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Distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) and dioxin-like polychlorinated biphenyls (dioxin-like PCBs) in the soil in a typical area of eastern China

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ABSTRACT

The distribution and concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dioxin-like PCBs, also called co-PCBs) in a typical area of eastern China were evaluated by analysis of 21 soil and 6 sediment samples. The range of WHO-TEQ values for the PCDD/Fs and dioxin-like PCBs in 17 soil samples representing the background investigation in the study area was 0.017–5.04 pg g^{-1} (dry weight, dw), with a mean value 0.967(±1.361) pg g^{-1} and medium value 0.348 pg g^{-1}, which indicates that the levels of PCDD/Fs and dioxin-like PCBs over the major part of this district were low. However, the WHO-TEQ values (6.52–16.7 pg g^{-1} dw) for PCDD/Fs and dioxin-like PCBs in soil samples to the leeward of a known contaminated disassembly industrial park were much higher than that of the background investigation, and the levels of sediment samples downstream of this area were in the range 2.25–34.6 pg g^{-1} (dw). The levels of WHO-TEQ in soil and sediment samples decreased with an increase in distance from the researched pollution source. The principal component analysis demonstrated that the PCDD/Fs and dioxin-like PCBs in major part of contaminated sediment and soil samples derived from the correlative matrix. Yet the different distribution patterns of them in part of sediment samples strongly indicate that other potential sources may be exist, further researches should be done to get more information about the sources and the distributions of the PCDD/Fs and PCBs.

1. Introduction

The highly toxic polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), which are unwanted by-products of various combustion processes and chemical reactions involving chlorinated compounds [1], can be transferred to other locations through the transmission and deposition of particulates in ambient air [2–4]. The dioxin-like polychlorinated biphenyls (dioxin-like PCBs, PCB-81, 77, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, IUPAC number) mainly come from the commercial products which are used in an industrial capacity, transformers and oil painting and which are sometimes deposited in the environment. They are generally monitored in agricultural fields, environmental soil and sediment [5–15]. It is well known that the soil quality has always been important for soil microbial, plant and animal life, including humans. Soil pollutants can pass to vegetation and enter food chains. Furthermore, the soil has high affinity for hydrophobic organic pollutants and can act as a natural sink. Therefore, it is very important to evaluate the environmental quality of soil concerning with the distribution and contamination of PCDD/Fs and PCBs.

Because of the rapidly developing industrial and agricultural activities, municipal development, increased usage of chemicals, and insufficient recognition of environmental protection over the past 20 years, the pollution of the soil and sediment in certain district of eastern China may be very serious. Of particular concern has been done about the pollution of oil with PCBs in the 1990s and the long-term practice of disassembling electronic solid waste in several villages and towns of this district, the pollution of PCDD/Fs and PCBs was quite serious [16–22]. Cai et al. [5] summarized the status of soil contamination by PCDD/Fs, PCBs and other pollutants in China. PCBs in soil samples occurred generally at concentrations lower than 100 μg kg^{-1} dry weight (dw), quite high concentrations of PCDD/Fs and PCBs were observed in some contaminated sites. Luo et al. [16] investigated the composition and the pollution of the PCDD/Fs in typical farmland and found the concentration of two

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Table 1
The characteristic and the polluted situation of different samples

Series	Characteristic of sample	Vegetation of sampling site	Pollution of sampling site
S-1	Brown farmland soil	Rice	Near farmhouse, no special polluted source
S-2	Gray farmland soil	Vegetable	Near farmhouse, no special polluted source
S-3	Brown forest soil	Forest	No special polluted source
S-4	Gray farmland soil	Rice	No special polluted source
S-5	Dark black farmland soil	Vegetable	Outskirts, no special polluted source
S-6	Brown meadow soil	Meadow	No special polluted source
S-7	Dark black farmland soil	Deserted farmland	Outskirts, near a PCB capacitor disassembly site
S-8	Brown forest soil	Greening land	Outskirts, no special polluted source
S-9	Brown meadow soil	Meadow	Neat a market town, no special polluted source
S-10	Dark brown greening land soil	Meadow	The city zone, no special polluted source
S-11	Gray farmland soil	Rice	Near farmhouse, no special polluted source
S-12	Gray forest soil	Forest	Foothill land, no special polluted source
S-13	Brown meadow soil	Meadow	Foothill land, no special polluted source
S-14	Brown meadow soil	Meadow	Near outskirts, no special polluted source
S-15	Gray farmland soil	Crop	Near farmhouse, no special polluted source
S-16	Gray farmland soil	Crop	Near farmhouse, no special polluted source
S-17	Brown greening land soil	Meadow	The city zone, no special polluted source
S-18	Dark brown farmland soil	Deserted farmland	Northwest of the pollution source, about 2.5 km distance
S-19	Dark brown farmland soil	Deserted farmland	Southwest of the pollution source, about 2.5 km distance
S-20	Dark brown farmland soil	Deserted farmland	About 5.0 km to pollution source
S-21	Gray farmland soil	Deserted farmland	Suburb, near the pollution source
R-1	Gray sediment		Another branch of main stream
R-2	Black sediment		20 km of downstream of site S-21
R-3	Black sediment		10 km of downstream of site S-21
R-4	Black sediment		Branch of main stream near site S-21
R-5	Gray sediment		Main stream, 30 km of downstream of site S-21
R-6	Gray sediment		Main stream, 40 km of downstream of site S-21

