PCDD/Fs, dl-PCBs and PBDEs in urban areas from Spain

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Introduction

Given the concern raised by Persistent Organic Pollutants (POPs), the Stockholm Convention (SC) entered into force in 2004 as a global treaty to protect human health and the environment from POPs. Spain was a pioneer in developing and putting into effect a National Implementation Plan (NIP). Among different activities undertaken by the Spanish Ministry of the Environment, a monitoring program on POPs is running since 2008 in order to evaluate the effectiveness of SC's measurements for POPs elimination at a national scale. Under the Spanish Monitoring Program (SMP), POPs are monitored following the recommendations of the Global Monitoring Plan (GMP) based on the use of polyurethane foam disk passive air sampling (PUF-PAS) (1, 2). In the SMP air sampling is conducted seasonally (winter, spring, summer, fall) at urban and background sites virtually reaching the entire national territory (3, 4).

In this work, data on selected POPs (i.e. PCDD/Fs, dl-PCBs and PBDEs) included in the SC POP list in very different moments (e.g. PCDD/Fs and dl-PCBs in 2004, PBDE-209 in 2017), are evaluated in air sampled in urban areas from Spain and compared to the situation found in background/rural areas across the country. Spatial and temporal observations are provided for the period 2008-2015.

Materials and methods

From summer 2008 to fall 2015, a total of 321 air samples (and their associated 321 field blanks) corresponding to 30 field-campaigns were obtained every three months around each season's change from five urban sites and seven background (rural/remote) sites in Spain using PUF-PAS. Urban sampling points were chosen in populous urban centers characterized for a highly developed industrial fabric. Background sampling sites corresponded with European Monitoring and Evaluation Program (EMEP) stations, located far from populated spots and with no direct influence of industrial activities.

One PUF disk at each sampling site was used for air sampling and subsequent PBDE analysis. Three PUF disks at each site were used for sampling and subsequent PCDD/F and dl-PCB analysis. PUF disk pre-treatment, transport conditions and deploying plus collecting procedures in the field were optimized to avoid potential contamination of PUFs and are thoroughly described elsewhere (3). Fourteen PBDEs (PBDE-28, -47, -66, -85, -99, -100, -153, -154, -183, -184, -191, -196, -197, -209) were identified and quantified by GC-LRMS. Detailed instrumental conditions as well as the whole sample treatment procedure can be found in Muñoz-Arnanz et al. (2016). 17 PCDD/Fs (2,3,7,8-chlorinated congeners), and 12 dl-PCBs (#CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, -189) were analyzed by GC-HRMS. Further details are provided in Muñoz-Arnanz et al. (5).

Air concentrations were calculated based on the validated approximation of 4 m^3/day as sampling rate per PUF disk (6-8). PBDE results are given in pg/m^3. PBDE concentrations below the method detection limit (MDL) based on field blank results were set to ½ MDL (4). All results are given in fg/m^3 for PCDD/Fs and TEQs, and in pg/m^3 for dl-PCBs. For these chemicals, concentrations below the MDL were set to 2/3 MDL (8). Final concentration data were analytical and field blank corrected.

Data treatment and analysis were performed with IBM SPSS.24. To evaluate the influence of sampling year, season, sampling site and environmental variables that can regulate air-pollution and sampling rates of PUFs (temperature, humidity, precipitation and wind speed), General Linear Model (GLM) analyses, as detailed in Roscales et al. (4), were used.

Results and discussion:

PBDEs: All targeted PBDEs were found above the MDL in the air samples, but detection frequencies (% > MDL) strongly varied among PBDE congeners and sampling sites. As expected, urban sites, showed detection frequencies that at least doubled those of background sites for all PBDEs. In the GLM analysis, a significant effect of sampling year and site, but not of season was detected on total PBDE (∑PBDEs) air concentrations. In addition, a significant effect of locality type, the interaction locality type*year and a negative and positive relationship with precipitation and wind speed, respectively, were detected on ∑PBDE concentrations.

