MONITORING OF PCDD/Fs AND PCBs IN CONTAMINATED AIR WITH ACTIVE AND PASSIVE SAMPLING

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Abstract
Contaminated air, produced by burning PVC containing plastic floor and electronic scrap, was monitored with active sampling, using XAD-2, and passive sampling, applying semipermeable membrane devices (SPMDs) and fresh unpolluted spruce needles, for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs). It was found that the emitted polychlorinated dibenzofurans (PCDFs) were dominant compared to polychlorinated dibenzo-p-dioxins (PCDDs) collected from the contaminated air in all samples. However the PCDD/F and PCB homologue pattern were different between the active and passive samples. Triolein-containing SPMDs can absorb much more PCDD/Fs and PCBs than spruce needles when they were exposed to contaminated air simultaneously. The logarithm of the concentrations of PCDD/Fs and PCBs in SPMDs and in spruce needles at the same sampling time exhibited a significant linear correlation, with correlation coefficients larger than 0.86 for PCDD/Fs and 0.92 for PCBs. SPMDs and spruce needles are effective passive air samplers for PCDD/Fs and PCBs and can complement each other in passive air sampling. In addition the active emission sampling during the combustion process provides information of the total concentrations (gas and aerosol) of the flue gas.

Introduction
Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are mainly formed as by-products of manufacturing and combustion processes involving the use, production or disposal of chlorine or chlorine-derived chemicals, especially, combustion processes. They are dispersed through the atmosphere and finally precipitated into soil, water and vegetation by wet, dry deposition and diffusive processes[1]. Polychlorinated biphenyls (PCBs) have two sources: PCB mixtures manufactured in past industrial activities, and by-products in the process of combustion[2]. PCDD/Fs and PCBs have been implicated in causing a range of health problems in the immune, endocrine, nervous and reproductive system of humans and animals[3]. With the rapid growth of the electronic industry, a large quantity of electronic products becomes obsolete each year. Electronic waste (E-waste) becomes the most rapidly growing waste problem in the world[4]. The aim of this study was to monitor the profiles of PCDD/Fs and PCBs coming from PVC and E-waste combustion with active and passive sampling, and to compare the relationship between the two passive sampling methods.

Materials and Methods
Sampling. The combustion system consisted of a small domestic stove from which the exhaust gas was introduced into an exposure chamber. A mixture with the following proportion was used for combustion to produce exhaust gas containing PCDD/Fs and PCBs: wood (20 kg, dry weight), PVC (0.564 kg, plastic floor) and electronic scrap (0.564 kg, computer mainframe shell). The combustion process lasted for 8 h; afterwards the inlet fan was switched off. In order to keep the trees alive and avoid aerosol impact, the spruce trees and semi-permeable membrane devices (SPMDs) were placed into the exposure chamber 30 h after the incineration. Three isokinetic emissions samplings were performed in the stovepipe, 0.65 m above the combustion chamber, by the help of an automatic sampling system MRU 4000 (GSM, Neuss, Germany). The volumetric portions of the gas components were measured on-line with a gas analyzer TESTO 350 (Lenzkirch, Germany). The system was adjusted to an optimal gas flow rate of 1.5-2 m^3/h and each sampling lasted 30 min[6]. The cooled probe method was used to take samples and determine PCDD/PCDFs and PCBs according to DIN EN 1948[5]. Batteries of cartridges were connected to collect the PCDD/Fs and PCBs on the soot particles (pre-heated glass wool) and in the gaseous phase (XAD-2 resin).

SPMDs field blanks were transported to the sampling sites in clean air tight jars, but were not deployed and kept in the dark. Sampling took place after 19, 44, 116, 188 and 404 h for SPMDs and spruce needles.
Pretreatment and Analysis. The SPMD samples and 20 g of each spruce needle sample were extracted overnight by shaking in 100 mL of cyclohexane or 100 mL of n-hexane/dichloromethane (1:1, V:V), respectively, by use of a rotating shaking machine at 200 rpm. The XAD-2 samples were extracted for 24h with toluene in a Soxhlet apparatus. $^{13}C_{12}$-labeled internal standards of PCDD/Fs and PCBs were added to the solution or onto the cartridge at the beginning of all extractions. The clean up procedure and HRGC/HRMS analysis are described elsewhere[7].

