MONITORING ATMOSPHERIC LEVELS OF PCDD/Fs, PCBs AND PCNs USING ACTIVE AND PASSIVE AIR SAMPLERS

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Introduction

For atmospheric monitoring of POPs, high volume air samplers are currently used as conventional sampling techniques. However, the important cost of the sampling equipment, as well as the requirement of a pump and source electricity are some disadvantages of this method. Moreover, only momentary concentrations can be known. Therefore, it is necessary to collect many samples in order to get real information of POP levels in air. On the other hand, meteorological variations, as well as punctual emissions, can modify POP air concentrations in short-time periods. Passive samplers are useful sampling tools for POPs making possible to integrate ambient concentrations over various weeks/months. Among the different types of passive samplers, polyurethane foam (PUF) disks are especially attractive because of their low cost and simple manipulation. These devices allow semi-quantitative comparisons of POP levels.[1] The aim of this study was to assess the air concentrations of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in two zones of Barcelona, Spain, one of them near a municipal solid waste incinerator (MSWI) and with a intense traffic. Another goal was to evaluate the use of passive samplers as a complementary tool to monitor the levels of these POPs in different areas.

Materials and Methods

In March/April 2005, PCDD/Fs PCBs and PCNs were monitored in ambient air at four sampling locations in Barcelona. Three sites were urban/industrial (Nos. 1, 2 and 3), while the remaining was a semi rural area (Site 4). Ambient air samples were collected using high volume active samplers (Tisch TE-1000) complying with US EPA TO-9. The airflow was calibrated to 0.225 m^3/min. For PCDD/Fs, the total volume of air sampled ranged from 600 to 700 m^3 for a sampling duration of aprox. 55 hr. For PCBs and PCNs, the sampling period was 24 hr. Moreover, 4 PUF passive samplers were deployed at the same sampling points during three months (March-June 2005). Passive samplers consisted on a PUF disk (14 cm diameter, 1.35 cm thick) contained within a stainless steel shelter.

The levels of PCDD/Fs, PCBs and PCNs were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) following the VDI 3499 method. The complete samples (one filter and two PUFs plugs) were spiked with $^{13}C_{12}$ isotopic labelled internal standards. The filter and PUF plugs were then ASE extracted with toluene three times. The system was purged during 120 sec. The volume of the sample extract was reduced to about 1 ml by means of a Zymark-Turbovap. The extract was subjected to an acid/base clean-up procedure followed by micro columns of silica gel and alumina. The dioxin containing fraction (or that corresponding to PCB/PCN) was concentrated near to dryness by a gentle stream of dry nitrogen. The final extract was spiked with the isotopic labelled internal standard and then analysed by HRGC/HRMS. The spectrometer was equipped with a fused silica capillary column DB-dioxin (30 m x 0.25 mm x 0.15 μm) for PCDD/Fs analysis. For PCB and PCN analysis a capillary column DB MS (30 m x 0.25 mm x 0.25μm) was used. The HRMS operated under positive EI conditions (35-45 eV) and selected ion monitoring (SIM) mode at resolving power range from 6.000 to 10.000 amu. The mass range available was 0-2.000 amu. For total I-TEQ calculations, for those congeners below the detection limit the respective concentration was assumed to be one-half of the detection limit.

Results and Discussion

Table 1 shows the levels of PCDD/Fs, PCBs and PCNs of the Hi-vol air samples. Total PCDD/F I-TEQ were 24 and 13 fg I-TEQ/m^3 in the urban/industrial (range: 20.6-27.7 fg I-TEQ/m^3) and the background sites, respectively. These levels were similar or even lower than those found in previous studies of various suburban/industrial sites of Catalonia.[2] The main contributor to total I-TEQ was 2,3,4,7,8-PeCDF, accounting for 35-39%. The most abundant congener was OCDD contributing with 47% to the total concentration (28-61%), followed by 1,2,3,4,6,7,8-HpCDD with 13% (11-17%), and OCDF with 10% (9-11%). A pattern of decreasing PCDF concentrations with increasing chlorination level, and increasing PCDD concentrations with increasing chlorination level were noted. The sum of the 7 ICES-PCB congeners was higher at the industrial site (mean value 170 pg/m^3) than at the background site (127 pg/m^3). In this study, PCB 180 was found under its detection limit in all samples, while PCB 118 was only detected at site 3 (13 pg/m^3). PCB 28 was the most abundant congener in both areas. Decreasing PCB concentrations with rising chlorination degree was observed in the urban/industrial sites. In contrast, higher concentrations of most heavy PCBs (138 and 153) were found at the background site. Regarding background PCN levels, these were lower than those found at the urban/industrial sites (2.4 and 3.8 pg/m^3, respectively). The most abundant homologues were the tri- and tetraCNs, while hexa- to octaCNs presented value under their respective LOD.

