04	0.80	0.52	0.67	0.14	0.40	0.52	0.57	1.19	0.82	0.67	0.60	0.43	4.21	0.21
1,2,3,4,7,8-HxCDF	0.56	0.83	0.73	0.36	0.26	0.91	0.75	0.46	0.43	1.12	0.41	0.09	0.60	0.74	3.56	0.44
1,2,3,6,7,8-HxCDF	0.54	0.81	0.63	0.48	0.60	0.33	0.52	0.45	0.42	0.84	0.64	0.48	0.61	0.67	3.32	0.39
2,3,4,6,7,8-HxCDF	0.58	0.95	0.65	0.23	0.54	0.73	1.61	0.80	0.57	1.37	0.81	0.64	0.66	0.72	4.12	0.30
1,2,3,7,8,9-HxCDF	0.19	0.34	0.17	0.13	0.18	0.23	0.20	0.24	0.12	0.28	0.17	0.16	0.18	0.16	1.14	0.05
1,2,3,4,6,7,8-HpCDF	1.76	3.26	1.96	1.47	1.79	1.69	2.10	1.98	1.60	2.86	1.97	1.62	1.95	2.31	14.1	1.35
1,2,3,4,7,8,9-HpCDF	0.19	0.31	0.28	0.17	0.23	0.30	0.17	0.24	0.11	0.28	0.23	0.14	0.13	0.19	1.39	0.18
OCDF	1.49	2.87	1.66	1.45	1.89	1.13	2.86	1.97	2.47	2.94	2.09	1.00	1.89	2.59	6.74	1.22
Sum of 17 congeners	41.9	61.2	49.4	35.7	48.4	38.3	44.3	39.2	36.5	49.2	41.7	25.0	42.8	45.2	101	72.0
TCDD	5.27	6.11	4.80	3.82	4.33	3.78	3.00	2.99	3.26	6.37	3.67	3.08	3.18	3.95	16.8	4.89
PeCDD	4.74	8.19	5.23	3.77	5.34	4.87	3.74	4.08	3.45	6.80	4.53	2.35	3.21	4.16	23.8	2.77
HxCDD	5.28	13.9	6.47	3.97	6.15	3.87	4.70	4.90	4.45	7.94	6.32	4.06	5.30	6.48	36.9	4.55
HpCDD	6.75	14.8	8.00	5.80	7.57	5.82	7.26	6.06	5.99	9.24	7.26	4.15	6.39	7.32	23.6	8.96
OCDD	31.3	41.4	37.0	27.1	37.1	28.5	31.0	28.3	26.2	31.7	29.4	17.0	31.5	32.1	40.9	62.7
TCDF	11.7	8.86	12.7	8.16	12.1	10.2	9.11	7.11	7.34	14.0	9.59	9.76	6.01	9.45	42.5	11.1
PeCDF	7.58	10.3	8.23	6.58	6.86	3.62	5.87	5.51	4.78	10.9	6.75	5.97	4.86	6.82	37.9	3.47
HxCDF	5.13	8.98	5.91	3.84	5.06	6.31	7.55	5.10	4.45	9.40	6.17	4.77	5.11	6.11	36.4	3.47
HpCDF	2.30	4.54	2.74	1.94	2.36	2.48	2.60	2.82	2.28	4.07	2.59	1.96	2.47	2.88	19.7	1.80
OCDF	1.49	2.87	1.66	1.45	1.89	1.13	2.86	1.97	2.47	2.94	2.09	1.00	1.89	2.59	6.70	1.22
$\Sigma_{PCDD/Fs}$	81.5	120	92.7	66.4	88.8	70.6	77.7	68.8	64.7	103	78.4	54.1	69.9	81.9	285	105
I-TEQ	0.82	1.43	1.09	0.62	0.83	0.76	0.78	0.80	0.70	1.35	0.98	0.67	0.84	0.75	5.04	0.56

[a] The concentrations measured below the detection limits were accepted as half of the corresponding detection limit and they were shown in italics in the table.
[b] Back is referred to background.

