RESEARCH ARTICLE

Polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and polycyclic aromatic hydrocarbons around a thermal desorption plant in China

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Abstract This study was launched to establish comprehensive environmental monitoring on the levels and patterns of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and polycyclic aromatic hydrocarbons (PAHs) both in soil and ambient air around a thermal desorption plant in China. All 209 congeners of PCBs, 136 congeners of PCDD/Fs (P=4 to 8) and 16 EPA priority PAHs were analyzed. The concentration of PCBs ranged from 20.0 to 536 ng g^{-1} (or 0.077–5.27 pg WHO-TEQ g^{-1}) in soil and from 972 to 991 ng Nm^{-3} (or 0.245–0.374 pg WHO-TEQ Nm^{-3}) in air samples, much higher than the levels in cities. A single soil sampling point could have been affected by some transfer of PCBs from the untreated soil by the fingerprint characteristics and the statistical analysis. Establishing blank values prior to the start-up of new plant is a safe and sure method to establish subsequent impacts on the environment. During the treatment of hazardous waste, strict control of all waste materials and all emissions is required.

Keywords Thermal treatment · PCBs · PCDD/Fs · PAHs · Contaminated soil

Introduction

Polychlorinated biphenyls (PCBs) were widely produced and used between 1929 and 1979 because of their intrinsic qualities, such as stability, low vapor pressure, and flammability.

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Japan was the first country to ban their PCB production in 1974, after the Yu-sho rice oil-poisoning incident. The Stockholm Convention on persistent organic pollutants (POPs) confirmed that their usage is to be phased out and their emission is to be minimized (Porta and Zumeta 2002). Considerable interest in their environmental effects and remediation methods spread quickly all over the world.

China historically produced about 10,000 t of PCBs (Xing et al. 2005), largely used as dielectric fluid in transformers and capacitors. Since 1974, China banned production of PCBs containing chemicals and electrical equipment. In 1980s, electrical equipment containing PCBs were forbidden to use and were stored in caves or buried. Due to spill, evaporation loss, and inappropriate management, some areas have been heavily contaminated by PCBs (China SEPA 2003). It is necessary to remediate such sites; however in China, remedial strategy, soil treatment plants, and management experience are all lacking.

Thermal desorption is an efficient remediation technology for removing volatile and semi-volatile organic species from contaminated soil. In the USA, it has been widely applied at Superfund sites to remediate both in situ and ex situ. Under anoxic conditions, desorption of semi-volatile compounds (PCDD/Fs; PCBs) is accompanied by dechlorination and decomposition (Hagenmaier et al. 1987; Weber et al. 2002; Misaka et al. 2006). While in the presence of oxygen, PCBs could be potential precursors of PCDFs, which formed via oxygen insertion. The formation pathways of PCDFs include loss of ortho-Cl$_2$, loss of HCl involving a 2,3-chlorine shift, loss of ortho-H$_2$, and dechlorination (Weber and Sakurai 2001; Sato et al. 2010; Zhao et al. 2012).

In 2010, a first thermal desorption plant for treating PCB-contaminated soil was built in Zhejiang Province, China. This plant (capacity of 75 t soil per day) was operated as a Sino-American demonstration project. It started operation in

February 2011. Until August 2012, about 1100 t of PCB-contaminated soil had been cleaned. In order to ascertain the potential spreading of pollution and evaluate the environmental safety during the thermal desorption, investigation covered several pollutants were carried out in the soil and air samples at boundary of the plant. Also, this assessment could provide useful experience for further contaminated soil treatment as well as hazardous waste management and disposal in China.

Materials and methods

Study area

The thermal desorption plant covers an area of 6000 m^2 and is surrounded by hills on three sides. Lan River forms a large reservoir at a distance of less than 200 m. PCDD/Fs, PCBs, and PAHs were analyzed simultaneously in the contaminated soil being treated (S_{PCB}), five soil samples (S_1 to S_5), and ambient air (A_1, A_2) situated at short range around the plant (Fig. 1). Diesel oil is used for indirect heating of the PCB-contaminated soil, tumbling in a rotary kiln. The combustion products do not contact the soil. The off-gas rises from the soil; it is cooled, condensed, and scrubbed. In the middle of the plant, there is a covered depot for contaminated soil (capacity of 100 m^3), which has no sidewalls (Fig. 2). Evaporated PCBs as well as small particles entrained by wind gusts could spread around the plant.

Samples collection

Soil samples and ambient air were collected on 21st and 22nd of February 2012, and their positions were recorded by a handheld GPS, with ~10-m accuracy. The ambient

Fig. 2 Covered depot of contaminated soil

temperature ranged from 5 to 10 °C with a slight breeze from the southeast to the northeast. Two samples (S_3, S_4) were situated in the downwind direction within 50 m from the plant; two other samples were taken upwind (S_1, S_2). A background sample (S_5) was collected about 1.2 km north of the plant. PCB-contaminated soil was sampled from the storehouse. The procedure of Yan et al. (2008) was followed in sampling and analysis. The soil samples were freeze-dried and stored at −20 °C until analysis.

