

POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN ATMOSPHERE COLLECTED FROM BACKGROUND AREA IN CHINA IN 2011-2012

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Introduction

The Stockholm Convention on POPs under the United Nations Environment Program (UNEP) identified a group of POPs termed the “dirty dozen” to be removed from the global environment. Article 16 of the Stockholm Convention on POPs requires the Conference of the Parties to perform an effectiveness evaluation starting four years after entry into force of the Convention and then at periodic intervals. To assist member countries with this task, UNEP Chemicals published a guidance document for the global monitoring of POPs (UNEP,2007). In this document, air is recommended for investigating POP levels in the environment. The guidance also suggests collect air samples from background with high volume air samplers with a size-selective inlet for collecting only those particles smaller than 10 micrometers diameter.

Monitoring of dioxins by this method maybe helpful to know the usually pollutions of POPs in background air and the long range transport of POPs. Only china followed this method in the first time global monitoring of POPs in background area. The aim of this study was to investigate the concentrations and profiles of background atmospheric PCDD/Fs in China. Samples were collected between 2011 and 2012 at 6 background sites in different provinces. This study implements the national monitoring plan for POPs, and provides data to assess regional and global environmental transport of POPs. Nonetheless, this study is also helpful for monitoring trends and making an assessment of the effectiveness of source reduction measures.

Material and Methods

Two samples and a field blank were collected from 6 background area (Site A and E located in remote, Site B, C loacted in a park of urban area, Site D loacted in suburb area and site F loated in

coastal area) in 2011-2012. So 12 samples were collected. Air samples were collected using high-volume samplers designed to collect both vapor and particle bound phases. A typical air sampling high volume sampler with a size-selective inlet for collecting only those particles smaller than 10 micrometers diameter was used for sample collection for more than 3 days. In these samplers, air is first drawn through a Whatman 102-mm binderless quartz micro-fiber filter where atmospheric particles of $<10\mu\text{m}$ in diameter are trapped. Air then passes through a polyurethane foam plug (PUF) used to remove the vapors from the air stream. The airflow rate was calibrated to $0.220\text{ m}^3/\text{min}$ prior to initiation of the sampling and checked at the conclusion of each sampling event. An average flow rate of $0.220\text{ m}^3/\text{min}$ was recorded during the period sampled. A total volume of air about 1000m^3 was processed. According to the US EPA method TO-9A (EPA, 1999a), GMFs were heated in a muffle at $450\text{ }^\circ\text{C}$ for 12 h before sampling and then stored in aluminum foil until use. Filters and PUFs were pre-treated to ensure to be free of contamination and volatilization losses. PUF plugs were rinsed with water and then Soxhlet extracted for 24 h with acetone, dried in a vacuum desiccator, and stored in solvent rinsed aluminum cans. After sampling, PUF plugs were resealed in their original containers while GMFs were placed in aluminum foil. Samples were then returned to the laboratory and stored at $-20\text{ }^\circ\text{C}$ until extraction.

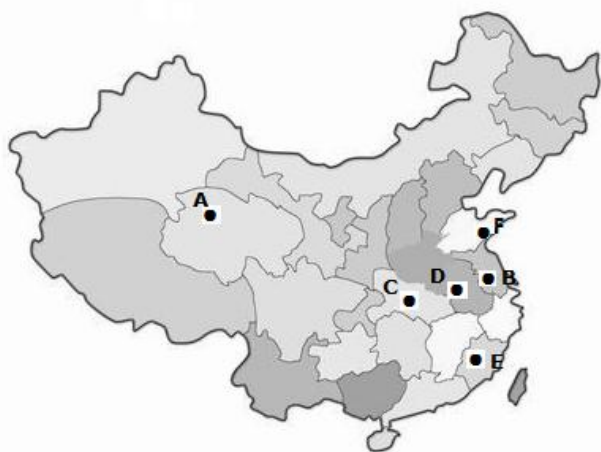


Figure.1 sampling location

The entire analytical process was performed according to US EPA method 1613B. The filter and PUF were combined for sample preparation and spiked with ^{13}C -labeled compound solution (Wellington Laboratories, Canada). The sample was then extracted with dichloromethane and

hexane (1:1, v/v) using accelerated solvent extraction (ASE 300, Dionex, USA). After concentration, an automated sample preparation system (Power-Prep™, Fluid Management System, USA) was employed for sample cleanup. This cleanup process included a series of three columns: multilayer acid/base/neutral (ABN) silica, basic alumina, and carbon columns. Then the fraction obtained was concentrated under a gentle stream of purified nitrogen and the solvent was changed to nonane (10 µL) in a minivial. For quantification of recovery, the sample extract was spiked with ¹³C-labeled internal standard (Wellington Laboratories, Canada) immediately prior to instrumental analysis. PCDD/Fs were analyzed by an Agilent 6890 gas chromatograph coupled with Micromass Autospec Ultima high-resolution mass spectrometry by tracing the M+, (M+2)+, or the most intensive ions of the isotope cluster. PCDD/F congeners were analyzed by a 60 m DB5 MS column (60 m * 0.25 mm i.d. * 0.25 µm). The carrier gas was helium at 1.2 mL/min. Injection volume was 1 µL in splitless mode with a 60 s splitless period. The MS was operated over 10 000 resolution with EI (35 eV), and data were obtained in the selected ion monitoring (SIM) mode. The instrument stability and relative response factor variance were obtained from the analysis of calibration standard solutions during each sample batch. For quality control, the retention times of the analytes in a sample had to be within 2 s of the retention times of the internal standards. Isotope ratios of the two monitored ions for each compound had to be within 15% of the theoretical chlorine values.