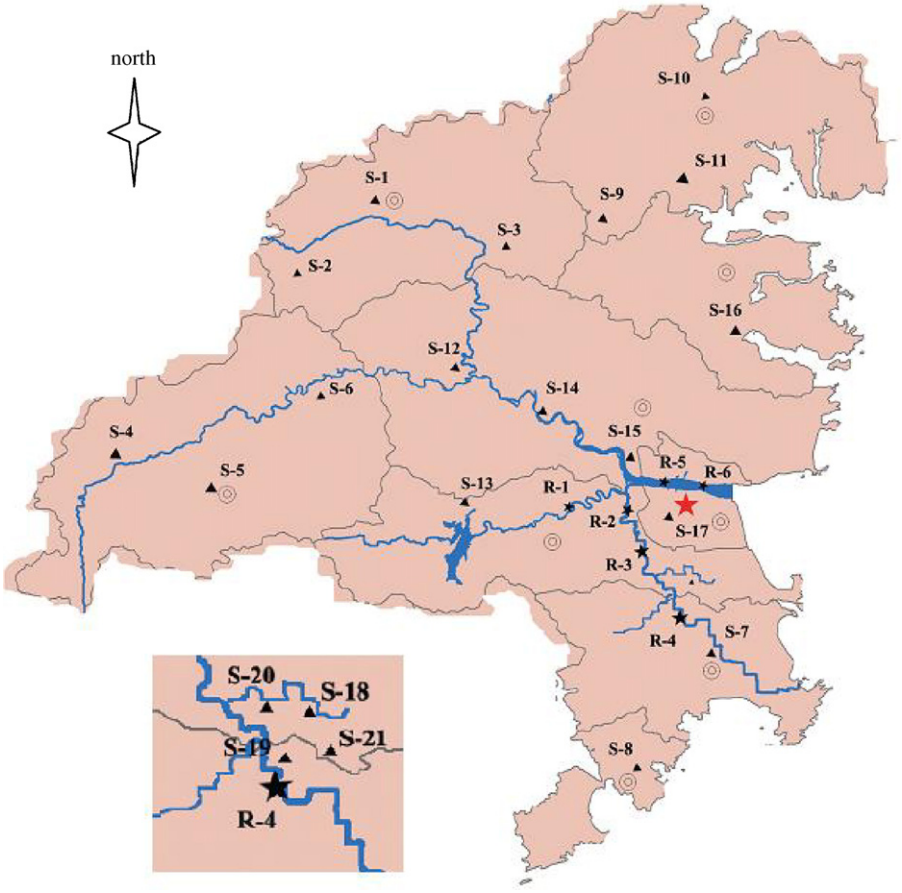

Fig. 1. The distribution of sampling site.

Table 2
Total PCDDs/Fs and PCBs concentrations (pg g^{-1} dw) in background investigation samples of selected species

Species	OCDD	ΣPCDDs	ΣPCDFs	ΣPCDD/Fs	ΣCo-PCB	ΣPCBs	WHO-TEQ(PCDD/Fs)	WHO-TEQ(PCDD/Fs + PCBs)
S-1	169	206	18.9	224	ND[a]	37.2	0.127	0.127
S-2	31.0	31.0	12.5	43.5	ND	58.6	0.070	0.070
S-3	37.1	66.0	28.5	94.5	ND	18.6	0.090	0.090
S-4	75.6	127	75.7	203	ND	25.3	0.128	0.128
S-5	1,488	1,668	45.7	1,713	ND	58.0	0.741	0.741
S-6	1,626	1,724	26.6	1,750	ND	92.0	0.466	0.466
S-7	47.7	154	156	310	9531	54,475	3.86	5.04
S-8	3,289	3,416	22.2	3,438	ND	94.0	0.838	0.838
S-9	711	757	24.5	782	ND	42.5	0.360	0.360
S-10	15,323	15,540	8.96	15,548	ND	52.0	2.503	2.503
S-11	715	764	54.0	818	ND	294	0.348	0.348
S-12	174	180	9.98	190	ND	33.5	0.017	0.017
S-13	79.4	96.8	12.5	109	ND	24.5	0.236	0.236
S-14	14,920	15,391	24.1	15,416	ND	74.5	2.223	2.223
S-15	5.32	10.1	14.8	25.0	ND	39.8	0.343	0.343
S-16	5.00	7.39	22.2	29.6	ND	32.6	0.283	0.283
S-17	14,311	14,532	-	14,532	ND	42.9	2.628	2.628
Mean ± S.D.	3118 ± 5666	3216 ± 5769	32.8 ± 36.7	3249 ± 5758	–	3264 ± 13197	0.898 ± 1.15	0.967 ± 1.361
Medium value	174	206	23.2	310	–	42.9	0.348	0.348

[a] ND means the results was below the limit of detection.

soil samples was 20.82 and 21.32 WHO-TEQ pg g^{-1} (dw) individually. Chu et al. [17,18] analyzed the composition and distribution of the PCBs in typical polluted soil and found that the concentration of total PCBs was 788 ng g^{-1} (dw). Zhao et al. [19] measure the levels of 23 PCB congeners and 6 OCPs in human milk and three food types collected from Luqiao and Pingqiao in Zhejiang Province, China. Data showed that the PCB levels in milk samples from Luqiao were significantly higher than those from localities in other Chinese provinces and comparable to those in developed or industrialized countries. Li et al. [20] investigated the cumulative levels of PCBs in blood samples of mothers and children in southern China, the average concentration of 13 kinds of PCBs was found to be 192 μg kg^{-1} lipid for children and 176 μg kg^{-1} lipid for mothers. However, the distribution of PCDD/Fs and dioxin-like PCBs in soil and sediment in this district was seldom found.

