PCDD/Fs, DIOXIN-LIKE PCBs AND PBDEs IN AIR. PRELIMINARY RESULTS OF THE SPANISH MONITORING PROGRAM ON POPs UNDER THE STOCKHOLM CONVENTION AFTER FOUR YEARS MONITORING

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Introduction

The Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) is a global treaty to protect human health and the environment from POPs. These highly toxic chemicals remain in the environment for long periods, and are bioaccumulative and ubiquitous since they undergo long-rate transport. The SC, which was adopted in 2001 and entered into force in 2004, requires Parties to take measures to eliminate or reduce the release of POPs into the environment. Spain, as a member State, ratified it in 2004[1].

The main objective of the Spanish Monitoring Programme is to establish a national monitoring network able to characterize the current status and temporal trends of POPs and in turn to evaluate the effectiveness of measures taken to reduce POP emissions[2]. Initial work has focused on POPs monitoring in air based on PAS (Passive Air Sampling) in selected points across the national territory covering remote and urban sites. The program by now is using existing sampling networks in Spain (e.g. EMEP) by means of a very close and successful collaboration with the Spanish Agency of Meteorology (AEMET). The implemented monitoring program intends to become a long-term and stable program analyzing the occurrence of POPs in air and soil samples as well as seeking to expand into other environmental matrices.

Polyurethane foam (PUF) disks as passive air samplers allow for semi-quantitative evaluation of atmospheric POP levels. Some advantages like their low cost and easy manipulation explain their common use today in air monitoring studies[3]. Since 2008 and following the recommendations of the Global Monitoring Plan (GMP), Spain implemented a permanent program of air monitoring based on PAS. In this study, air levels of PCDD/Fs, dioxin-like PCBs and PBDEs during the first four years of monitoring (2008-2012) in urban and rural locations throughout the Spanish national territory are presented.

Material and Methods

Sampling

PUF disks (14 cm diameter, 1.35 cm thick) were first pre-cleaned by Soxhlet extraction with solvents of high purity. To avoid contamination, they were transported in glass containers and assembled in stainless steel domed chambers at the sampling sites. Six remote/rural locations and four urban sites were chosen as sampling points. At each sampling point, four PUFs were deployed and collected every 3 months around each season's change. After collection, three of them were pooled and used for PCDD/Fs and dioxin-like PCBs determination. The fourth one was used for PBDE analysis.

Analytical Procedure

Samples were Soxhlet extracted during 24 h with petroleum ether. Further cleanup was performed by using acidic and basic silica gel multilayer columns. The analysis of all the 17 2,3,7,8-substituted PCDD/Fs and dioxin-like PCBs was performed by gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) on a Trace GC ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy) coupled to a high resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany). Positive electron ionization

(EI+) was used operating in selected ion monitoring mode (SIM) mode at 10,000 resolving power. Quantification was carried out by the isotopic dilution technique. A total of 14 PBDEs were identified and quantified by gas chromatography coupled to low resolution mass spectrometry (HRGC-LRMS) using a 6890 N gas chromatograph coupled with a 5975 quadrupole mass spectrometer (Agilent, Palo Alto, CA) operating in selected ion monitoring mode (SIM) with electron capture negative ion chemical ionization (ECNI).

Data analysis

The influence of sampling location (remote or urban), season (winter/fall *vs.* summer/spring) and year was simultaneously evaluated by means of a separated generalized linear model analysis (GLM) using total PCDD/F, dioxin-like PCB or PBDE concentrations (previously ln transformed to adjust to normal distribution) as response variable. Sampling location and season were considered fixed factors and the temporal sequence was included as a covariable in the model.

Results and Discussion

The range, median and average concentrations for the target compounds in remote and urban areas selected in our study are shown in Table 1. PCDD/Fs showed the lowest levels, in the order of fg/m^3. Sampling location showed a significant effect on contaminant levels since the average concentration of PCDD/Fs, dioxin-like PCBs and PBDEs found in air was generally higher in urban than in rural areas. Air concentrations for all the POPs considered in the present study, fall within the range of those reported in previous studies conducted in remote and urban areas[4-6].