Results and Discussion
The results of PCDD/Fs and WHO-TEQ for the active and passive samples are summarized in Table 1. PCB concentration and WHO-TEQ data detected in the samples are summarized in Table 2. The SPMDs values in Table 1 and 2 were the mean of two replicates. The XAD-2 values (active sampling) are the mean of three samples taken during time sections of the total combustion period.

Table 1: Concentrations of PCDD/Fs and WHO-TEQ in passive and active samples

Compounds	SPMDs (pg sample^{-1}) Mean values (n=2)					Spruce needles (pg g^{-1}, wet weight)					XAD-2 (pg m^{-3}) Mean values (n=3)
	19 h	44 h	116 h	188 h	404 h	19 h	44 h	116 h	188 h	404h	
2,3,7,8-TCDD	1.5	0.88	1.6	1.5	2.6	0.04	0.04	0.12	0.08	0.17	35501
1,2,3,7,8-PCDD	1.3	0.67	1.4	1.2	2.0	0.08	0.05	0.09	0.14	0.1	155000
1,2,3,4,7,8-HxCDD	1.4	1.1	0.98	1.0	1.1	0.06	0.06	0.07	0.07	0.07	88498
1,2,3,6,7,8-HxCDD	0.55	0.72	0.91	0.49	1.1	0.05	0.07	0.06	0.05	0.09	109291
1,2,3,7,8,9-HxCDD	0.98	0.61	0.80	0.35	0.84	0.06	0.04	n.d.	0.05	0.04	130560
1,2,3,4,6,7,8-HpCDD	5.1	4.4	5.7	4.5	7.1	0.43	0.5	0.46	0.4	0.44	348902
OCDD	11.9	9.1	12.1	9.5	12.6	0.94	1.00	0.96	0.84	0.86	247756
2,3,7,8-TCDF	4.2	3.0	6.2	6.7	18.3	0.31	0.35	0.82	1.1	1.7	243658
1,2,3,7,8-PCDF	1.7	1.5	2.6	2.5	5.1	0.15	0.15	0.29	0.27	0.53	717781
2,3,4,7,8-PCDF	2.8	2.3	2.8	2.2	4.2	0.15	0.14	0.23	0.4	0.51	467970
1,2,3,4,7,8-HxCDF	3.0	2.3	3.5	2.4	4.1	0.22	0.20	0.26	0.25	0.36	653807
1,2,3,6,7,8-HxCDF	3.1	2.5	3.6	2.7	4.5	0.15	0.18	0.30	0.28	0.36	683412
1,2,3,7,8,9-HxCDF	0.24	0.79	1.0	0.42	1.1	0.03	0.05	0.08	0.05	0.07	155729
2,3,4,6,7,8-HxCDF	3.0	2.8	3.4	2.3	4.1	0.20	0.16	0.23	0.25	0.25	390866
1,2,3,4,6,7,8-HpCDF	8.9	7.2	9.7	8.1	11.4	0.70	0.83	0.90	0.83	0.81	891596
1,2,3,4,7,8,9-HpCDF	0.85	0.95	2.2	1.2	1.3	0.11	0.14	0.10	0.13	0.19	103437
OCDF	6.9	6.4	7.9	6.6	9.0	0.52	0.68	0.50	0.67	0.63	229219
WHO-TEQ	6.1	4.3	6.7	5.7	10.7	0.3	0.3	0.5	0.7	0.9	719445

n.d.: not detected.