background soil and soil samples, respectively, followed by the remaining high-chlorinated congeners including 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. This distribution profile was in agreement with those previously reported by other investigators [3,6–9,12,13,17]. Though OCDD was the dominant congener in other relevant surveys, the average concentrations of OCDD found in soil samples within 3 km of MSWIs showed a great variation from 7.3 pg g^{-1} in Veneto, Italy to 1.5 ng g^{-1} in Columbus, USA [9,16]. The average OCDD concentration of this study (36 pg g^{-1}) was comparable with those in Adige Valley and Po Valley, Italy and Tarragona, Spain [6,7,16]. Interestingly, 2,3,7,8-TCDD, the most toxic congener, exhibitted the lowest concentrations among all congeners, which was also consistent with the results in other studies [6,7,16,17]. Moreover, a smaller variation of concentrations was observed in 2,3,7,8-TCDD compared with that of OCDD. Generally, the average concentration of 2,3,7,8-TCDD in soil samples ranged from 0.01 to 0.53 pg g^{-1}, except for those found in Columbus, USA [9]. In the present study, the 2,3,7,8-TCDD was detected in 13 out of 31 samples, with the highest and average concentrations of 0.17 and 0.07 pg g^{-1}, respectively. As can be seen in Table 1, the main contributors of TEQ of this study were the 2,3,4,7,8-PeCDF (accounting for 33% of the total TEQ), which was in accordance with those reported elsewhere [3,6–9,12,16,17].

It should be noted that in order to get an explicit interpretation of the results, the aforementioned three samples (i.e., WSW, NW and N) were treated as outliers and excluded in the following discussion except for multivariate analysis.

3.2. PCDD/F source identification

3.2.1. Distribution of PCDD/F levels

According to the plot of the distance V.S. average concentration axes (Fig. 2a), 30 soil samples (including three background controls) were roughly divided into nine groups with increasing distances (i.e., 200, 300, 450, 700, 1000, 1250, 2000, 3000 and 6500 m) from the stack. The mean concentrations of PCDD/Fs in soil samples progressively decreased as a function of distance from the incinerator. The maximum PCDD/F levels were observed at 200–750 m from the MSW incineration plant, being comparable with the results obtained in other investigations [3,12]. The highest levels near the stack might be attributed to the wet deposition of the PCDD/Fs [3].

The wind direction was another major parameter of concern in the influence of MSWIs on the environment. PCDD/F concentration of 25 soil samples in seven directions are averaged and depicted in the downwind frequency V.S. concentration axes (Fig. 2b). As shown in Fig. 2b, the PCDD/F concentrations were partially influenced by the downwind frequencies. It seemed that the downwind frequencies showed roughly direct proportionality with the concentrations of PCDD/Fs. For instance, the downwind frequencies of W and E based on the pluriannual observations were 12 and 2%, respectively. Correspondingly, the average PCDD/F concentrations in soil samples in west and east direction were 1.11 and 0.72 pg I-TEQ g^{-1}. Therefore, the declining trend of PCDD/F levels with the increased distances