In order to obtain an overall view of pollution by PCDD/Fs and dioxin-like PCBs in soil of the studied district of eastern China, and the pollution in soil and sediment of a typical contaminated area of this district, this study evaluated the distribution and concentrations of PCDD/Fs and dioxin-like PCBs of 21 soil samples and 6 sediment samples in the area.

2. Materials and methods

2.1. Sampling and sample preparation

Seventeen samples of surface soils (approximately 0–20 cm depth) were collected from different parts of the study district, a well-known area with the disassembly of electronic solid waste in eastern China, using a geographic information system (GIS) grid (20 × 20 km) for the background investigation of the PCDD/Fs and PCBs pollution of the district. The influence of a typical source (a long-term disassembling electronic solid-waste industrial park with several simple solid-waste incinerators) on the soil and surface water system of the typical contaminated area of this district was investigated by collecting four surface soil samples to the leeward of the main direction of the wind and six sediment samples (surficial sediments, approximately 8 cm in depth) downstream of the pollution source. The characteristics and degree of pollution of the different samples are shown in Table 1, and the distribution of the sampling sites is shown in Fig. 1.

All the samples were air-dried and ground through a 20-mesh of sieve before solvent extraction.

2.2. Analytical methods

The analyses of PCDD/Fs, dioxin-like PCBs and total PCBs were carried according to the EPA 8280 method and the references of [23–25]. In brief, 20 g of homogenized sample was Soxhlet-extracted for 20 h using toluene. A blank and a parallel sample were included in each batch of five or six samples. Before extraction, ^{13}C-labelled PCDD/Fs internal standards (including $^{13}C_{12}$-2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-2,3,7,8-TCDD), $^{13}C_{12}$-1,2,3,7,8-pentachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-1,2,3,7,8-PeCDD), $^{13}C_{12}$-1,2,3,4,7,8-hexachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-1,2,3,4,7,8-HxCDD), $^{13}C_{12}$-1,2,3,6,7,8-hexachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-1,2,3,6,7,8-HxCDD), $^{13}C_{12}$-1,2,3,4,6,7,8-heptachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD), $^{13}C_{12}$-octachlorinated dibenzo-*p*-dioxin ($^{13}C_{12}$-OCDD), $^{13}C_{12}$-2,3,7,8-tetrachlorinated dibenzofuran ($^{13}C_{12}$-2,3,7,8-TCDF), $^{13}C_{12}$-2,3,4,7,8-pentachlorinated dibenzofuran ($^{13}C_{12}$-2,3,4,7,8-PeCDF), $^{13}C_{12}$-1,2,3,4,7,8-hexachlorinated dibenzofuran ($^{13}C_{12}$-1,2,3,4,7,8-HxCDF), $^{13}C_{12}$-1,2,3,6,7,8-hexachlorinated dibenzofuran ($^{13}C_{12}$-1,2,3,6,7,8-HxCDF), $^{13}C_{12}$-2,3,4,6,7,8-hexachlorinated dibenzofuran ($^{13}C_{12}$-2,3,4,6,7,8-HxCDF), $^{13}C_{12}$-1,2,3,4,6,7,8-heptachlorinated dibenzofuran ($^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF), and $^{13}C_{12}$-octachlorinated dibenzofuran ($^{13}C_{12}$-OCDF), Wellington Laboratories) for PCDD/Fs, or ^{13}C-labelled PCBs internal standards ($^{13}C_{12}$-PCB-81, 77, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, 28, 52, 101, 118, 153, 138, and 180, Wellington Laboratories) for dioxin-like PCBs and total PCBs [23,24], were spiked into the sample individually. After concentrating the extracts, the samples for dioxin and dioxin-like PCBs were subjected to cleanup using a multilayer silica gel column (sil/sil+33% NaOH (0.1 mol/L)/sil/sil+44% H_2SO_4 (concentrated)/sil/anhydrous Na_2SO_4 from button to upper of the column) and basic super-active Al_2O_3 columns (MP Biomedicals Germany) in series; PCDD/Fs samples were further purified by another micro basic super-active Al_2O_3 column. The total PCBs sample underwent cleanup by a multilayer silica gel column only. The eluent was concentrated to near dryness and transferred into vials with a known quantity of $^{13}C_{12}$-labelled injection standard as recovery standard ($^{13}C_6$-1,2,3,4-TCDD for PCDD/Fs, $^{13}C_{12}$-PCB-79