Generally, the concentrations of the PCDF congeners were higher than the PCDD congeners within the same degree of chlorination, except for OCDD and OCDF, and the total amount of PCDDs was lower than that of PCDFs in all samples. OCDD, OCDF, 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were the main contributors in all the congener profiles of the passive samples. 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8-PCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF, OCDF, OCDD and 1,2,3,4,6,7,8-HpCDD were the main contributors in all the congener profiles of the active samples.
The composition of PCBs was similar in SPMDs and spruce needles samples, except PCB#157, PCB#189 in the 19 h sampling and PCB#169 at all the sampling times. PCB#52, PCB#28, PCB#101, PCB#153, PCB#138 and PCB#118 were the main contributors in all congener profiles of the passive samples. PCB#101, PCB#77, PCB#138, PCB#81, PCB#118, PCB#156 and PCB#105 were the main contributors in all congener profiles of the active samples. Although the concentrations of PCB#157, PCB#189 and PCB#169 were quite low in the passive samples, there were not as low in the active samples.

The main contributors in the congener profiles were different between active and passive samples, because the active sampling not only sampled the gaseous phase but also particles, whereas the passive sampling mainly sampled the gaseous phase. A correlation between the logarithm of the concentrations of PCDD/Fs and PCBs in SPMDs (C_{SPMDs}) and that in spruce needles ($C_{spuce\ needles}$) of the same sampling period was observed when applying equation 1. PCB#169 was not included in all correlation analysis; PCB# 157 and PCB#189 were not included in the 19h sampling for PCBs, because the concentrations of these compounds were quite low and associated thereby with high variances.

$$\log C_{SPMDs} = a \log C_{spruce\ needles} + b \quad (1)$$

The correlation between the logarithm of the concentrations of PCDD/Fs and PCBs in SPMDs and that in spruce needles at the same sampling times was quite good, with being better for the PCBs than for the PCDD/Fs at trace levels. The correlation coefficients were higher than 0.86 for PCDD/Fs and 0.92 for PCBs. SPMDs and spruce needles are effective passive air samplers for PCDD/Fs and PCBs and can complement each other in passive air sampling.

Table 2: Concentrations of PCBs and WHO-TEQ in passive and active samples

Compounds	SPMDs (pg sample^{-1}) Mean values (n=2)					Spruce needles (pg g^{-1}, wet weight)					XAD-2 (pg m^{-3}) Mean values (n=3)
	19 h	44 h	116 h	188 h	404 h	19 h	44 h	116 h	188 h	404h	
PCB #28	1030	1190	1850	2290	4700	69.8	87.6	104	92.2	104	144793
PCB #52	1750	2120	3730	4860	10160	126	128	170	155	168	13072
PCB #101	1950	1870	2400	2580	4530	128	135	154	165	167	1238252
PCB #138	1070	935	1010	952	1150	55.2	58.3	53.1	53.6	50.3	560572
PCB #153	1550	1400	1420	1420	1680	77.8	68.9	71.4	63.1	56.6	147184
PCB #180	441	401	408	402	482	27.7	18.7	17.7	19.4	17.4	87617
PCB #77	135	147	269	275	627	15.7	15	24.9	30.4	41.7	940838
PCB #81	25.3	42.2	116	97.0	249	2.5	2.6	8.2	10.6	16.6	451356
PCB #126	9.5	13.6	20.8	20.3	50.5	1.1	1.3	2.5	3	5	397556
PCB #169	4.0	3.9.	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	0.40	0.52	110445
PCB #105	206	183	224	225	351	27.8	29.1	28.2	30.5	29.9	239647
PCB #114	26.7	28.4	41.9	46.0	96.7	3.5	2.7	3.8	4.3	5	166204
PCB #118	600	538	626	606	833	69.4	67.4	62.9	67	62.6	336672
PCB #123	29.9	45.0	29.9	50.6	92.3	2.4	2.2	2.9	2.3	3.9	74819
PCB #156	105	90.0	101	102	127	7.0	5.7	5.4	6.3	2.1	239229
PCB #157	13.7	13.7	16.0	15.8	27.1	n.d.	1.4	1.3	1.6	1.9	122176
PCB #167	52.7	44.6	49.3	52.6	62.3	3.9	2.9	2.5	3.1	3.4	102224
PCB #189	9.6	10.3	10.3	9.4	14	n.d.	0.56	0.77	0.57	0.72	123376
WHO-TEQ	1.2	1.6	2.3	2.3	5.4	0.1	0.2	0.3	0.3	0.5	41342

n.d.: not detected.

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