PERSISTENT ORGANIC POLLUTANTS (PCDD/Fs, PCBs AND PBDEs) IN AMBIENT AIR FROM BARCELONA (CATALONIA, SPAIN). SEASONAL VARIATION

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Introduction

Barcelona is a city located in central coast of Catalonia (Spain) with more than 1.5 million people living there. The city spreads out from the Mediterranean Sea to Collserola Mountains for 100 km^2. The surrounding area is highly industrialized and, additionally, the impact of traffic is very high. Our study was focused on the characterization of POPs (PCDD/Fs, DL-PCBs, NDL-PCBs and PBDEs), both in the vapor and the particulate phase. Since some authors have detected seasonal influence on the levels of these compounds in air[1-3], the study considered this factor and, also, the possible influence of climatological conditions.

Materials and methods

Sampling

The sampling station was located in the upper part of Barcelona, in the neighborhood of Sarrià. Two main roads (the road that crosses Collserola Mountains starting in Sarrià, and the road that surrounds Barcelona) were close to the sampling point. Sampling was carried out between October 2009 and August 2010. Sampling was performed with a high volume sampler (MCV, Barcelona, Spain). Particle phase was retained by a quartz-fiber filter, followed by a polyurethane foam (PUF) block for vapor phase absorption. Table 1 shows sample codes and some of their characteristics.

Table 1. Codes and characteristics of samples analysed.

Code	Date	Sampling time (hours)	Volume sampled (m^3)	Comments
A1	19/10/09	11	751	---
A2	10/11/09	24	1564	---
A3	02/12/09	24	1644	---
A4	21/01/10	24	1645	---
A5	02/02/10	24	1633	---
A6n	10/02/10	12	859	Night sampling
A7n	24/02/10	13	921	Night sampling
A7d	25/02/10	10	743	Day sampling
A8n	15/03/10	13	849	Night sampling
A8d	16/03/10	10	653	Day sampling
A9	18/05/10	24	1742	---
A10	01/07/10	24	1605	---
A11	16/08/10	24	1639	---

Analysis

Following compounds were analysed in the samples: NDL-PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180), DL-PCBs (PCB 81, PCB 77, PCB 123, PCB 118, PCB 114, PCB 105, PCB 126, PCB 167, PCB 156, PCB 157, PCB 169, PCB 189), PCDD/Fs (2,3,7,8-chlorosubstituted congeners) and PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209).

Analytical procedure was based on international methods (US EPA 1613, US EPA 1614, UNE-EN 1948) and consisted of following steps: (1) pre-treatment of different parts of the sample, (2) spiking with $^{13}C_{12}$-labelled extraction standards (Wellington Laboratories, Canada), (3) Soxhlet extraction with toluene for 48 h (4) extract clean-up in multilayer silica column (5) fractionation of the extract by HPLC equipped with a pyrenyl column[4] (6) concentration of each fraction under nitrogen stream and addition of $^{13}C_{12}$-labelled recovery standards (7) instrumental determination of PCDD/F, DL-PCB, NDL-PCB and PBDEs by HRGC-HRMS and quantitation by the isotopic dilution method. For each sample, filter and PUF were analysed separately in order to evaluate pollutant concentrations in particulate and vapour phase. Particulate matter was measured gravimetrically according to the method UNE-EN 12341. In addition, climatological conditions were measured by an Advanced Weather Station Model WMR100 (Oregon Scientific) located in the sampling point.

Results and discussion

Total concentrations

Table 2 shows the concentrations (average, minimum and maximum) of NDL-PCBs, DL-PCBs, PCDD/Fs and PBDEs (with and without BDE 209) obtained in the samples. Each concentration is the sum of the different congeners analyzed and it is expressed as upperbound.

Table 2. Concentration of POPs in the samples analyzed.

Pollutants	Average	Minimum	Maximum
NDL-PCB (pg/m^3)	42.9	23.3	88.3
DL-PCB (pg/m^3)	5.55	2.00	11.5
TEQ*-DL-PCB (fg TEQ/m^3)	2.94	1.67	6.30
PCDD/F (pg/m^3)	0.63	0.13	3.30
TEQ*-PCDD/F (fg TEQ/m^3)	27.4	13.7	48.8
PBDE (w/o 209) (pg/m^3)	3.41	1.50	5.80
PBDE (w 209) (pg/m^3)	21.9	6.90	47.8

**TEQ concentration has been calculated by using 2005 TEF*[5]

As it is usual in air samples, concentrations of NDL-PCBs and PBDEs are higher than those of PCDD/Fs. In general, concentrations of POPs detected in the samples are similar or lower than those found by other authors in areas close to Barcelona [3, 6-7] or in other cities around the world [8-12].