Table 3
PCDD/Fs and Co-PCBs congener (pg g^{-1} dw) profile of soil samples

	S-18	S-19	S-20	S-21	Mean ± S.D.	Medium value
sum TetraCDD	45.2	21.5	74.0	42.3	–	–
sum PentaCDD	22.1	32.4	32.1	44.5	–	–
sum HexaCDD	18.9	20.2	28.3	9.38	–	–
sum HeptaCDD	65.2	39.9	53.0	–	–	–
OctaCDD	315	78.7	180	61.8	–	–
sum TetraCDF	217	145	432	61.1	–	–
sum PentaCDF	102	104	166	47.5	–	–
sum HexaCDF	44.2	49.3	87.7	20.8	–	–
sum HeptaCDF	32.1	18.2	26.0	–	–	–
OctaCDF	<12.4	<12.4	15.5	<12.4	–	–
ΣPCDD/Fs	862	509	1,095	287	688 ± 360	686
2,3,7,8-TetraCDD	<1.6	<1.6	<1.6	<1.6	–	–
1,2,3,7,8-PentaCDD	<2.4	<2.4	<2.4	5.02	–	–
1,2,3,4,7,8-HexaCDD	4.21	5.20	<4.1	<4.1	–	–
1,2,3,6,7,8-HexaCDD	6.40	<4.1	4.53	<4.1	–	–
1,2,3,7,8,9-HexaCDD	<4.1	<4.1	<4.1	<4.1	–	–
1,2,3,4,6,7,8-HeptaCDD	36.8	29.5	25.4	<8.5	–	–
OctaCDD	315	78.7	180	61.8	–	–
2,3,7,8-TetraCDF	4.52	12.0	8.56	2.98	–	–
1,2,3,7,8-PentaCDF	3.20	4.56	3.90	<2.4	–	–
2,3,4,7,8-PentaCDF	6.60	5.90	7.02	4.00	–	–
1,2,3,4,7,8-HexaCDF	4.45	4.78	5.45	<4.1	–	–
1,2,3,6,7,8-HexaCDF	4.89	8.82	6.55	<4.1	–	–
1,2,3,7,8,9-HexaCDF	<4.1	<4.1	<4.0	<4.1	–	–
2,3,4,6,7,8-HexaCDF	<4.1	6.60	6.16	<4.1	–	–
1,2,3,4,6,7,8-HeptaCDF	10.60	10.5	13.0	<8.5	–	–
1,2,3,4,7,8,9-HeptaCDF	<8.5	<8.5	<8.5	<8.5	–	–
OctaCDF	<12.4	<12.4	15.5	<12.4	–	–
3,3′,4,4′-TeCB(#77)	92.1	289	38	2,239	–	–
3,4,4′,5-TeCB(#81)	31.6	<4.1	<4.1	115	–	–
2,3,3′,4,4′-PeCB(#105)	166	772	609	4,433	–	–
2,3,4,4′,5-PeCB(#114)	<4.5	<4.5	<4.5	274	–	–
2,3′,4,4′,5-PeCB(#118)	298	978	1,325	8,439	–	–
2,3,4,4′,5-PeCB(#123)	45.3	105	133	825	–	–
3,3′,4,4′,5-PeCB(#126)	<4.5	<4.5	<4.5	65.0	–	–
2,3,3′,4,4′,5-HxCB(#156)	101	52.0	147	1,188	–	–
2,3,3′,4,4′,5′-HxCB(#157)	<6.8	<6.8	<6.8	283	–	–
2,3′,4,4′,5,5′-HxCB(#167)	<6.8	72.0	73.8	503	–	–
3,3′,4,4′,5,5′-HxCB(#169)	<6.8	<6.8	<6.8	<6.8	–	–
2,3,3′,4,4′,5,5′-HpCB(#189)	<10.2	<10.2	<10.2	<10.2	–	–
ΣCo-PCB	734	2,268	2,675	18,364	6010 ± 8278	2,472
WHO-TEQ(PCDD/Fs)	6.41	7.32	7.23	7.75	7.18 ± 0.56	7.28
WHO-TEQ(PCDD/Fs + PCBs)	6.52	7.56	7.55	16.7	9.58 ± 4.77	7.56
ΣPCBs	1334	23,088	18,192	12,7852	42617 ± 57583	20,640

for dioxin-like PCBs and total PCBs, Wellington Laboratories). Before concentration, 10 μL nonane was added into eluent to avoid the loss of PCBs. Measurements of tetra- to octa-PCDD/Fs, dioxin-like PCBs and total PCBs were performed using a high-resolution gas chromatograph (DB-5 MS column and CP SIL 88 column for PCDD/Fs, 60 m, 0.32 mm i.d., 0.1 μm film thickness for DB-5MS column, and 50 m, 0.25 mm i.d., 0.2 μm film thickness for CP SIL 88 column; DB-XLB column for dioxin-like PCBs and total PCBs, 60 m, 0.32 mm i.d., 0.25 μm film thickness) interfaced to a Agilent 5973I low-resolution mass spectrometer (HRGC/LRMS). Identification of 2,3,7,8-substituted PCDD/Fs and dioxin-like PCBs was performed using retention times of the ^{13}C-labelled standard and isotope ratios M/(M+2) or (M+2)/(M+4). Non-2,3,7,8-substituted PCDD/Fs and non-dioxin-like PCBs (total PCBs, from the congeners tri to heptachlorinated biphenyls) were also identified. Recoveries of internal standards generally varied between 65 and 115% and the relative deviation of parallel samples of different congeners were less than 20%. The concentrations of the different congeners of PCDD/Fs and dioxin-like PCBs in the blank samples were too low to detectable. The detection limit was 1.6–12.4 pg g^{-1} from congeners tetra to octachloro dibenzo-*p*-dioxins (OCDD) and dibenzofurans (OCDF), and 4.1–10.2 pg g^{-1} for dioxin-like PCBs.

3. Results and discussion

3.1. Background investigation of the pollution of dioxin

PCDDs, PCDFs, dioxin-like PCBs, total PCBs and WHO-TEQ values of PCDD/Fs and dioxin-like PCBs in the selected samples for background investigation of this district are summarized in Table 2.