Sampling site was the factor explaining the largest variability of ∑PBDEs, with concentrations significantly greater in urban than in background sites (Figure 1). Previous studies found similar spatial patterns and related increasing PBDE air concentrations to population density (9-11). Our results also pointed out urban areas as significant sources of PBDEs, probably due to diffuse emissions derived from PBDE-treated materials such as vehicles' upholstery and house products and furnishings (12).

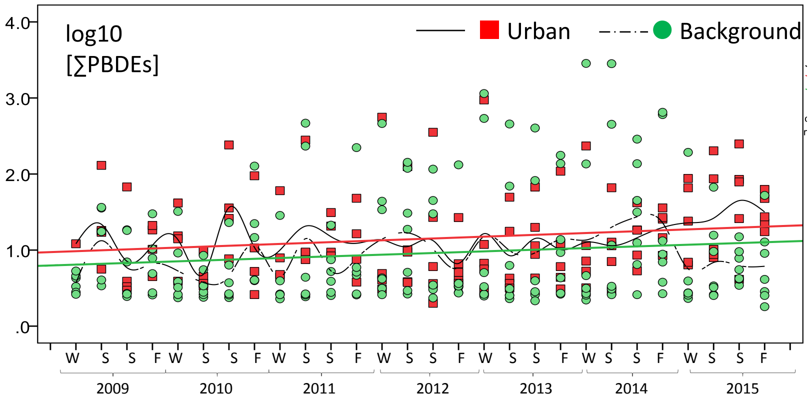

Figure 1. Temporal trends and seasonal (Winter, Spring, Sumer, Fall) variations of ∑PBDEs pg/m^3 in air samples from Spain at urban (red) and background (green) sites. Straight lines represent regression year*∑PBDEs. Sinuous lines represent mean seasonal trends.

Regardless of the sampling site or year, the deca-brominated PBDE-209 showed the greatest contribution, followed by tetra- and penta-PBDEs. Despite the estimated reduction in Europe in the usage and emissions of PBDE-209 since 2004 (13), steady or increasing temporal trends irrespective of the sampling site from 2008 to 2015 were found in this study. In the case of lighter PBDEs, (tri- to hexa-substituted) steady concentrations were found during the study period. However, compared to PBDE-209, in the case of these PBDEs greater differences in their concentrations were found between urban (high levels) and background areas (low levels).This seems to underline the role of highly populated areas as ongoing sources for lower brominated PBDEs, which was not so evident for other study congeners such as PBDE-209.

Seasonal patterns were much clear in urban than in background areas (Figure 1). This could be explained by the major abundance of potential T-dependent sources in highly populated areas as well as to major building ventilation rates that can act as active PBDE indoor-outdoor sources in hot seasons (10, 14, 15).

In spite of increasing regulations on the production and usage of PBDEs during the last 15 years, the temporal evolution of ∑PBDEs air concentrations was highly dependent on the sampling site and did not reflect significant trends from 2009 to 2015 (Fig. 1). PBDE-209 was by far the congener found at the greatest concentration, being, thereby, responsible for the main spatiotemporal patterns in ∑PBDEs (Figure 1). Our results only pointed out a significant reduction in air levels of PBDE congeners related to the octa-PBDE formulation. Larger temporal series are yet needed to accurately evaluate when restrictions and regulations on PBDEs translate into a significant decrease in their presence.

PCDD/F and dl-PCB concentrations: All target congeners were more frequently detected in urban sites. Sampling site showed the greatest effects in the models, with significant greater concentrations in urban compared to background sites during the entire study period. Higher concentrations at urban sites compared to those at background sites have been reported in similar studies using PUF-PAS sampling approaches (8, 16-19) pointing out the major presence of PCDD/F sources in urban areas compared to remote background regions. Regarding seasonality, in background sites maximum and minimum concentrations mostly occurred in cold seasons (winter or fall) and hot seasons (summer or spring), respectively. This pattern was not so clear in the study cities.