Seasonal variation

Graphics in Figure 1 show the seasonal variation for the concentrations of the pollutants studied in the vapor phase (PUF), particulate phase (filter) and total concentration.

NDL-PCB and DL-PCB were found mainly in the vapor phase, even in winter. However, if individual congeners are studied, some differences are observed. While less chlorinated congeners (PCB 28, PCB 52, PCB 77) were found in the vapor phase (more than 75%) in all the samples, other congeners with more chlorine atoms (PCB 180, PCB 189) showed important variations in the proportion detected in the PUF in the different seasons: from 30-50% in winter to 80-90 % in summer. Total concentrations of NDL-PCB and DL-PCB increased during the summer, probably due to the evaporation of those pollutants from terrestrial environment at higher temperatures.

For PCDD/F, an opposite trend was observed: the concentration in the vapor phase was, proportionally, very low compared to particulate phase. In addition, while the PUF concentration remained almost constant during the year, the PCDD/F concentration in particulate showed important variations. They can be explained by changes in the sources (e.g. domestic heating in winter, differences between traffic load in winter and summer), but also by particle deposition due to rain (Figure 2) or degradation due to sun UV-light. Some differences are also observed in the congener profile between samples collected in the winter and those sampled in the summer.

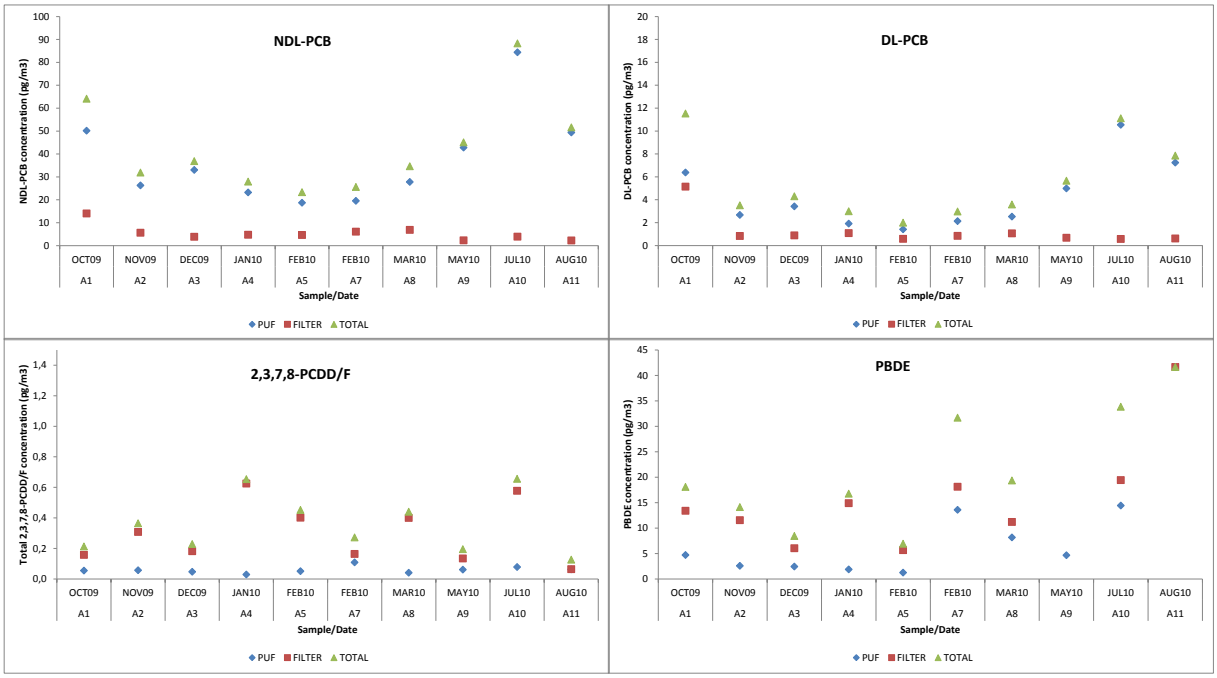

Figure 1. Seasonal variation of POP concentration in vapor and particle phase.