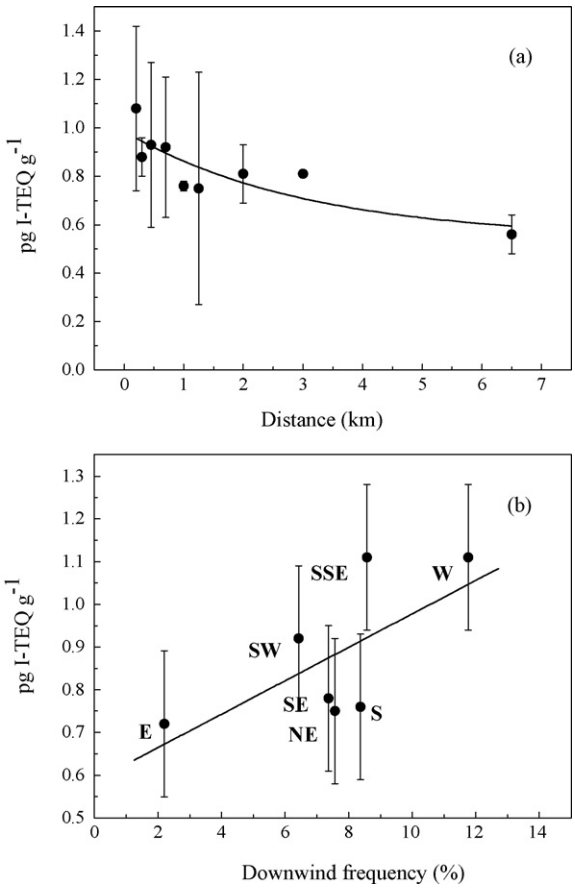

Fig. 2. Trend of PCDD/Fs levels in the soil with increasing distances (a) and with the downwind frequencies from the MSWIs (b), with the error bars indicating the standard deviations.

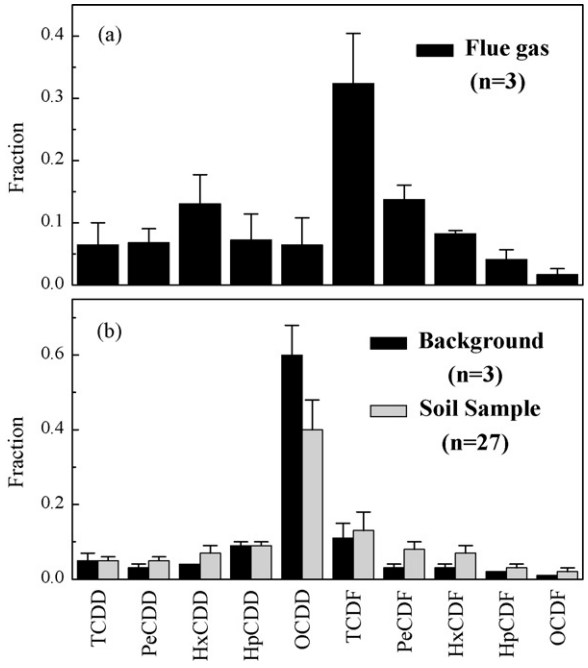

Fig. 3. PCDD/F homologue patterns in flue gas sample (a) and background soil and soil samples collected near the incinerators (b), with error bars indicating the plus standard deviations.

and with the decreased downwind frequencies strongly indicated the existing effect of PCDD/F emissions of FBIs on the surrounding soils.

3.2.2. Comparison of homologue patterns

The PCDD/F homologue patterns of flue gas are shown in Fig. 3a. It was a typical MSWI gas profile with a dominant homologue of TCDF and relatively low PCDDs [25]. It has been reported that the homologue patterns of flue gas were similar from various thermal processing facilities, including MSWIs, HWIs, industrial waste incinerators (IWIs) and automobiles, where PCDF levels were higher than PCDDs [25,29]. The ratio of PCDFs to PCDDs (2.30) of this study confirmed that finding. By contrast, the ambient air tends to have a typical homologue pattern of high-chlorinated PCDDs (e.g., OCDD) and relatively low levels of PCDFs [1].

In this study, OCDD accounted for approximately 60% of the background soil (Fig. 3b), indicating a typical 'background profile' [25]. On the contrary, the profile of averaged soil samples analyzed in this study had higher fractions of PCDFs than those of background soil samples, even though OCDD was the most abundant. It is well known that the soil is the environmental sink that reflects cumulative deposition of PCDD/Fs during long term [12]. Therefore, the discrepancies in homologue patterns between flue gas and ambient air and their subsequent differences between background soil and soil samples clearly suggest that the agricultural soils have been affected by the combustion sources such as MSWIs, HWI and automobiles.