Two air samples were collected with high-volume air samplers (Model HV-1000F, SIBATA) in compliance with USEPA method TO-9A. Sample A_2 was collected upwind and A_1 downwind, in the opposite direction. The sampler was fitted with a glass fiber filter followed by a glass cartridge containing two polyurethane foam plugs. The flow rate was set at 0.7 m^3 min^{-1}, and after 24 h of sampling, the total volume collected was 1008 m^3 air. These samples were stored at −20 °C before further analysis.

Samples extraction and analysis

About 10.0 g dry weight (dw) of each soil sample (<60-mesh fraction) was extracted by accelerated solvent extraction (ASE 300, Dionex, Sunnyvale, CA) following the selective pressured liquid extraction (SPLE) method (Eljarrat et al 2003). Air sample filters and cartridges were also Soxhlet extracted for 24 h with 300 ml toluene.

PCBs analysis

After ASE or Soxhlet extraction and acid/base treatment, the samples were cleaned up using multi-silica gel and Florisil columns, as in the USEPA method 1668. The solution was analyzed for PCBs by HRGC/HRMS (JEOL JMS-800D,
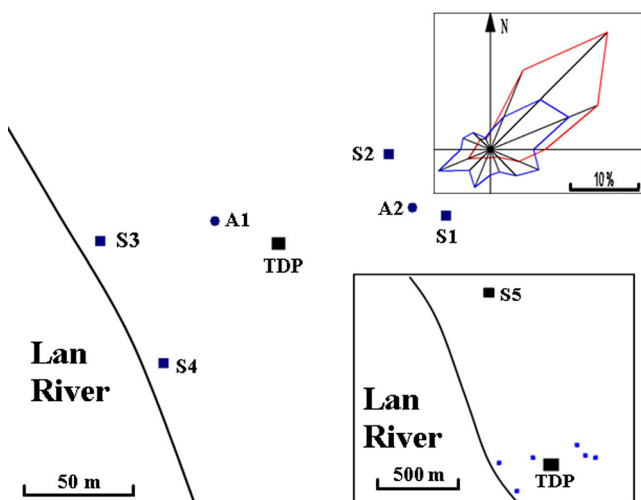
Fig. 1 Sampling sites and wind rose (*blue lines* indicate wind frequency in winter; *red* lines indicate wind frequency in summer; *TDP* thermal desorption plant)

Japan) with a DB-5MS column (60 m×0.25 mm×0.25 μm). All 209 congeners from mono- (MCB) to deca-chlorinated (DeCB) were detected (Frame 1997) and quantified by adding a mixture of internal standards, purification standards, and injection standards, before extraction, purification, and analysis, respectively. The recovery of each internal standard was between 64 and 128 % and those of each purification standard between 78 and 124 %, in accordance with analytical quality requirements. The toxic equivalency factors (TEFs) of the World Health Organization (WHO) were used for calculating the toxic equivalency quantity (TEQ) of PCDDs, PCDFs, and PCBs (Van den Berg et al. 2006).

PCDD/Fs analysis

The analysis of PCDD/Fs was described by Yan et al. (2008), and the elution order of the various congeners was determined according to study by Fishman et al. (2011).

After extraction and acid/base treatment, the samples were cleaned up using a multi-silica gel column and an alumina column, as in USEPA method 1613 and USEPA method 23. The congeners of the tetra- to octa-chlorinated homologue groups as well as the toxic 2,3,7,8-substituted PCDD/Fs were identified and quantified by HRGC/HRMS (JEOL, JMS-800D). The recovery of internal standards varied between 60 and 110 % for all samples.

PAHs analysis

PAHs analysis, clean-up, and fractionation were realized using columns packed with deactivated silica gel (Lundstedt et al. 2000; Johansson and van Bavel 2003). A GC-MS-MS (Varian 1200, USA) with a

DB5-MS capillary column (30 m×0.25 mm×0.25 μm) was used for determining the 16 EPA-PAHs. Each extract (1 μL) was injected in a splitless mode. High-purity helium was used, at a flow rate of 2 ml min^{-1}. The temperature of injector and transfer lines were 270C and 290 °C, respectively. The initial oven temperature was set at 60 °C for 1 min, followed by heating to 280 °C at a rate of 20 °C min^{-1} and then maintained for 5 min at this temperature. The recovery of surrogate standards for PAH determinations was in ranges of 80 to 115 %.

Data and statistical analysis

Statistical analysis was based on the SPSS software version 15.0. The individual samples were clustered hierarchically as Zhang et al. (2006).

The weight average chlorination level of PCBs (in weight units) was defined by

$$\text{Chlorination Degree} = \frac{\sum_{i=0}^{10} C(C_{12}H_iCl_{10-i}) \times (10-i)}{\sum_{i=0}^{10} C(C_{12}H_iCl_{10-i})}$$

Results and discussion

All data are presented and analyzed in a sequence of (1) PCBs, the potential pollutant, (2) dioxin-like PCBs (dl-PCBs), (3) PCDD/Fs, (4) 2,3,7,8-PCDD/Fs, and (5) PAHs, including the total carcinogenic PAHs and B[a]P$_{eq}$.