3.1.1. PCDDs and PCDFs concentrations in soil

As shown in Table 2, the range of the concentration of PCDDs was 7.39–15,540 pg g^{-1} (dw), with a mean of 3216(±5769) pg g^{-1} (mean ± S.D.) and a medium value of 206 pg g^{-1}, which was much greater than those of PCDFs in soil samples (range of 8.96–75.7 pg g^{-1}, mean value 34.8(±36.9) pg g^{-1}, medium value 23.2 pg g^{-1}). The PCDD/F congener profiles in most of the samples were dominated by OCDD, which contributed >80% to the total PCDD/Fs concentrations. This phenomenon was quite similar to that reported for soil samples collected from southern China [26] and sediment samples collected from Hong Kong [27]. In contrast to PCDDs, levels of PCDFs were very low generally. However, relatively higher PCDFs levels were observed in samples S-7, S-15 and S-16. Wagrowski and Hites suggested that, when PCDFs are predominant, the profile is classified as “source”, whilst “sink” profiles

Table 4
PCDD/Fs and Co-PCBs congener (pg g^{-1} dw) profile of sediment samples

	R-1	R-2	R-3	R-4	R-5[a]	R-6[a]	Mean ± S.D.	Medium value
sum TetraCDD	14.3	78.2	95.5	51.6	21.9	20.9	–	–
sum PentaCDD	12.2	75.5	87.5	57.2	18.0	14.9	–	–
sum HexaCDD	–	52.9	49.0	48.4	15.1	17.0	–	–
sum HeptaCDD	–	26.2	55.0	115.7	24.3	22.0	–	–
OctaCDD	21.8	41.4	170	163	102	96.4	–	–
sum TetraCDF	45.2	55.9	260	139	47.0	34.5	–	–
sum PentaCDF	16.7	46.7	151	336	38.4	26.2	–	–
sum HexaCDF	–	40.9	128	149	19.5	13.9	–	–
sum HeptaCDF	–	38.0	99.5	338	17.8	21.0	–	–
OctaCDF	<12.4	12.5	25.1	113	32.5	43.5	–	–
ΣPCDD/Fs	110	468	1,121	1,510	336	310	643 ± 548	402
2,3,7,8-TetraCDD	<1.6	<1.6	3.84	<1.6	0.16	0.27	–	–
1,2,3,7,8-PentaCDD	<2.4	<2.4	<2.4	<2.4	0.55	0.62	–	–
1,2,3,4,7,8-HexaCDD	<4.1	<4.1	3.00	2.32	0.63	0.64	–	–
1,2,3,6,7,8-HexaCDD	<4.1	5.20	5.10	4.58	1.14	1.07	–	–
1,2,3,7,8,9-HexaCDD	<4.1	4.40	4.24	4.44	0.96	0.65	–	–
1,2,3,4,6,7,8-HeptaCDD	<8.5	15.4	30.27	66.2	10.0	9.28	–	–
OctaCDD	21.8	41.4	170	163	102	96.4	–	–
2,3,7,8-TetraCDF	2.64	3.10	6.10	5.15	1.94	1.15	–	–
1,2,3,7,8-PentaCDF	2.66	<2.4	1.52	23.59	1.01	1.42	–	–
2,3,4,7,8-PentaCDF	3.02	<2.4	2.06	31.02	1.42	1.47	–	–
1,2,3,4,7,8-HexaCDF	<4.1	8.90	10.85	18.64	3.59	2.48	–	–
1,2,3,6,7,8-HexaCDF	<4.1	8.80	12.1	25.7	2.25	1.72	–	–
1,2,3,7,8,9-HexaCDF	<4.1	<4.1	<4.1	1.76	0.32	0.24	–	–
2,3,4,6,7,8-HexaCDF	<4.1	7.90	12.5	37.7	1.53	1.27	–	–
1,2,3,4,6,7,8-HeptaCDF	<8.5	19.9	49.7	227	10.8	14.20	–	–
1,2,3,4,7,8,9-HeptaCDF	<8.5	<8.5	18.3	31.4	1.18	1.44	–	–
OctaCDF	<12.4	12.5	25.1	113	32.5	43.50	–	–
3,3′,4,4′-TeCB(#77)	123	1,021	1,236	2,340	<4.1	<4.1	–	–
3,4,4′,5-TeCB(#81)	42.5	98.3	<4.1	<4.1	39.9	54.6	–	–
2,3,3′,4,4′-PeCB(#105)	654	4,500	3,792	7,260	22.3	51.4	–	–
2,3,4,4′,5-PeCB(#114)	56.4	268	230	620	<4.5	<4.5	–	–
2,3′,4,4′,5-PeCB(#118)	992	8,900	8,720	18,010	85.3	206	–	–
2,3,4,4′,5-PeCB(#123)	241	670	744	1,744	<4.5	20.9	–	–
3,3′,4,4′,5-PeCB(#126)	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	–	–
2,3,3′,4,4′,5-HxCB(#156)	168	2,145	2,428	2,170	21.0	<6.8	–	–
2,3,3′,4,4′,5′-HxCB(#157)	43.0	1,287	1,751	556	36.7	23.1	–	–
2,3′,4,4′,5,5′-HxCB(#167)	64.5	989	808	990	34.1	9.43	–	–
3,3′,4,4′,5,5′-HxCB(#169)	<6.8	<6.8	<6.8	<6.8	<6.8	<6.8	–	–
2,3,3′,4,4′,5,5′-HpCB(#189)	<10.2	<10.2	<10.2	<10.2	<10.2	<10.2	–	–
ΣCo-PCB	2384	19,878	19,709	33,690	239	365	12711 ± 13821	11,046
WHO-TEQ(PCDD/Fs)	1.91	4.19	11.3	30.0	2.94	2.88	8.87 ± 10.9	3.56
WHO-TEQ(PCDD/Fs + PCBs)	2.25	7.46	15.0	34.6	2.98	2.92	10.9 ± 12.6	5.22
ΣPCBs	5234	80,967	128,756	235,409	726	4470	75927 ± 93819	43,100

[a] PCDD/Fs analysis with HRGC/HRMS by Zhejiang University, China (JMS-800D, DB-5MS, 60 m, 0.32 mm i.d., 0.1 μm film thickness).

are dominated by PCDDs [28]. Investigation shows that high PCDFs levels in sample S-7 may be traced to an abandoned solid-waste incinerator and the disassembling of capacitor with PCBs solution nearby during last century. Yet the open burning of the residue of crops might be the main source of PCDD/Fs in sample S-15 and S-16.