In order to compare active and passive sampling, the levels of PCDD/Fs, as well as PCB and PCNs sequestered amounts in the 4 passive air samplers are summarized in Table 2. With respect to PCDD/Fs, as expected, the background site showed lower concentrations (2.30 pg I-TEQ) than the industrial area (mean value 3.63 pg I-TEQ). Total tetra- and pentaDFs and tetraCDDs were the main contributors to total PCDD/Fs. Light congeners are predominant in the gas phase. In turn, PCDDs tend to be more associated with the particulate phase than the equivalent PCDF homologue groups. Among PCDD individual congeners, OCDD was the predominant (48-75% of the total PCDD/Fs, mean value 60%), followed by 1,2,3,4,6,7,8-HpCDD (7-11%, mean value 10%). With respect to furans, OCDF contributed with 3-5% of the total 2,3,7,8-substituted congeners (mean value 4%). These results show that most compounds associated with particles are also sequestered by the samplers. Similar results were also observed in studies where PUF passive samplers were used.[3] In relation to PCBs, it is not possible to report results from site 3 because of analytical problems. PCB 28 was the most abundant congener in the three sites. Sites 1 and 2 showed decreasing PCB concentrations with increasing number of chlorine atoms. In the background site, as also observed in the active sampling, hexa- and hepta-CBs (Nos. 138, 153 and 180) were found in higher quantities than tetraCBs (52 and 101). These findings are in agreement with those concerning active samples and they reflect a punctual source of the heaviest congeners in site 4. With respect to PCNs, in site 2 only sum of tri- and tetraCNs could be detected. These results reflect the extremely low PCN concentrations in ambient air. The atmospheric levels of PCNs were probably too low to allow collection of a sufficient amount to be detected in a 90-day-sampling. Therefore, it would be necessary a longer sampling period in order to detect PCNs in ambient air. Furthermore, it would be suitable to achieve lower analytical detection limits.

In order to study PUF passive samplers as a complementary tool for PCDD/F, PCB and PCN monitoring, sampling rates were calculated in accordance with passive samplers theory, where it has been demonstrated that sampling rates of chemicals with $K_{OA} > 10^{8.5}$ remain linear (and defined by the mass transfer coefficient) over 100 days at few m^3/day.[4] Under these conditions of linearity, the sampling rates for the target compounds can be calculated according the following simple expression:

$$R_{cal} = N_{PS}/ C_V t$$

where R_{cal} is the sampling rate (m^3/day) measured at the calibration site, N_{PS} is the amount of compound accumulated in the sampler (ng), C_V is the concentration of that compound in the vapour phase (ng/m^3) and t is the time of exposure (days). Subsequently, calculated rates are used to estimate air concentrations using the same devices. Table 3 shows the uptake/rates for each congener. As expected, high substituted PCDD/F congeners showed very high rates when only the gas phase was considered. Otherwise, when total air concentrations were taken into account the rates obtained (0.7-5.1m^3/day) were lower than those obtained for most gas phase congeners (tetra and penta) (1.7-7.2 m^3/day). Data for hepta- and octa- congeners were rather heterogeneous,

Table 1. Levels of PCDD/Fs (fg/m^3), PCBs and PCNs (pg/m^3) determined by Hi-vol air sampling in Barcelona (March-April 2005).