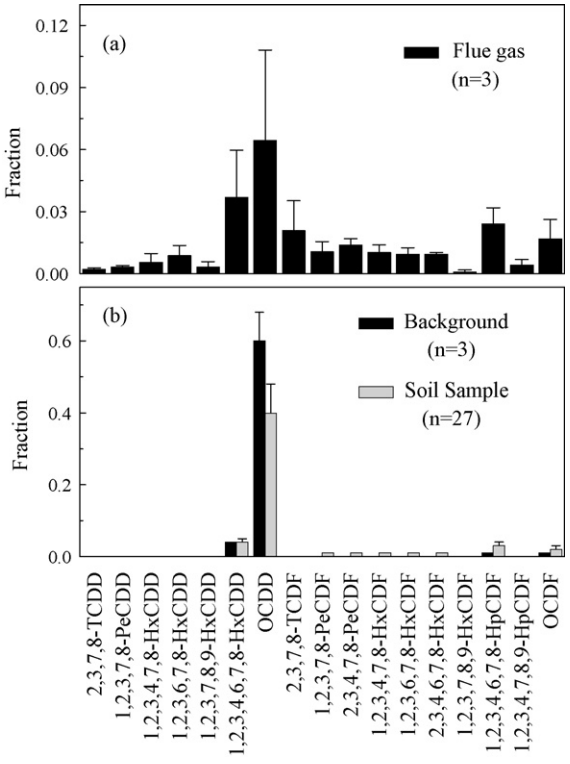

Fig. 4. PCDD/F congener patterns in flue gas samples (a) and background soil and soil samples collected near the incinerators (b), with error bars indicating the plus standard deviations.

3.2.3. Comparison of congener patterns

As numerous procedures can be chosen to obtain a congener profile, and there is no single agreed-upon convention [13]. In this paper, all data were normalized to the sum of [PCDDs] + [PCDFs] = 1 before analysis [17,25,30]. The congener profile of flue gas (Fig. 4a) was dominated by OCDD and 1,2,3,4,6,7,8-HpCDD, followed by 1,2,3,4,6,7,8-HpCDF and OCDF, being in agreement with the previous findings, where the profiles of individual 2,3,7,8-substituted congener concentrations were quite similar in spite of the wide range of I-TEQ from different combustion sources [31]. These congeners are bound primarily to aerosols or adsorbed on the particulate matter and then are much easier to be settled on the soil than those of low-chlorination [13]. A typical congener profile of ambient air is also dominated by the aforementioned four congeners, but has much higher fractions of OCDD and lower fractions of 1,2,3,4,6,7,8-HpCDF, OCDF and tetra- to hexa-PCDFs [25].

The average congener profiles of background soil and soil samples in this study were a good reflection of the differences and similarities of congener profiles between flue gas and ambi-