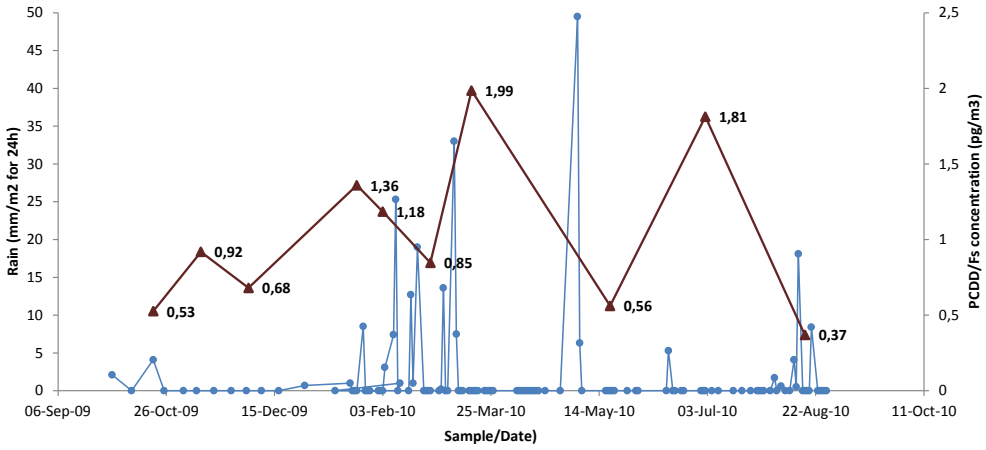

Figure 2. Rain deposition (mm/m^2 for 24h) and PCDD/F concentration during the studied period.

For total PBDE, concentration in particle phase was higher than in vapor phase, due to the presence of BDE 209 (most predominant congener) mainly in particle phase. For the other congeners, at much lower levels of concentration, the proportion detected in PUF increased in summer months until 70-80%. Total PBDE concentration increased from winter to summer, with levels of 47.8 pg/m^3 in August sample.

Daily variations

Differences in concentration between day and night were evaluated by collecting 12-h samples. Although the variability between samples made difficult to state a conclusion, for PCBs (NDL and DL), day samples seemed to present higher concentrations, while for PCDD/Fs and PBDEs concentrations seemed to be higher during the night (Figure 3).

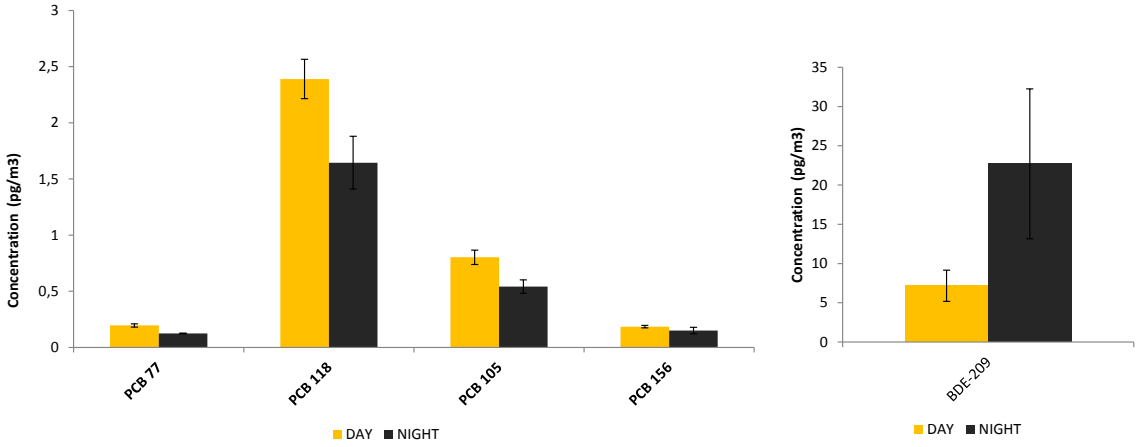

Figure 3. Concentration of PCB 77, PCB 118, PCB 105, PCB 156 and BDE 209 in day and night samples.

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