	Urban/Industrial			Background
	S1	S2	S3	S4
2.3.7.8-TCDF	12.9	14.8	21.5	11.0
1.2.3.7.8-PeCDF	10.6	13.3	16.8	9.1
2.3.4.7.8-PeCDF	17.2	14.9	21.8	9.8
1.2.3.4.7.8-HxCDF	17	14.2	19.5	7.6
1.2.3.6.7.8-HxCDF	19.7	17.4	24.4	10.6
2.3.4.6.7.8-HxCDF	1.9	1.8	1.6	1.5
1.2.3.7.8.9-HxCDF	18.8	15.3	23.4	9.7
1.2.3.4.6.7.8-HpCDF	64.2	52.4	69.5	22.7
1.2.3.4.7.8.9-HpCDF	5.7	6.6	7.9	4.5
OCDF	108.3	66.1	77.4	21.6
2.3.7.8-TCDD	<1.5	<1.5	<1.8	<1.5
1.2.3.7.8-PeCDD	3.6	2.7	3.5	1.5
1.2.3.4.7.8-HxCDD	3.7	2.8	3.5	1.5
1.2.3.6.7.8-HxCDD	12.1	11.9	11.8	4.4
1.2.3.4.7.8-HxCDD	9.1	7.5	7.6	2.1
1.2.3.4.6.7.8-HpCDD	149.6	97.3	92.9	30
OCDD	705.9	234.5	242	79.8
pg I-TEQ/m^3	24.3	20.6	27.7	12.5
PCB 28	66	60	56	28
PCB 52	42	36	26	16
PCB 101	24	22	30	22
PCB 118	<10	<10	13	<10
PCB 138	13	16	24	25
PCB 153	14	18	24	26
PCB 180	<10	<10	<10	<10
Σ ICES PCB	169	158	178	127
Sum of Di-CNs	7	3.3	3.4	1.6
Sum of Tri-CNS	17.5	10.9	12.3	6.8
Sum of Tetra-CNs	21.5	<1.7	7.6	4.3
Sum of Penta-CNs	1.6	<1.7	<1.6	1.6
Sum of Hexa-CNs	<1.6	<1.7	<1.6	<1.6
Sum of Hepta-CNs	<1.6	<1.7	<1.6	<1.6
Octa-CNS	<1.6	<1.7	<1.6	<1.6
Σ PCN	2.4	5.9	3.2	2.4

Table 2. Levels of PCDD/Fs. PCBs and PCNs determined by sequestered passive samplers (pg/PUF) in Barcelona (March-June 2005).

	Urban/Industrial			Background
	S1	S2	S3	S4
Sampling period (day)	97	91	97	97
2.3.7.8-TCDF	4.1	2.8	2.1	<2.7*
1.2.3.7.8-PeCDF	2.7	2.6	2.7	0.9
2.3.4.7.8-PeCDF	2.4	2.9	3.3	1.8
1.2.3.4.7.8-HxCDF	3.6	2.2	2.4	2.4
1.2.3.6.7.8-HxCDF	3.4	2.6	3.6	1.8
2.3.4.6.7.8-HxCDF	<0.5	<0.5	<0.6	<0.9
1.2.3.7.8.9-HxCDF	1.8	1.3	0.9	<0.9
1.2.3.4.6.7.8-HpCDF	10.0	7.5	5.4	4.2
1.2.3.4.7.8.9-HpCDF	0.7	<1.0	<1.5	<0.9
OCDF	10.5	3.3	3.3	<6.0*
2.3.7.8-TCDD	<0.5	<0.5	<0.6	<0.6
1.2.3.7.8-PeCDD	0.5	<0.5	0.9	<0.6
1.2.3.4.7.8-HxCDD	0.5	<0.5	<0.6	<0.9
1.2.3.6.7.8-HxCDD	1.5	<0.5	<0.6	<0.9
1.2.3.4.7.8-HxCDD	1.1	<0.5	<0.6	<0.9
1.2.3.4.6.7.8-HpCDD	23.3	6.8	7.2	4.2
OCDD	195.0	32.2	69.9	32.7
pg I-TEQ	4.01	3.13	3.76	2.30
PCB 28	16.4	17.2	ND	12.3
PCB 52	9.6	11.0	ND	7.5
PCB 101	7.3	8.6	ND	6.9
PCB 118	2.0	3.0	ND	<3.0
PCB 138	4.6	6.1	ND	8.4
PCB 152	5.0	6.7	ND	9.9
PCB 180	2.0	2.6	ND	8.4
ΣICES PCB	46.9	55.2	-	54.9
Sum of Di-CNs	<1.0	<1.0	ND	<1.0
Sum of Tri-CNS	<1.0	1.70	ND	1.20
Sum of Tetra-CNs	2.60	4.10	ND	<1.0
Sum of Penta-CNs	<1.0	<1.0	ND	<1.0
Sum of Hexa-CNs	<1.0	<1.0	ND	<1.0
Sum of Hepta-CNs	<1.0	<1.0	ND	<1.0
Octa-CNS	<1.0	<1.0	ND	<1.0
Σ PCN	5.6	8.3	-	4.2