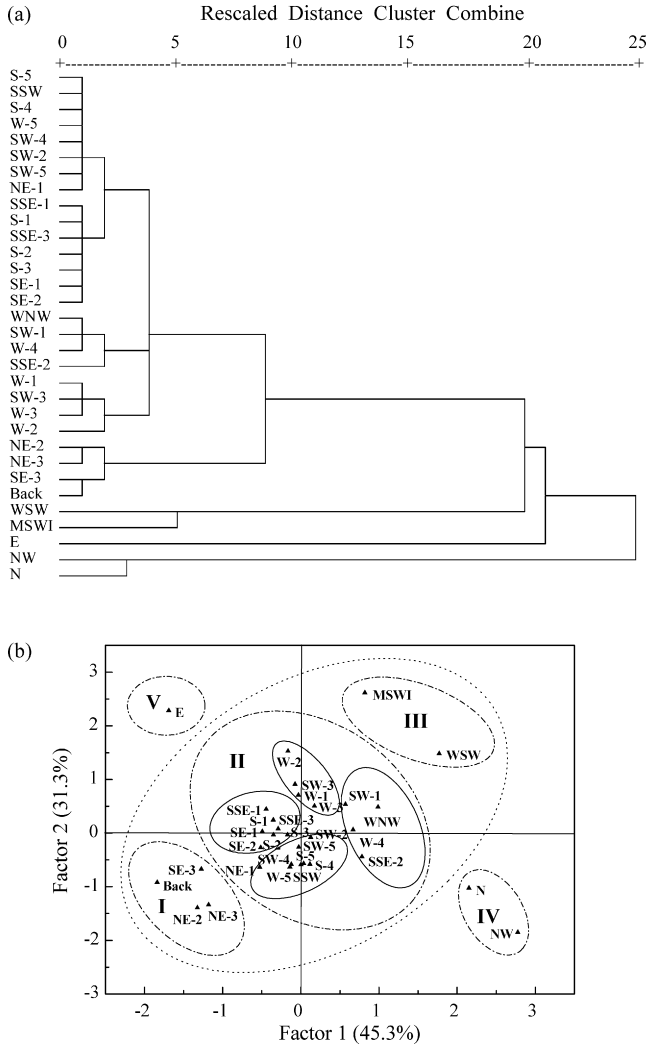

Fig. 5. Plot of hierarchical cluster analysis (a) and principal component analysis (b) of flue gas and soil samples.

ent air (Fig. 4b). For both background soil and soil samples, as described above, OCDD was the predominant congener, followed by the 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. However, the average congener profile of soil samples collected in the vicinity of the MSW incineration plant has lower fraction of OCDD and higher fractions of PCDFs than those of the background soil, especially for the congener of 1,2,3,4,6,7,8-HpCDF and OCDF. This confirmed the assumption that the agricultural land around the MSW incineration plant had been affected by the above-mentioned combustion sources.

3.2.4. Multivariate analysis of homologue patterns

Multivariate analysis including PCA and HCA were applied to further investigate the influence of PCDD/F emissions of FBIs on the surrounding soils, and to identify the other possible potential emission source of PCDD/Fs. The results of PCA showed that the first two principal components (PCs) accounted for 76.6% of the total variance (Fig. 5a). The first principal component (PC1, explaining 45.3% of the total variance) was correlated with HxCDD, HpCDF, PeCDD and HxCDF, while the second principal component (PC2, explaining 31.3% of the total variance) was positively correlated with TCDD and TCDF. A total of five groups were clearly identified in dendrogram and scatterplot resulting from the PCA and HCA (Fig. 5). Three groups (I, II and III) containing 30 soil samples within a radius of 7 km were constituted into a main cluster with only a few samples appearing as outliers (Groups IV and V), demonstrating that most of soil samples in the area studied were affected by the FBIs, but to different degrees.

A large variation of homologue patterns was observed among the five groups of soil samples (Fig. 6). Group I was associated with an OCDD-dominant homologue group with relatively lower levels of both low-chlorinated PCDDs and high-chlorinated PCDFs, resembling a typical background soil type [25]. For convenience of comparison, homologue profile of Group I was presented in every sub-illustrations. Group II (Fig. 6a) was also dominated by OCDD, but with relatively higher levels of the rest nine homologue groups than that of Group I, especially for low-chlorinated PCDFs, indicating the potential influence of combustion emissions of PCDD/Fs on agricultural soils. Group III (Fig. 6b) contained only one soil sample (WSW), being dominated by the low-chlorinated PCDFs and high chlorinated PCDDs (OCDD and HxCDD). This homologue profile was intermediate between the patterns of background soil and those of MSWI fly ash, demonstrating that the highest PCDD/F levels observed in this sampling site might be more attributed to uncontrolled dispersion of fly ash than the regularly deposition of PCDD/Fs [25]. Group IV (Fig. 6c) was again the OCDD-dominant homologue group but with higher levels of high chlorinated PCDD/Fs than Group II (except for OCDD), which resembles the differences between a typical automobile/HWI and MSWI emission homologue profile [25]. Since the two sampling sites (N and NW) in Group IV were located adjacent to motorways with heavy traffic and downwind of the HWI, the discrepancies of homologue profiles between Groups IV and I might be explained by the emission gases of the HWI and motor vehicles [32]. Soil sample (E) in Group V (Fig. 6d) exhibited a TCDF-dominant homologue patterns with rest of the profile similar to that of Group I. This unique homologue profile was caused by the unusually high level of the isomer 2,4,6,8-TCDF (45.1 pg g^{-1}), an indicator isomer in the impurities of a pesticide named 1,3,5-trichloro-