3.1.2. PCB concentration in soil

The concentrations of total PCBs were in the range of 18.6–127, 852 pg g^{-1} (dw), with a mean value of 3264(±13,197) pg g^{-1} and a medium value of 42.9 pg g^{-1} (Table 2), and dioxin-like PCBs in all analyzed soil samples was lower than the detection limit of the method except for soil sample S-7, in which the concentration was 9531 pg g^{-1} (dw). Except for sample S-7, the pollution of PCBs over the major part of this district was relatively mild. The source of the pollution in sample S-7 was also traced to the disassembling of capacitor with PCBs solution in last century.

3.1.3. WHO-TEQ concentrations in soil samples

As shown in Table 2, the range of WHO-TEQ values for PCDD/Fs and dioxin-like PCBs was 0.017–5.04 pg g^{-1} (dw), mean value was 0.967(±1.361) pg g^{-1} and medium value was 0.348 pg g^{-1}. The relatively low levels of the WHO-TEQ data meant that the pollution of PCDD/Fs and dioxin-like PCBs in main area of the studied district was not obvious, yet the WHO-TEQ of the S-7 soil sample was somewhat higher than the recommended value in soil, which is <5 pg g^{-1} [29]. In contrast with PCDD/Fs, the WHO-TEQ levels for dioxin-like PCBs in soil samples of background investigation were only 10% or less of total WHO-TEQ except for sample S-7. However, the contribution of dioxin-like PCBs to total WHO-TEQ in the S-7 soil sample was almost 30%.

3.2. Evaluation of PCDD/Fs and dioxin-like PCBs pollution in a typical area of this district

In the 1990s, Chu et al. [17,18] reported PCBs pollution observed in several villages of this district due to the disassembling of capacitor and transformer which contained PCBs solution. Later, the disassembly of electronic solid waste became widespread and several industrial parks were formed in these villages, although this kind of activity was restricted by the government in a way. The residue of the solid waste after disassembly was burnt in simple solid-waste incinerator or even open burning. Quantities of hazardous pollutant were emitted from the incinerator and polluted the soil and water [16,20–22]. In this report, the levels and distribution of PCDD/Fs and PCBs in soil adjacent to one of typi-

cal contaminated disassembly industrial park in this district were evaluated. The influence in sediment of downstream was also evaluated. The concentrations of PCDD/Fs and PCBs of the soil to the leeward of the main direction of the wind in this typical source are shown in Table 3, and the levels of the sediment downstream are listed in Table 4.

3.2.1. Congener profiles of PCDDs, PCDFs and dioxin-like PCBs in soil

As shown in Table 3, the concentration of the PCDD/Fs was in the range 287–1094 pg g^{-1} (dw), with a mean value of 688(±360) pg g^{-1} (dw) and a medium value of 686 pg g^{-1} (dw). These levels are only third of those reported by Luo et al. [16] (average 2639 pg g^{-1}), and only 20th of Guiyu (another disassembling site of electronic solid waste in south China, average 10,081 pg g^{-1} [12]). Unlike the background investigation samples, the PCDD/F congener profiles in these samples were not dominated by OCDD. The level of PCDD congeners, except for TCDDs and PeCDDs, generally increased with an increase of their chlorine substitution. On the other hand, the profile of PCDF congeners was different from PCDDs, decreasing with an increase of their chlorine substitution.

The concentrations of total PCBs were in the range of 1334–127, 852 pg g^{-1} (dw), with a mean value of 42,617(±57,583) pg g^{-1} (dw) and a medium value of 20,640 pg g^{-1} (dw), which was also lower than the report of Guiyu (62 mg kg^{-1}) so far [12]. The concentrations of dioxin-like PCBs were in the range of 734–18,364 pg g^{-1} (dw), with a mean value of 6010(±8278) pg g^{-1} (dw) and a medium value of 2472 pg g^{-1} (dw). The most abundant congener of dioxin-like PCBs was PCB-118, with 44.8% ± 3.8 of the total dioxin-like PCBs.

The WHO-TEQ values for PCDD/Fs and dioxin-like PCBs were in the range of 6.52–16.7 pg g^{-1} (dw), and the levels for PCDD/Fs were in the range of 6.41–7.75 pg g^{-1} (dw), with a mean value of 7.18(±0.56) pg g^{-1} (dw) and a medium value of 7.28 pg g^{-1} (dw), which was much lower than the report of Guiyu (average of 122 I-TEQ pg g^{-1} [12]). Generally, the WHO-TEQ levels of dioxin-like PCBs were less than 10% in soil samples S-18, S-19 and S-20. However, the contribution of dioxin-like PCBs to total WHO-TEQ in the S-21 soil sample was more than 50% for the high concentration of dioxin-like PCBs (18,364 pg g^{-1}). An interesting finding from Table 3 is that the concentrations of four soil samples decreased in order of S-18 < S-19 ≅ S-20 < S-21. This indicates that the WHO-TEQ levels decreased with an increase in distance from the researched pollution source. However, if the contribution of dioxin-like PCBs is ignored, an increase in the distance to the leeward of the polluted source showed no obvious correlation with concentrations of PCDD/Fs. This kind of distribution of PCDD/Fs was possibly due to the contribution of other PCDD/Fs pollution sources.