Table 1. Range, median and average concentrations of PCDD/Fs, dioxin-like PCBs and PBDEs in remote and urban sampling points selected in the present study.

	Sampling point	**Range**	**Median**	**Average**
PCDD/Fs (fg/m^3)	Remote	2.43 - 300	29.5	52.4
	Urban	30.1 – 995	110	233
PCBs (fg/m^3)	Remote	10.1 – 30,500	1,240	2,600
	Urban	95.9 – 35,100	5,230	7,940
PBDEs (pg/m^3)	Remote	0.01 - 464	2.56	26.1
	Urban	0.07 - 557	7.98	43.4

Regarding PCDD/Fs, the general tendency during the studied period (2008-2012) was quite similar in both urban and remote locations and did not show significant temporal trends (Figure 1a). On the contrary, dioxin-like PCB concentrations (Figure 1b) showed a significant decreasing tendency from 2008 to 2012 in both remote and urban areas as showed by the GLM analysis.

The season of the year was a significant factor in the model explaining the occurrence of PCDD/Fs in air. The seasonal profile for PCDD/Fs was characterized by higher concentrations in winter and fall compared to those in spring and summer. This pattern was especially noted in remote compared to urban locations as shown in Figure 1a. This behavior has been previously described[5] and might be mainly associated to the higher ratio of combustions due to operational heating systems during the cold seasons. Moreover, OH radical is postulated to photochemically react and degrade PCDD/Fs in the atmosphere. Thus the lower atmospheric concentration of this radical that takes place in fall and winter seasons in the northern hemisphere may be contributing to the observed seasonal variations for PCDD/Fs. On the contrary, dioxin-like PCBs showed the highest levels in spring and summer both in urban and remote areas. However, the pattern was not as marked as in the case of PCDD/Fs and thus, the season of the year did not show a significant effect in the model. This fact could be related to the greater degree of volatilization that these compounds experience under higher temperatures.

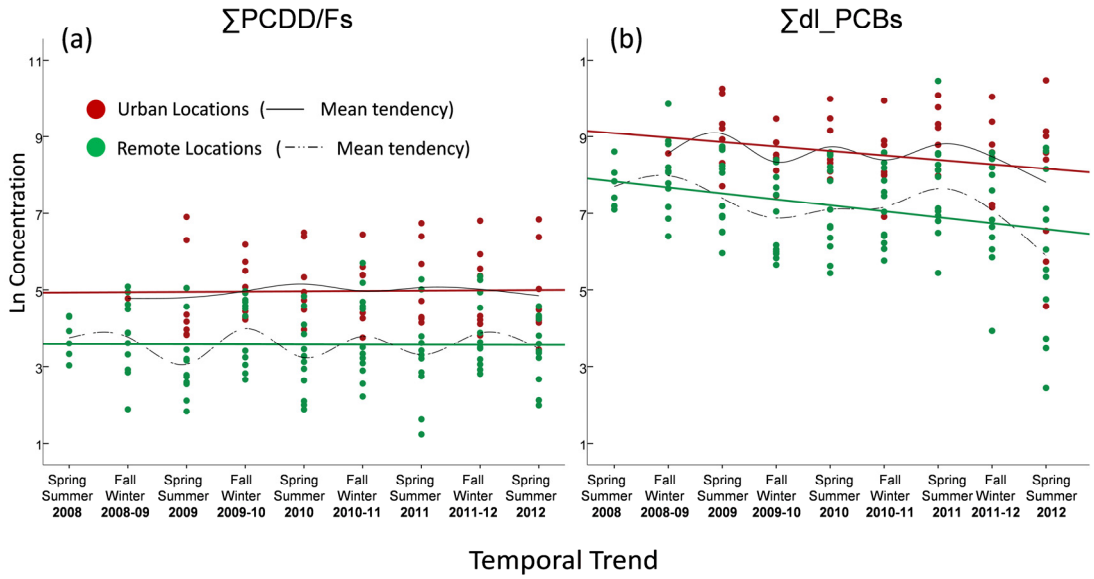

Figure 1. Temporal trends of PCDD/Fs (1a) and dioxin-like PCBs (1b) in remote and urban areas selected in this study during the period 2008-2012.