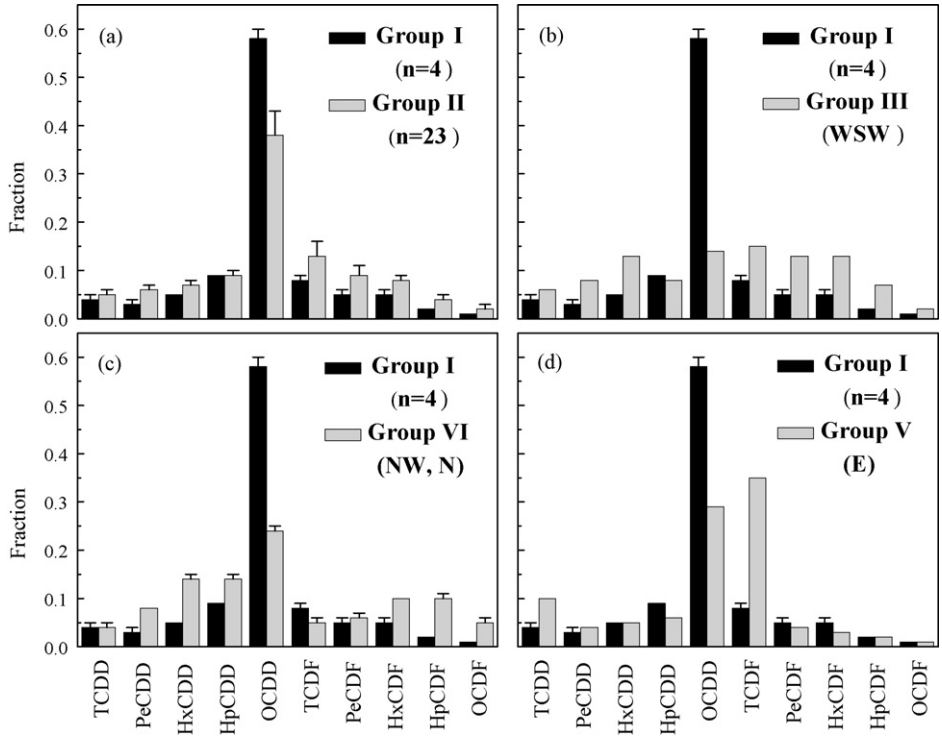

Fig. 6. PCDD/F homologue patterns of soil samples in each group, with error bars indicating the plus standard deviations.

2-(4-nitrophenoxy) benzene (CNP) [33,34], indicating that soil from this sampling site might be polluted by the application of the CNP. Therefore, it could be concluded from the multivariate analysis of homologue patterns that most of the soil samples in the studying area were directly affected by the FBIs, and other sources such as automobiles, HMI and CNP seemed to play an important role in agricultural soils adjacent to these potential sources.

4. Conclusions

The investigation of PCDD/Fs levels in agricultural soil in the vicinity of fluidized bed incinerators were initially conducted in Hangzhou, China. Although baseline data prior to the construction of the MSWIs were not available, the comparison of current results with the previously reported investigations conducted in the MSWIs of similar surroundings and rural areas indicate a low contamination of the soil around the FBIs. The PCDD/F levels decreased with the increasing distances and with the decreasing downwind frequencies from the MSWIs. The comparisons of homologue and congener patterns and the multivariate analyses of soil samples strongly suggested that most of the soil samples were influenced by the MSWIs. Moreover, historical PCDD/F emission of HMI and motor vehicles as well as the application of CNP seemed to play an important role in soil samples adjacent to these potential sources.

With the MSW incineration plant running, the PCDD/F emission and pollution are an ongoing problem and consequently need continuous monitoring. Atmospheric PCDD/F monitoring in the vicinity of the FBIs and a second round of sampling and analysis of soil samples in the same sites will be conducted in the near future in order to give a better interpretation of the possible PCDD/F emission sources that accounted for the PCDD/F levels in the agricultural soils around the FBIs. The data and results acquired in this study are a reference for the future controls of MSWIs activity and also could be used in the background risk assessment of PCDD/F exposure in the residents living near the MSWIs.