Several steps were taken to assure that the data collected in this study are of high quality including collection of field and lab blanks, duplicates from collocated samplers and breakthrough samples. Field and laboratory blanks were taken with each set of samples and processed in an identical manner to the samples. The method detection limit (MDL) is determined by the background amounts on these blanks rather than the instrumental detection limit. None of the lower chlorinated congeners were detected in the blanks. OCCD was the most prevalent congener in the blanks. However, their concentrations in the blanks corresponded to less than 8% of the concentrations found in the air samples. Concentrations of duplicates obtained at the collocated sites were in good agreement with each other. Of the 17 congeners, 2,3,7,8-TCDD was the most difficult to measure because the concentrations are extremely low. Recoveries of each chemical during clean-up procedure were calculated separately from surrogates and were also determined. The average recoveries for the ¹³C₁₂-PCDD/PCDFs were in the range of

56-122%.

Results and discussion

Table 1 summarizes the full data set of over 12 air samples collected from 6 background areas in 2011-2012. Total (gas +particle) concentrations of Σ PCDD/Fs ranged from 435-25210 fg/m³. The (gas +particle) concentrations of Σ 2,3,7,8-PCDD/Fs were 105 fg/m³ and 5490 fg/m³ in air samples. The highest Σ 2,3,7,8-PCDD/Fs concentration were found at location C and the lowest concentration were found at location. During the regular sampling periods, major contributors of atmospheric PCDD/Fs measured at background area include 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD.

Table 1 The concentrations of PCDD/Fs in air of background area

	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2	F1	F2
2378-TCDF	9	3	107	116	122	198	69	<2	<4	5	41	43
12378-PeCDF	7	2	186	152	209	247	101	154	<4	<3	48	44
23478-PeCDF	8	6	210	213	253	343	120	139	5	<2	77	57
123478-HxCDF	13	7	233	246	251	303	154	215	8	6	92	77
123678-HxCDF	10	6	188	209	218	292	132	167	5	5	77	73
234678-HxCDF	14	7	333	236	230	300	125	177	5	6	77	72
123789-HxCDF	<3	<1	59	71	60	78	38	50	<3	<1	19	20
1234678-HpCDF	56	30	744	786	661	910	471	732	27	24	239	270
1234789-HpCDF	7	4	98	116	89	117	64	88	3	4	43	30
OCDF	59	25	560	604	401	582	416	480	42	35	241	230
2378-TCDD	<4	<2	7	4	20	22	<6	5	<4	<1	<11	<6
12378-PeCDD	<3	<2	24	<7	29	55	20	17	<4	<1	<11	<11
123478-HxCDD	<2	<1	18	22	27	36	12	12	4	<1	<7	<7
123678-HxCDD	<2	<1	42	52	56	67	31	25	<1	2	12	16
123789-HxCDD	<2	<1	32	30	44	56	24	22	<2	3	12	13
1234678-HpCDD	15	5	202	234	266	341	119	129	5	12	69	64
OCDD	56	10	307	431	1145	1545	339	170	73	59	120	129
Totals Tetra-Furans	239	98	4507	3796	5108	7501	2355	3422	235	241	1684	1517
Totals Tetra-Dioxins	176	32	1541	1817	1645	2102	1052	893	119	117	908	710
Totals Penta-Furans	269	63	3375	3437	4032	5259	2018	2666	134	141	1218	1035
Totals Penta-Dioxins	143	24	564	1839	1045	1680	822	577	57	45	296	259
Totals Hexa-Furans	130	60	2346	2426	2148	2855	1352	1960	56	55	744	696
Totals Hexa-Dioxins	69	44	936	1125	1228	1423	539	552	26	32	294	328
Totals Hepta-Furans	95	51	1420	1281	1019	1382	738	1193	42	39	399	405
Totals Hepta-Dioxins	58	57	529	625	725	882	321	359	23	25	190	277
2378-PCDD/Fs	252	105	3349	3522	4077	5490	2234	2579	177	160	1164	1138
PCDD/Fs	1,293	465	16,085	17,381	18,495	25,210	9,952	12,273	807	788	6,093	5,586
WHO-TEQ	11.7	6.6	211.1	186.3	229.3	334.3	127.1	144.2	8.3	4.7	72.1	62.3

To normalize concentrations and the toxicity of the different PCDD and PCDF congeners, World

Health Organization (WHO) toxicity equivalent factors (WHO-TEFs) (Van den Berg et al., 2006) were used to calculate the WHO toxicity equivalent for the samples. The WHO-TEQ were calculated where the measurement results were below the limits of detection, their concentrations were taken as 0.5 of the value. The dioxin levels varied from 4.7 to 334.3fg WHO-TEQ/m³. The dioxins levels in site A and E in this study were in the same magnitude with those analyzed in previous study and site D were much higher than previous data (Wu et al., 2009). The highest levels were observed in site C located in a park of urban area and the lowest levels were observed in Site E located in a remote area which is far away from city. Among all PCDD/F congeners, 1,2,3,4,7,8,9-HpCDF, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were the major contributors of total WHO-TEQ.

Acknowledgements

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