Total PBDE concentrations in air did not show significant temporal or seasonal trends, likely because of the heightened variability observed in some localities. However, BDE-209 - found as the most abundant congener in our study (Figure 2a)-increased significantly (correlation analysis) from 2008 to 2012 in both remote and urban areas (Figure 2b). This tendency likely indicates the progressive substitution in Europe of penta- and octa-PBDE formulations (banned in 2004) for the deca- formulation, which shows a congener abundance profile dominated by BDE-209. In fact, our results agree with other studies reporting a major presence of BDE-209 in environmental samples[7, 8].

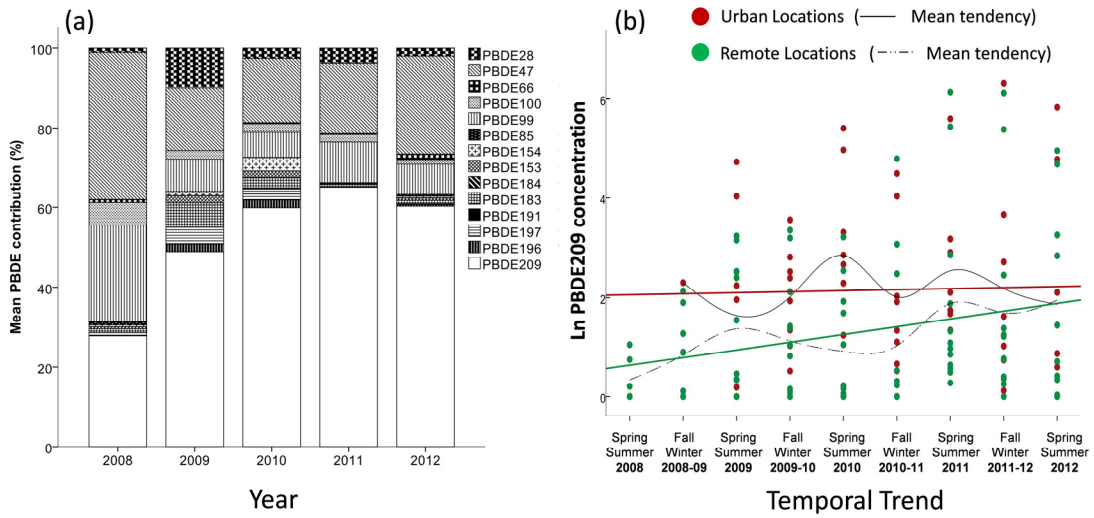

Figure 2. a) Relative contribution of the individual BDE congeners to total PBDE content, b) Temporal trends of BDE-209 (2008-2012) in remote and urban areas selected in this study.

Conclusions

Our preliminary results suggest that POP concentrations in Spanish air are usually higher in urban compared to rural areas. Dioxin-like PCB concentrations decreased from 2008 to 2012 while some PBDE congeners (i.e. BDE-209) increased during the same period. Although no temporal trends were detected for PCDD/Fs, significant seasonal variations related to cold and warm periods were found.

Long-term air monitoring programs for POPs become essential in order to gain a solid knowledge regarding not only their geographical distribution but also their seasonal behavior. Even more important, the maintenance of these monitoring plans is absolutely necessary for a proper evaluation of the fate and temporal trends of these POPs.

Acknowledgements

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