3.2.2. Congener profiles of PCDDs, PCDFs and dioxin-like PCBs in sediment

As shown in Table 4, the concentrations of the PCDD/Fs were in the range 110–1510 pg g^{-1} (dw), with a mean value of 643(±548) pg g^{-1} (dw) and a medium value of 402 pg g^{-1} (dw). The concentrations, except for sample R-1, which was used for research into other potential sources of PCDD/Fs pollution in the sediment, were R-6 < R-5 < R-2 < R-3 < R-4, increasing with a decrease in the distance from the typical pollution area. The PCDD/Fs levels were lower than that of sediment taken from the Hong Kong coastline [27] and higher than that of sediment from Nansi Lakes [30]. Generally, the level of PCDD/Fs congeners, except for TCDDs, increased with an increase in their chlorine substitution for PCDDs and decreased with an increase in their chlorine substitution for PCDFs. However, the distribution pattern of sample R-4 was different from that of the other samples. The level of PCDFs congeners

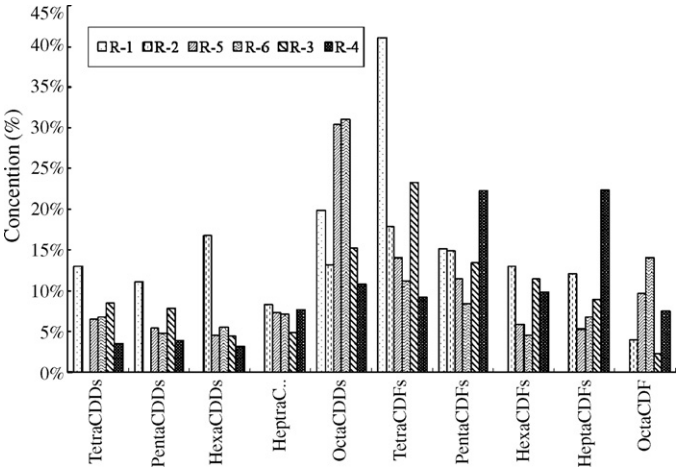

Fig. 2. The profile of the PCDD/Fs congener of sediment in the downstream of typical pollution area.

increased with an increase in their chlorine substitution; the most abundant congeners of PCDD/Fs were PeCDFs and HpCDFs.

The composition of PCDD/Fs in sediment is shown in Fig. 2. It appears that the composition of PCDD/Fs between samples R-1, R-2, R-3, R-4 in branch of the main stream and samples R-5, R-6 in main stream was different. The ratios of ΣPCDDs/ΣPCDFs for R-1, R-2, R-3 and R-4 were <1.0, and the ratios were >1.0 for R-5 and R-6, which means that the potential sources of PCDD/Fs in R-5 and R-6 were not only those of the typical study area, but possibly other sources as well. Through investigation of the industrial pollution source along the main stream, some potential source, just like hazardous solid-waste incinerator, dye industry, pharmaceutical industry, etc., may also contributed to the pollution of PCDD/Fs. Further work should be done to research the pollution of the main stream.

The concentration of PCBs in sediment samples was in the range of 447–235,409 pg g^{-1} (dw) and dioxin-like PCBs was in the range of 239–33,690 pg g^{-1} (dw). Fig. 3 shows the distribution of different dioxin-like PCB congeners in sediment. The most abundant congener of dioxin-like PCBs in sediment samples was PCB-118 with 46.7% ± 8.6 of total dioxin-like PCBs, which was very similar to the distribution in the soil. The variation in the concentrations

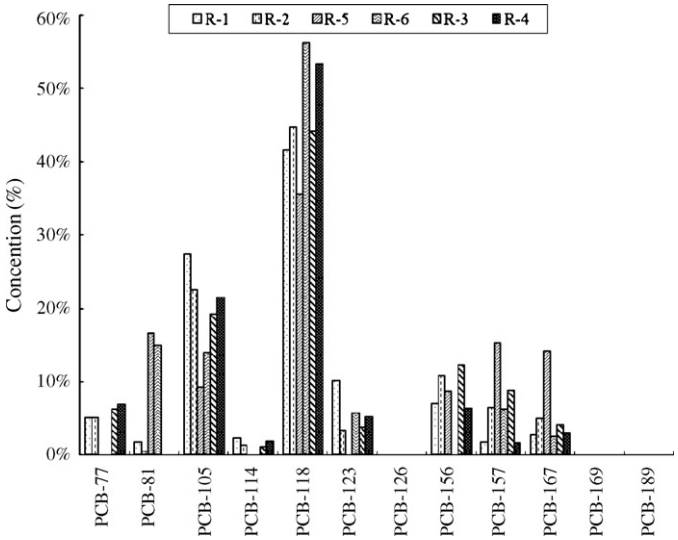

Fig. 3. The profile of the dioxin-like PCBs congener of sediment in the downstream of typical pollution area.

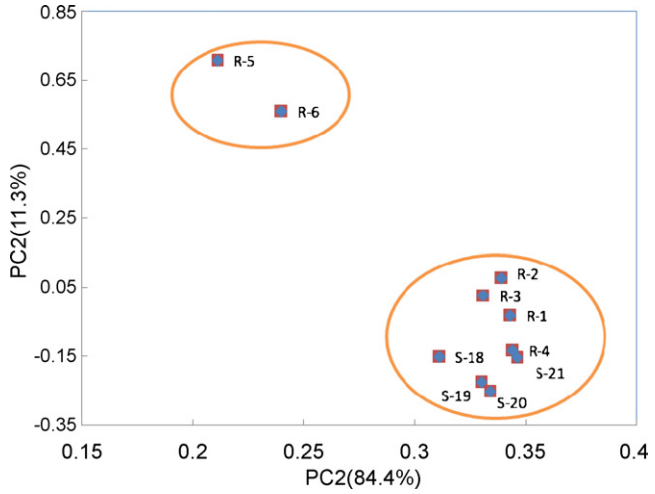

Fig. 4. The correlation of the dioxin-like PCBs profile of soil and sediment samples.

in sediment was R-5 < R-6 < R-1 < R-3 ≅ R-2 < R-4, which was a little different from that of the PCDD/Fs. The highest levels of PCBs were found in sample R-4. Compared with the concentration of dioxin-like PCBs at site R-1, which was 2384 pg g^{-1} dw, means that the research area was not the only potential source of PCBs in sediment. Other workshops for disassembling capacitors and transformers may also exist nearby.