PCDD/Fs showed a marked decreasing trend from 2009 to 2015. The low concentration range found in our study (20.0–1010 fg/m^3) seems to indicate that stricter legislation and the improvement of industrial processes contributed to reduce most of the non-intentional sources attributed to these compounds (20). OCDD was the most prevalent compound with concentrations up to two orders of magnitude above other congeners, followed by 1,2,3,4,6,7,8-HpCDD and OCDF in almost all air samples. The high prevalence of OCDD in urban areas was previously reported by Mari et al. 2008 (21) and can be attributed to the major presence of combustion sources (vehicles, industrial facilities, etc.) in densely populated and industrialized cities.

In the case of dl-PCBs, GLM analysis showed a significant effect of year, sampling site and season for both non- and mono-*ortho* PCB concentrations. Overall, urban sites showed significantly higher concentrations than background areas during the entire study period (Fig. 2). In terms of temporal behavior, non-*ortho* PCBs showed a significant decreasing trend from 2009 to 2015 regardless of the locality type (Fig. 2). A concentration decrease was more noticeable in urban than in background places, being the negative relationship between year and non-*ortho* PCBs significant only in urban sites. For mono-*ortho* PCBs, no significant relationship was found between sampling year and their concentrations, showing instead a steady flat temporal behavior regardless of the locality type. This suggests the existence of different sources for mono-*ortho* and non-*ortho* PCBs, which is in agreement with the latter being more associated to non-intentional emissions. The significant decrease of non-*ortho* PCB concentrations could be indicative of the effectiveness of local and global regulations as indicated before for PCDD/Fs.

TEQs: Sampling site was by far the factor that explained the largest variability of ΣTEQ concentrations, with values higher in urban than background areas during the entire sampling period (Figure 2).

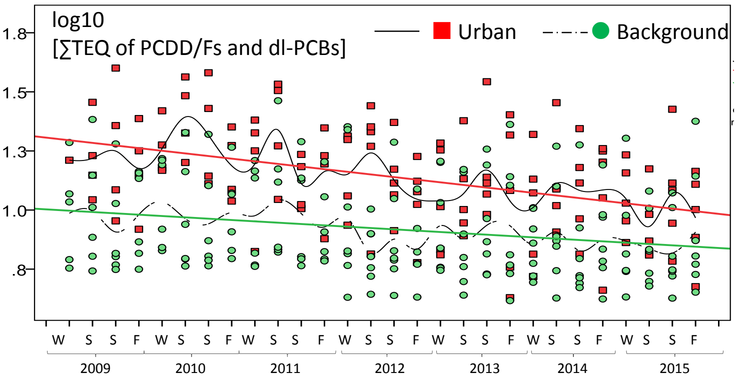

Figure 2. Temporal trends and seasonal (Winter, Spring, Sumer, Fall) variations of ∑TEQs fg/m^3 in air samples from Spain at urban (red) and background (green) sites. Straight lines represent regression year*∑TEQs. Sinuous lines represent mean seasonal trends.

As reported in previous studies, significant greater concentrations found at urban areas reflected a major presence of PCDD/F sources in densely populated areas. For instance, Schuster et al. (5) found the highest TEQ concentrations at urban sites compared to background sites, attributing these differences to distinct in site characteristics and potential/regional sources. ΣTEQ concentrations significantly decreased progressively from 2009 to 2015. Data from studies in Spain conducted before 2000 along with our results from 2009 to 2015 suggest a clear reduction in time for ΣTEQs, a positive trend probably driven by collective intentional efforts to protect human and environment health, and achieved under the global efforts for POP regulation and their subsequent implementation.

Outline:

The most encouraging outcome -considering the objectives of the SC- is how PCDD/Fs and dl-PCBs are reaching low concentration values as shown by their temporal trends, converging at urban and background sites in Spain. This seems to indicate how regulation measures both at regional and global extents are being effective. Given that depending on each chemical family, POPs exhibit diverse trends and behaviors, as shown for PBDEs, larger temporal series are still needed. Therefore, the continuation of the monitoring activities is of the outmost importance in order to further contrast and reassure the positive results obtained.

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