Table 1 Concentration of PCBs in soil (in ng g^{-1}) and air samples (in ng Nm^{-3})

	S_1	S_2	S_3	S_4	S_5	S_{PCB}	A_1	A_2
MoCB	0.10	0.18	0.33	0.22	0.16	$7.89×10^3$	5.59	5.42
DiCB	5.38	6.53	29.80	7.44	6.18	$5.13×10^5$	276.9	304.6
TrCB	14.52	18.06	281.6	14.75	10.88	$3.04×10^6$	565.2	556.6
TeCB	6.87	8.35	190.1	3.89	2.60	$1.83×10^6$	118.6	119.4
PeCB	0.78	0.66	29.42	0.22	0.11	$1.49×10^5$	5.59	5.36
HxCB	0.08	0.08	3.44	0.04	0.02	$1.04×10^4$	0.39	0.35
HpCB	0.02	0.03	0.82	0.02	0.01	$2.31×10^3$	0.17	0.14
OcCB	0.01	0.01	0.27	0.01	<0.01	720	0.02	0.01
NoCB	<0.01	<0.01	0.09	<0.01	<0.01	230	0.01	<0.01
DeCB	0.01	<0.01	0.01	0.01	0.01	120	<0.01	<0.01
PCBs	27.8	33.9	536	26.6	20.0	$5.56×10^6$	972	992

Fig. 3 PCBs isomer distribution and weight average chlorination degree in soil and air samples
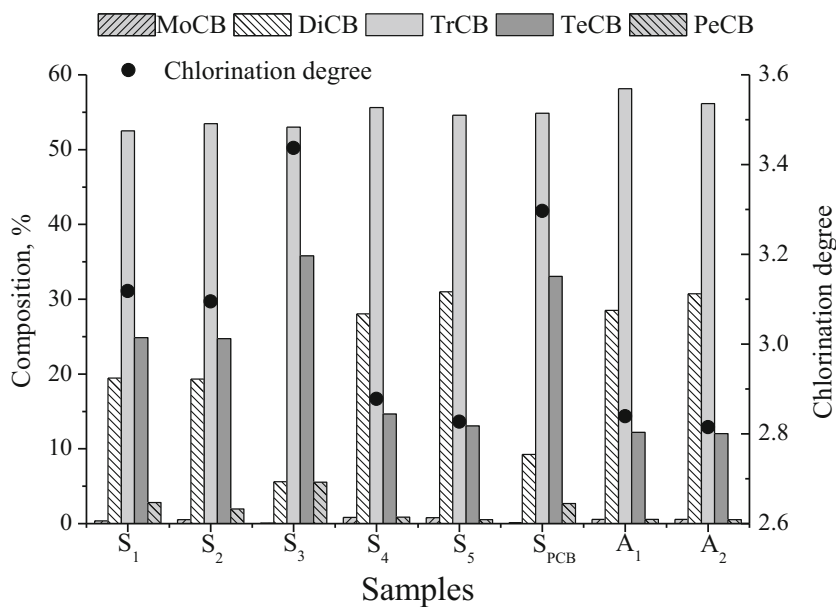
PCBs in soil and ambient air

Table 1 shows total PCB (209 congeners) values in soil and air samples. The PCB levels in air (972 ng m^{-3} (A_1) and 992 ng m^{-3} (A_2)) are two orders of magnitude higher than those in an e-waste dismantling area in southeast China (4.23 to 11.35 ng m^{-3}, Li et al. 2008). The concentrations of PCBs range from 20.0 ng g^{-1} in background sample S_5 to 536 ng g^{-1} in soil sample S_3. Sample S_3 attains 20 to 30 times of the load of the other samples; yet, it is still one ten-thousandth of the soil to be thermally treated (S_{PCB}). Spreading of PCB-contaminated soil particles could explain this outlier. The

spreading of PCB-vapors is less likely to produce such sharp difference between soil samples.

All PCB-levels recorded are a factor 10 higher than those urban soil in Kunming (1.84 ng g^{-1}) and Shanghai (1.73 ng g^{-1}), and a factor 20 more than in background and rural samples in Zhejiang (1.14 ng g^{-1}) (Ren et al. 2007). Sample S_3 exceeds the threshold of 60 ng g^{-1} PCBs in ambient soil established by the USSR Ministry of Health in 1991 (Bobovnikova et al. 1993) by a factor 9.