The WHO-TEQ levels for PCDD/Fs and dioxin-like PCBs were in the range of 2.25–34.6 pg g^{-1} (dw), and the levels of PCDD/Fs were in the range of 1.91–30.0 pg g^{-1} (dw). The major contributors to the WHO-TEQ levels were PCDD/Fs in sediment samples R-1, R-4, R-5 and R-6, however, the contributions of dioxin-like PCBs to total WHO-TEQ in sediment samples R-2 and R-3 were 44 and 25%, respectively.

3.2.3. Correlation of PCDD/Fs, dioxin-like PCBs in soil and sediment

Principal component analysis (PCA) is a multivariate statistical method that is frequently employed in environmental science to reduce the dimensionality of a data set. In the present work, PCA was applied to evaluate the similarities and differences of distribution patterns of PCDD/Fs and dioxin-like PCBs for soil and sediment samples in the study area. Each sampling site and each chemical were assigned a score after PCA analysis, allowing the summarized data to be further plotted and analyzed. Figs. 4 and 5 show the patterns of dioxin-like PCBs and PCDD/Fs in different soil and sediment samples individually after PCA.

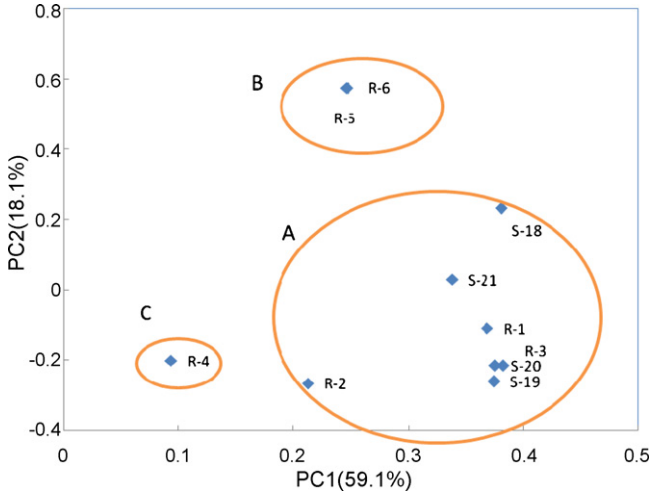

Fig. 5. The correlation of the PCDD/Fs profile of soil and sediment samples.

As seen in Fig. 4, the first principal components (PC1) and the second principal components (PC2) represented 80.4 and 11.3% of the total variance individually. It indicated that the dioxin-like PCBs in group A (include sample R-1, R-2, R-3, R-4, S-18, S-19, S-20, and S-21), which strongly associated with PC1, derived from the correlative matrix, and the sample R-5 and R-6 in group B, which associated with PC2, derived from another kind of matrix.

Fig. 5 shows that the sample R-1, R-2, R-3, S-18, S-19, S-20, S-21 fall in group A associated with PC1 which represents 59.1% of the total variance, conforming they have similar distribution patterns of PCDD/Fs and have a correlative matrix. Sample R-5 and R-6 fall in group B (PC2 18.1%) indicate they have another kinds of distribution patterns of PCDD/Fs and another kind of matrix. Yet the sediment sample R-4 was less strongly associated with group A or group B, which might be contributed to the difference distribution patterns of PCDD/Fs. Other potential source may also exist near the site of R-4. More effective and imperative activities should be done to get more information about the sources and the distributions of the PCDD/Fs in this typical polluted area.

4. Conclusions and future perspectives

(1) The range of WHO-TEQ values for PCDD/Fs and dioxin-like PCBs of soil in the background investigation of the researched district was 0.017–5.04 pg g^{-1} (dw), with a mean value 0.967 (±1.361) pg g^{-1} and medium value 0.348 pg g^{-1}, therefore, dioxin pollution was not obvious in this district.

(2) The WHO-TEQ values for PCDD/Fs and dioxin-like PCBs in soil samples adjacent to a typical polluted disassembly industrial park in this district were in the range of 6.52–16.7 pg g^{-1} (dw), which was much higher than that of the background investigation, and the levels decreased with an increase in distance from the researched pollution source.

(3) The WHO-TEQ values for PCDD/Fs and dioxin-like PCBs in sediment samples were in the range of 2.25–34.6 pg g^{-1} (dw), and the levels increased with a decrease in the distance from the typical pollution area studied.

(4) The principal component analysis demonstrated that the PCDD/Fs and dioxin-like PCBs in sample R-1, R-2, R-3, R-4, S-18, S-19, S-20, and S-21 derived from the correlative matrix (except for the PCDD/Fs in sample R-4). Yet the different distribution patterns of the PCDD/Fs in sample R-4 or the PCDD/Fs and dioxin-like PCBs in sample R-5 and R-6 were strongly indicated that other potential sources existed. More effective and imperative activities should be done to get more information about the sources and the distributions of the PCDD/Fs and PCBs in this typical polluted area.

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