Acknowledgements

The financial support by the Zhejiang Provincial Natural Science Foundation of China (X506312, X206955) is greatly acknowledged. The authors are thankful to Dr. Chen Chong and Yu Liang for their assistance in soil sampling.

References

[1] R. Lohmann, K.C. Jones, Dioxins and furans in air and deposition: a review of levels, behavior and processes, Sci. Total Environ. 219 (1998) 53–81.

[2] K. Olie, P.L. Vermeulen, O. Hutzinger, Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerations in the Netherlands, Chemosphere 6 (1977) 455–459.

[3] J.L. Domingo, M. Schuhmacher, M.C. Agramunta, J.M. Llobet, J. Rivera, L. Muller, PCDD/Fs levels in the neighbourhood of a municipal solid waste incinerator after introduction of technical improvements in the facility, Environ. Int. 28 (2002) 19–27.

[4] M. Schuhmacher, S. Granero, J.M. Llobet, H.A.M. De Kok, J.L. Domingo, Assessment of baseline levels of PCDD/F in soils in the neighbourhood of a new hazardous waste incinerator in Catalonia, Spain, Chemosphere 35 (1997) 1947–1958.

[5] M. Berlincloni, A.D. Domenico, Polychlorodibenzo-*p*-dioxins and polychloro-dibenrofurans in the soil near the municipal incinerator of Florence, Italy, Environ. Sci. Technol. 21 (1987) 1063–1069.

[6] M. Schuhmacher, S. Granero, A. Xifro, J.L. Domingo, J. Rivera, E. Eljarrat, Levels of PCDD/Fs in the soil samples in the vicinity of a municipal solid waste incinerator, Chemosphere 37 (1998) 2127–2137.

[7] M. Schuhmacher, J.L. Domingo, S. Granero, J.M. Llobet, E. Eljarrat, J. Rivera, Soil monitoring in the vicinity of a municipal solid waste incinerator: temporal variation of PCDD/Fs, Chemosphere 39 (1999) 419–429.

[8] M. Schuhmacher, S. Granero, J. Rivera, L. Muller, J.M. Llobet, J.L. Domingo, Atmospheric deposition of PCDD/Fs near an old municipal solid waste incinerator: levels in soil and vegetation, Chemosphere 40 (2000) 593–600.

[9] M. Lober, P. Pinsky, P. Gehring, C. Braverman, D. Winters, W. Sovocool, Relationships between dioxins in soil, air, ash, and emissions from a municipal solid waste incinerator emitting large amounts of dioxins, Chemosphere 37 (1998) 2173–2197.

[10] M. Coutinho, M. Conceicao, C. Borrego, M. Nunes, Atmospheric impact assessment and monitoring of dioxin emissions of municipal solid waste incinerators in Portugal, Chemosphere 37 (1998) 2119–2126.

[11] S. Ohta, O. Kuriyama, T. Aozasa, M. Nakao, H. Tanahashi, S. Miyata, Survey on levels of PCDDs, PCDFs, and non-*Ortho* co-PCBs in soil and sediment from a high cancer area near a batch-type municipal solid waste incinerator in Japan, B. Environ. Contam. Tox. 64 (2000) 630–637.

[12] J.L. Domingo, M. Schuhmacher, L. Muller, J. Rivera, S. Granero, J.M. Llobet, Evaluating the environmental impact of an old municipal waste incinerator: PCDD/F levels in soil and vegetation samples, J. Hazard. Mater. 76 (2000) 1–12.

[13] J.L. Domingo, S. Granero, M. Schuhmacher, Congener profiles of PCDD/Fs in soil and vegetation samples collected near to a municipal waste incinerator, Chemosphere 43 (2001) 517–524.

[14] J.L. Domingo, M. Schuhmacher, J.M. Llobet, L. Muller, J. River, PCDD/F concentrations in soil and vegetation in the vicinity of a municipal waste incinerator after a pronounced decrease in the emission of PCDD/Fs from the facility, Chemosphere 43 (2001) 217–226.