Figure 3 shows sufficient similarity between isomer group profiles to suggest similar sources of the PCBs recorded, i.e., commercial PCBs with mainly TrCB and

Table 2 Concentration of dl-PCB congener in soil (in pg g^{-1}) and air samples (in pg Nm^{-3})

	S_1	S_2	S_3	S_4	S_5	S_{PCB}	A_1	A_2
PCB 77	107.0	109.7	5638	32.65	14.04	3.03×10^7	451.5	411.8
PCB 81	6.05	6.57	316.8	2.19	1.17	1.65×10^6	43.51	25.70
PCB 126	1.33	1.40	42.99	1.22	0.66	1.9×10^5	2.79	1.59
PCB 169	0.31	0.22	<0.01	0.62	0.30	6.0×10^4	0.61	0.53
PCB 105	86.80	71.77	4267	18.76	7.47	1.69×10^7	206.4	189.5
PCB 114	6.36	6.14	3471	1.60	0.92	1.51×10^6	22.42	19.22
PCB 118	124.8	104.8	4805	33.20	11.71	2.85×10^7	438.3	373.4
PCB 123	4.21	4.46	269.1	1.51	0.41	1.0×10^6	27.88	27.61
PCB 156	2.87	2.60	136.9	1.18	0.91	4.4×10^5	9.82	6.69
PCB 157	0.92	0.71	38.21	0.43	0.43	1.4×10^5	3.15	2.23
PCB 167	0.99	1.18	55.72	1.17	0.61	2.0×10^5	5.70	3.61
PCB 189	0.38	0.47	6.37	0.48	0.38	5.0×10^4	<0.01	<0.01
Sum dl-PCBs	342	310	15921	95.0	39.0	8.09×10^7	1212	1062
TEQ, pg WHO-TEQ g^{-1}	0.161	0.164	5.27	0.146	0.077	2.7×10^4	0.374[a]	0.245[a]

[a] pg WHO-TEQ Nm^{-3}

Table 3 Concentration of PCDD/Fs in soil (in pg g^{-1}) and air samples (in pg Nm^{-3})

	S_1	S_2	S_3	S_4	S_5	S_{PCB}	A_1	A_2
TCDD	13.91	405.2	38.09	83.97	37.36	897.4	1.26	1.16
PeCDD	9.27	181.8	19.75	45.02	21.34	781.3	1.88	1.81
HxCDD	5.83	18.08	12.39	22.91	12.47	43.54	2.31	2.16
HpCDD	5.01	9.31	10.31	22.91	12.13	21.77	1.26	1.34
OCDD	50.86	118.5	101.6	154.1	102.7	38.70	1.09	1.22
TCDF	39.56	241.8	75.72	114.8	71.57	17331	23.32	23.99
PeCDF	36.22	49.97	40.97	85.64	35.88	4352	18.73	18.37
HxCDF	25.61	30.92	36.33	95.26	27.12	558.8	22.68	24.36
HpCDF	12.60	14.23	15.00	41.22	15.12	157.2	9.06	9.20
OCDF	0.12	0.21	1.94	2.20	0.30	4.84	<0.01	<0.01
PCDDs	84.91	733.0	182.1	328.9	186.0	1785	7.80	7.67
PCDFs	114.1	337.1	170.0	339.1	145.0	22404	73.80	75.93
136 PCDD/Fs	199	1070	352	668	336	24189	81.6	83.6

TeCB. And it also reveals some serious distinctions: the pair S_{PCB}, S_3 is higher in TrCB and TeCB, yet lower in DiCB.

The similarity between S_3 and S_{PCB} is impressive. S_{PCB} and S_3 samples show the highest chlorination level (3.30 and 3.44). While downwind sample S_4 (2.88), background sample S_5 (2.82), and air samples A_1 and A_2 (2.84 and 2.81) are the lowest.
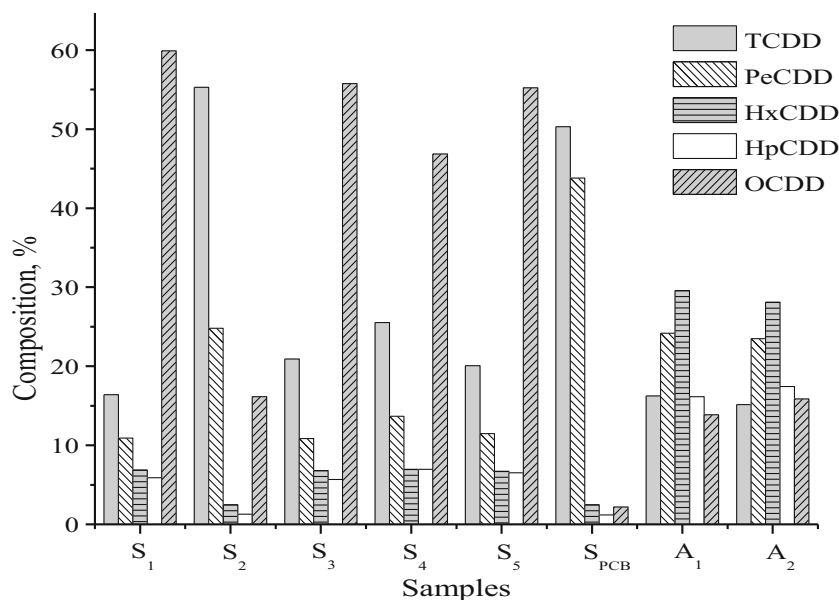
Dl-PCBs in soil and ambient air

Table 2 lists the concentration of dl-PCB congener and the PCB-related WHO-TEQ contribution of these 12 dl-PCBs as presented in soil and air samples. The concentration of the sum of dl-PCBs is 8.09×10^7 pg g^{-1} in S_{PCB}. Three congeners,

3,3′,4,4′-TeCB (#77), 2,3′,4,4′,5-TeCB (#118), and 2,3,3′,4,4′-PeCB (#105) are major contributors of the dl-PCBs.