ND: Not detected
*increased LOD because of matrix interferences

which was probably due to the particle size in each site. The finer the particle was, the easier it was probably sorbed by the samplers. In general terms, rates obtained for tetra- and penta- substituted congeners were homogeneous with a mean value of 3.5 m^3/day. These results were consistent with previous studies where other semipermeable membrane devices were found efficient samplers for vapour phase species with good reproducibility between samplers, but with a poorer reproducibility for particle associated species.[5] Mean of all congeners would mean 3.1 m^3/day. PCB uptake/rates ranged from 1.6 to 4.9 m^3/day. These results were similar to those found previously in indoor conditions (3-4 m^3/day).[4] An uptake rate of 3-4 m^3/day has been used in field-studies to assess PCB levels.[5]

Table 3. Sampling rates (m^3/day) for each PUF passive sampler and mean values.

	PS 1	PS 2	PS 3	PS 4	Mean
Congeners					
2,3,7,8-TCDF	3.4	2.5	1.7	-	2.5
1,2,3,7,8-PeCDF	3.9	4.0	3.9	2.0	3.5
2,3,4,7,8-PeCDF	3.0	3.9	4.2	4.2	3.8
1,2,3,4,7,8-HxCDF	9.4 (2.2)[a]	6.1 (1.4)[a]	6.2(1.5)[a]	13.9 (3.3)[a]	8.9 (2.1)[a]
1,2,3,6,7,8-HxCDF	7.6 (1.7)[a]	6.2 (1.4)[a]	8.0 (1.8)[a]	7.7 (1.8)[a]	7.4 (1.7)[a]
2,3,4,6,7,8-HxCDF	-	-	-	-	-
1,2,3,7,8,9-HxCDF	1.5	1.1	0.7	-	1.1
1,2,3,4,6,7,8-HpCDF	10.5 (1.7)[a]	8.4 (1.3)[a]	5.7 (0.9)[a]	12.0 (1.9)[a]	9.1 (1.5)[a]
1,2,3,4,7,8,9-HpCDF	11.6 (1.3)[a]	-	-	-	1.3
OCDF	40.6 (1.3[a])	13.6 (0.4)[a]	12.8(0.4)[a]		
2,3,7,8-TCDD	-	-	-	-	-
1,2,3,7,8-PeCDD	4.0	-	7.2	-	5.6
1,2,3,4,7,8-HxCDD	9.7 (1.5)[a]	-	-	-	9.7 (1.5)[a]
1,2,3,6,7,8-HxCDD	8.3 (1.3)[a]	-	-	-	8.3 (1.3)[a]
1,2,3,4,7,8-HxCDD	9.8 (1.4)[a]	-	-	-	9.8 (1.4)[a]
1,2,3,4,6,7,8-HpCDD	24.2 (2.1)[a]	7.5 (0.6)[a]	7.5 (0.7)[a]	16.4 (1.4)[a]	13.9 (1.2)[a]
OCDD	224.8 (5.1)[a]	39.6 (0.8)[a]	80.6 (1.8)[a]	186.2 (4.2)[a]	132.8 (2.9)[a]
PCB 28	2.8	3.1	-	4.5	2.6
PCB 52	2.9	3.5	-	4.9	2.8
PCB 101	3.8	4.8	-	4.2	3.2
PCB 118	1.6	2.6	-	-	2.1
PCB 138	3.4	4.8	-	4.4	3.2
PCB 152	3.4	4.9	-	4.9	3.3
PCB 180	-	-	-	-	-

[a]Sampling rate calculated using total air concentration (c_v+c_p).

In summary, it can be concluded that the urban/industrial areas under study showed low air levels of the POPs analyzed. It was also previously observed in soils and herbage of the same areas.[6] In relation to PUF disks, these devices allowed to establish differences among zone for POP levels.

Acknowledgments

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