[15] P.S. Cheng, M.S. Hsu, E. Ma, U. Chou, Y.C. Ling, Levels of PCDD/Fs in ambient air and soil in the vicinity of a municipal solid waste incinerator, in Hsinchu, Chemosphere 52 (2003) 1389–1396.

[16] S. Caserini, S. Cernuschi, M. Giugliano, M. Grosso, G. Lonati, P. Mattaini, Air and soil dioxin levels at three sites in Italy in proximity to MSW incineration plants, Chemosphere 54 (2004) 1279–1287.

[17] J.E. Oh, S.D. Choi, S.J. Lee, Y.S. Chang, Influence of a municipal solid waste incinerator on ambient air and soil PCDD/Fs levels, Chemosphere 64 (2006) 579–587.

[18] M. Schuhmacher, J.L. Domingo, Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator, Environ. Int. 32 (2006) 397–404.

[19] L.G. Zhang, X.F. Zhu, The present status of treatment for municipal wastes and its development trend in China, Ind. Safety Env. Protect. 32 (2006) 37–39, in Chinese.

[20] CAEPI, China development report on treatment industry of urban domestic refuse in 2004, China Environ. Protect. Ind. 10 (2005) 40–42 (in Chinese).

[21] J.H. Yan, T. Chen, X.D. Li, J. Zhang, S.Y. Lu, M.J. Ni, K.F. Cen, Evaluation of PCDD/Fs emission from fluidized bed incinerators co-firing MSW with coal in China, J. Hazard. Mater. 135 (2006) 47–51.

[22] USEPA, User's Guide for the Industrial Source Complex (ISC3) Dispersion Models. Report EPA-454/B-95-003, 1995.

[23] E. Eljarrat, A. De la Cal, D. Barcelo, Potential chlorinated and brominated interferences on the polybrominated diphenyl ether determinations by gas chromatography-mass spectrometry, J. Chromatogr. A. 1008 (2003) 181–192.

[24] USEPA, Method 1613 B: Tetra through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, USEPA Press, Washington, DC, 1994.
[25] H. Hagenmaier, C. Lindig, J. She, Correlation of environmental occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurens with possible sources, Chemosphere 29 (1994) 2163–2174.
[26] W. Rotard, W. Christmann, W. Knoth, Background levels of PCDD/F in soils of Germany, Chemosphere 29 (1994) 2193–2200.
[27] R.E. Alcock, K.C. Jones, Dioxins in the environment: a review of trend data, Environ. Sci. Technol. 30 (1996) 3133–3143.
[28] R. Duarte-Davidson, A. Sewart, R.E. Alcock, I.T. Cousins, K.C. Jones, Exploring the balance between sources, deposition, and the environmental burden of PCDD/Fs in the UK terrestrial environment: an aid to identifying uncertainties and research needs, Environ. Sci. Technol. 31 (1997) 1–11.
[29] J.E. Oh, K.T. Lee, J.W. Lee, Y.S. Chang, The evaluation of PCDD/Fs from various Korean incinerators, Chemosphere 38 (1999) 2097–2108.
[30] B.H. Kim, S.J. Lee, S.J. Mun, Y.S. Chang, A case study of dioxin monitoring in and around an industrial waste incinerator in Korea, Chemosphere 58 (2005) 1589–1599.
[31] R.E. Alcock, R. Gemmill, K.C. Jones, Improvements to the UK PCDD/F and PCB atmospheric emission inventory following an emissions measurement programme, Chemosphere 38 (1998) 759–770.
[32] B. Gullet, J.V. Ryan, On-road sampling of diesel engine emissions of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran, Organohalogen Compd. 32 (1997) 451–456.
[33] T. Sakurai, N. Suzuki, S. Masunaga, J. Nakanishi, Origin attribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment and soil from a Japanese freshwater lake area through congener-specific data analysis, Chemosphere 37 (1998) 2211–2224.
[34] S. Masunaga, T. Takasuga, J. Nakanishi, Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations, Chemosphere 44 (2001) 873–885.