The background sample S_5 has the lowest WHO-TEQ value 0.077 pg TEQ g^{-1}, and the TEQ of air samples are 0.374 and 0.245 pg TEQ Nm^{-3} for A_1 and A_2, respectively. The TEQ of S_3 achieves 5.27 pg TEQ g^{-1}, more than 30 times higher than other soil samples while similar with S_{PCB}, indicating the particle pollution by S_{PCB}.

PCDD/Fs in ambient air and soil

Commercial PCBs are always contaminated with (lower chlorinated) PCDFs and (to a minor extent) PCDDs. Thermal treatment is responsible for extensive formation of PCDFs (Weber and Sakurai 2001; Sato et al. 2010). Hence, it was important to analyze these compounds.

Fig. 4 Congener fingerprints of the PCDDs
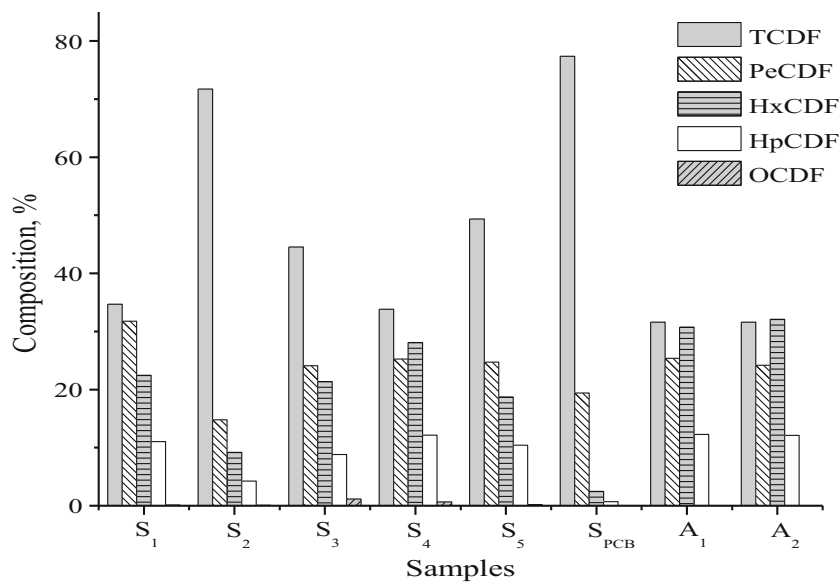
Fig. 5 Congener fingerprints of the PCDFs

Table 3 shows the concentration of PCDD/Fs in soil and air samples. Samples A_1 and A_2 are comparable to ambient air samples in China (2.6 to 120 pg m^{-3}) (Chen et al. 2011), yet higher than those at three sites in Italy (0.42–6.67 pg m^{-3}) (Caserini et al. 2004). The sum of PCDD/Fs ranged from 336 (S_5) to 1070 pg g^{-1} (S_2), higher than in Italy (16–255 pg g^{-1}) (Caserini et al. 2004).

S_{PCB} is roughly 50 times more contaminated with PCDD/Fs than the five soil samples. This ratio is much lower than those for PCBs, ranging from 10^4 (S_3) to 3×10^5 (S_5). Thus, S_{PCB} has a much higher potential for PCB-pollution than for PCDD/F-pollution.

Sample S_3 was heavily contaminated by PCBs, yet fails to show strong PCDD/F-pollution. This lower load of PCDD/Fs

Table 4 Concentration of toxic 2, 3, 7, 8-substituted PCDD/Fs in soil (in pg g^{-1}) and air samples (in pg Nm^{-3})

	S_1	S_2	S_3	S_4	S_5	S_{PCB}	A_1	A_2
2,3,7,8-TCDD	0.277	0.202	0.233	1.182	0.267	25	0.018	0.016
1,2,3,7,8-PeCDD	0.219	0.523	0.934	2.772	0.251	51.7	0.086	0.07
1,2,3,4,7,8-HxCDD	0.303	0.535	0.395	0.791	0.516	5.389	0.087	0.082
1,2,3,6,7,8-HxCDD	0.227	0.479	0.789	2.028	0.677	5.368	0.119	0.129
1,2,3,7,8,9-HxCDD	0.443	1.151	0.608	1.554	0.814	7.931	0.133	0.126
1,2,3,4,6,7,8-HpCDD,	2.215	4.485	4.207	10.851	5.704	12.41	0.621	0.684
OCDD	50.91	118.5	101.4	154.2	102.8	46.53	1.082	1.219
2,3,7,8-TCDF	1.014	11.234	2.908	3.633	2.859	1969.8	0.669	0.814
1,2,3,7,8-PeCDF	1.122	3.955	3.132	6.206	2.436	529.3	2.075	2.012
2,3,4,7,8-PeCDF	1.961	4.321	3.098	5.253	2.78	917.3	0.528	0.568
1,2,3,4,7,8-HxCDF	2.288	3.123	2.534	4.97	2.435	156.7	0.84	0.844
1,2,3,6,7,8-HxCDF	2.579	2.43	2.552	6.897	2.917	53.94	1.42	1.592
2,3,4,6,7,8-HxCDF	2.361	1.847	2.714	4.128	2.047	87.39	0.695	0.692
1,2,3,7,8,9-HxCDF	0.187	0.316	0.854	0.62	0.227	62.95	0.216	0.241
1,2,3,4,6,7,8-HpCDF	8.821	8.271	10.329	29.886	10.963	53.68	6.149	6.317
1,2,3,4,7,8,9-HpCDF	0.727	2.046	0.98	4.022	0.968	28.01	0.625	0.483
OCDF	0.125	0.211	1.947	2.227	0.289	0.213	0.001	0.001
2,3,7,8-PCDDs	54.56	125.86	108.53	173.36	110.98	154.3	2.146	2.326
2,3,7,8-PCDFs	21.19	37.75	31.05	67.84	27.92	3859.3	13.22	13.57
17 PCDD/Fs	75.76	163.62	139.6	241.2	138.9	4013.7	15.36	15.89
TEQ, pg WHO-TEQ g^{-1}	2.19	4.44	3.71	8.67	2.88	604	0.82[a]	0.84[a]

[a] pg WHO-TEQ Nm^{-3}

Table 5 Concentration of PAH congeners in soil (in ng g^{-1}) and air samples (in ng Nm^{-3})

Compound	PEF[a]	S_1	S_2	S_3	S_4	S_5	S_{PCB}	A_1	A_2
Naphthalene		317	315.4	112.5	352.4	178.6	295.1	51.46	48.84
Acenaphthylene		20.02	34.93	87.52	84.01	76.13	35.3	29.2	41.81
Acenaphthene		11.51	35.09	75.11	92.34	86.97	35.01	2.52	2.616
Fluorene		1620	1485	1363	1580	1290	1360	16.86	19.92
Phenanthrene		73.6	60.2	112.5	81.2	103.5	55.3	7.56	8.801
Anthracene		772.9	574.9	350	361.1	355.7	540.1	48.92	59.14
Fluoranthene		169.7	410	387.5	260.7	297.1	395.1	16.23	18.6
Pyrene		133.2	34.9	87.5	53	95.8	30.7	11.01	12.19
Benz[a]anthracene	0.1	25.3	37.2	57.1	33.5	56.2	20.2	7.839	9.921
Chrysene	0.01	56	150.1	237.5	146	117.9	150	14.49	18.29
Benzo[b]fluoranthene	0.1	10.2	11.4	5.3	6.2	4.7	ND	1.452	1.964
Benzo[k]fluoranthene	0.1	N.D.	N.D.	6.2	N.D.	N.D.	4.7	2.554	3.296
Benzo[a]pyrene	1	53.6	294.9	287.5	201.1	467	285	6.107	8.031
Indeno[1,2,3-cd]pyrene	0.1	88.1	85	162.5	46	51	70	0.256	0.308
Dibenzo[a,h]anthracene	1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.826	2.299
Benzo[g,h,i]perylene		N.D.	3.4	N.D.	N.D.	N.D.	N.D.	2.363	2.919
Total 16 PAHs		3351	3532	3331	3297	3180	3276	220.7	258.9
Total carcinogenic PAHs		233	579	756	433	697	530	34.52	44.11
Total B[a]Peq, ng TEQ g^{-1}		66.5	309.9	313	211	479.4	296	4.73[b]	6.07[b]

N.D. not detected, the detection limit ranging from 2.1 to 10.2 ng g^{-1}

[a] Dioxin-like PAHs

[b] ng TEQ Nm^{-3}

points at the presence of other PCDD/F-sources at the site investigated.

Figure 4 shows the PCDD-isomer distribution. The fingerprint of the air samples is atypical for atmospheric PCDDs and cannot be explained by the S_{PCB} finger-print: the PCDDs of S_{PCB} are basically TCDD and PeCDD; however, the air samples show a rather even PCDD-distribution.

Soil samples S_1, S_5, S_3, and S_4 show similar fingerprints. For the highest contaminated sample S_2, the relative importance of TCDD and PeCDD is much larger, explaining both the higher value and the different fingerprint, influenced by an unidenti-fied local source of PCDD-pollution.

Another indicative parameter is the ratio of PCDDs to total PCDD/Fs. S_{PCB} and also the air samples stand out, with very low PCDD-contribution (7.4 % for S_{PCB}, 9.2 % for A_2, and 9.6 % for A_1). On the opposite, S_2 is the soil sample with the highest PCDD/Fs load except S_{PCB}, while the ratio of PCDDs to total PCDD/Fs is 68.5 %. The difference in ratio demon-strates that the PCDD/Fs do not originate from the general PCB-contamination.

Normally, PCDFs are much more important than PCDDs as a contaminant of PCBs. The fingerprint of the air samples is unusual (Fig. 5). Almost all soil samples show a different PCDF distribution suggesting several different origins of the

PCDFs. The sample S_2 comes closest to the PCDF-profile of PCB-contaminated soil, probably a chance factor. Moreover, the soil samples are highly loaded with PCDDs, ruling out that they derive from the PCB-contamination of the site.

Toxic 2,3,7,8-PCDD/Fs in ambient air and soil

PCDD and PCDF are important indicators, and they imply the presence of several sources. Table 4 presents the toxic dioxins concentration. The sum of the 17 toxic 2,3,7,8-substituted PCDD/Fs concentrations in air amounts to 15.36 and 15.89 pg m^{-3} (0.82 and 0.84 pg WHO-TEQ m^{-3}) for A_1 and A_2, respectively. PCDFs dominate with ratios of PCDF/PCDD of 6.16 (A_1) and 5.83 (A_2). Congeners 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8-PeCDF, and 1,2,3,6,7,8-HxCDF are major contributors, accounting for 39.3±0.2 %, 13.1±0.6 %, and 9.6±0.6 % of the 2,3,7,8-substituted PCDD/Fs. This dramatically contrasts with PCDFs from thermal processes and from ambient air samples in China (Chen et al. 2011), in which OCDD often plays a dominant role. The PCDD/Fs homologue distribution in air was similar to the typical MSWI emis-sions given by Brzuzy and Hites (1996) and to those from ferrous and non-ferrous metals production (Buekens et al. 2000).
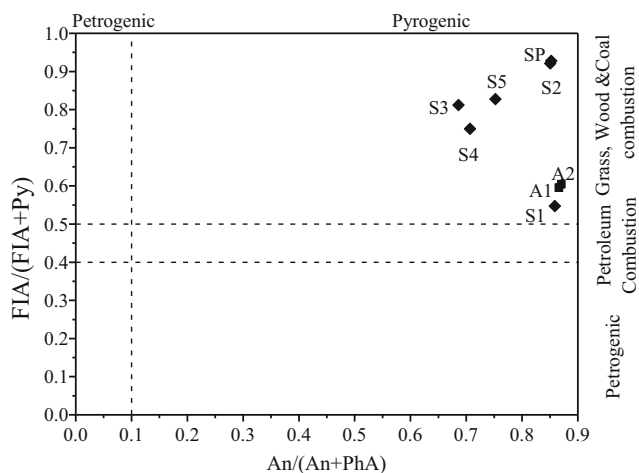
Fig. 6 PAHS cross plots for the ratios of An/(An+PhA) vs. FlA/(FlA+Py)

The 17 toxic PCDD/Fs congeners supply 2.19 to 8.67 pg WHO-TEQ g^{-1}, comparable with the topsoil in Taiwan (0.101 to 15.2 ng I-TEQ kg^{-1}) (Jou et al. 2007). OCDD is the main contributor with concentrations from 50.9 to 154 pg g^{-1}; these values are similar to the soil collected in the vicinity of a MSWI-plant in Spain (Nadal et al. 2002). PCDFs dominate the 2,3,7,8-substituted PCDD/Fs, with a ratio of PCDD/PCDF 0.04 for S_{PCB}. The congeners 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8-PeCDF are the main contributors, totally accounting for 85.1 % of 2,3,7,8-substituted PCDD/Fs. This can be attributed to transformation in soil from PCBs to PCDFs, or else to oxidation during former transformers service.

According to the international guidelines and regulations for agricultural soils summarized by Leung et al. (2007), these PCDD/Fs loadings are much lower than the US preliminary remediation goal of 1 ng TEQ g^{-1}.

However, this remediation level is extremely high, at the same level as undiluted MSWI fly ash.

PAHs in soil and ambient air

Table 5 shows the concentration of the 16 EPA PAHs and PAHs recognized as carcinogenic. Total PAHs in air are detected as 221 (A_1) and 259 ng Nm^{-3} (A_2), two times higher than those for centre London air (average of 118 ng g^{-1}) (Brown et al. 1996). The total 16 EPA PAHs detected in soil range closely, from 3180 to 3532 ng g^{-1} with average of 3338 ng g^{-1}. The PCB-contaminated sample S_{PCB} can be treated as a clue to contamination by PCBs and PCDD/Fs, yet not by PAHs: by chance, all soil samples (S_{PCB} included) show an almost identical 16 EPA PAH load, indicating that the PAHs in air and soil impossibly originate from PCB contaminated soil.

The PAHs levels in soil are much higher than those in Taizhou (330–790 ng g^{-1}) (Shen et al. 2009), Guangzhou (376 ng g^{-1}) (Chen et al. 2005), and Hong Kong (550 ng g^{-1}) (Zhang et al. 2006) and their levels are comparable to those of e-waste burning sites in Guangdong (average of 4940 ng g^{-1} for five samples) (Wang et al. 2012) and urban soils in Shanghai (average of 1970 ng g^{-1}) (Wang et al. 2013). However, they are lower than urban soils in Bergen, Norway (6780 ng g^{-1}) (Haugland et al. 2008) and Glasgow, Scotland (11,930 ng g^{-1}) (Morillo et al. 2007). The levels of carcinogenic PAHs are between 233 and 756 ng g^{-1}; benz[a]anthracene and chrysene always prevailed. Benzo[a]pyrene is an indicator of PAHs (Shen et al. 2010). The carcinogenic toxic equivalent quantity (TEQ) labeled as B[a]P$_{eq}$ is calculated using potency equivalence factors (Collins et al. 1998). The total B[a]P$_{eq}$ of PAHs range from 66.5 ng TEQ g^{-1} in S_4 to 479 ng TEQ g^{-1} in S_5.

Diagnostic ratios are useful indicators (Dickhut et al. 2000). In all samples, low molecular weight PAHs (LMW,

Fig. 7 Hierarchical dendrogram for soil samples using average linkage between groups and Pearson correlation as measure interval
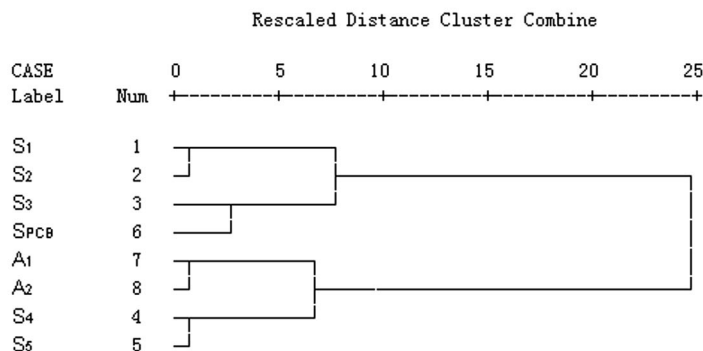
containing 2–3 rings) are represented more than high molecular weight PAHs (HMW, 4–6 rings). The LMW/HMW ratios range from 1.71 to 5.25 for soils and air samples with average of 2.74, showing predominantly petrogenic sources (Soclo et al. 2000; Rocher et al. 2004; Liu et al. 2009). The $A_n/(A_n + PhA)$ ratios range from 0.76 to 0.91 with an average of 0.83 (Fig. 6), indicating pyrogenic sources (Yunker et al. 2002; Zhang et al. 2004; Li et al. 2006). Furthermore, the FlA/(FlA+Py) ratios for soil samples range from 0.56 to 0.93 with average of 0.80; for air samples, it averages 0.60. These PAHs in air and soil may derive from combustion sources, such as hay, wood, and coal combustion.

Statistical analysis

Extensive data is available to try and check various hypotheses on the origins of the pollution of S_3. Statistical analysis may remain confined to the main classes of compounds, i.e., PCBs, dl-PCBs, PCDD/Fs, 2,3,7,8-PCDD/Fs, and PAHs. Extensive data analysis is conducted, yet the results are disappointing: there is very little correlation between PCB- and PCDD/F-data or PAHs. This inconsistency is probably due to the presence of multiple sources of pollution and the differences in environmental degradation levels. The best correlations are those between PCBs and dl-PCBs, PCDDs and PCDFs, and PAHs and carcinogenic PAHs.

As an example of statistical analysis, Fig. 7 shows a dendrogram for air and soil samples. Data on 209 PCB congeners of each sample are taken into account for cluster analysis: it shows similar trends as the chlorination degree of PCBs. Significant similarity is found between S_3 and S_{PCB}. Sample S_3, with the highest PCBs level in the investigated soils, may have been contaminated by direct spills of untreated soil.

Conclusions

This study assesses the environmental impacts from a thermal desorption plant, built for treating PCB-contaminated soil, after a first year of activity. Concentration levels, as well as fingerprints, are compared with the available data in China or abroad. The concentrations of PCDD/Fs and PAHs in the soil samples are similar to values in background sample. Similar concentrations are observed among the samples collected in upwind and downwind directions. One soil sampling point is polluted by PCBs, possibly originating from untreated contaminated soil stored in the thermal desorption plant.

Analysis of PCDD, PCDF, 2,3,7,8-PCDD/F loads and fingerprints makes clear that there are several and distinct PCDD/F sources and that the air is grossly dioxins-polluted, yet with an unusual fingerprint. Establishing blank values prior to the start-up of new plant is a safe method to establish the plant impact.

During the treatment of hazardous waste, strict control of all waste and all emissions is required and an environment impact assessment (EIA) study should be carried out before construction starts.

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