



## Invited paper

## Time trends of persistent organic pollutants in spanish air



Adrián de la Torre\*, Paloma Sanz, Irene Navarro, María Ángeles Martínez

Persistent Organic Pollutants Group, Environmental Department, CIEMAT, Avda. Complutense 40, 28040 Madrid, Spain

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## ABSTRACT

Passive air samplers consisting of polyurethane foam (PUF) disks were deployed in seven remote points and four urban locations to assess levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and some organochlorine pesticides including: 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT) and their metabolites (1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (DDE) and 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (DDD)), hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs), in the Spanish ambient air. Results revealed HCB (49 pg m<sup>-3</sup>; median) as the major pollutant, followed in decreasing order by HCHs (21 pg m<sup>-3</sup>), ΣDDT/E/Ds (20 pg m<sup>-3</sup>), PCBs (20 pg m<sup>-3</sup>), PBDEs (3.3 pg m<sup>-3</sup>) and PCDD/Fs (0.04 pg m<sup>-3</sup>), when urban and remote locations are evaluated together. Urban areas presented statistically significant ( $p < 0.05$ , Mann–Whitney U test) higher levels for all families studied, except for HCB, compared to remote locations revealing anthropogenic activities as potential sources for these chemicals. On the contrary, HCB concentrations seem to reflect background levels. Interestingly, results reveal a decreasing trend for PCBs, PBDEs and DDTs levels in remote areas, while this behaviour is only statistically significant in the case of the former chemicals in urban locations. The present study is framed in the Spanish air monitoring plan and represents the first complete analysis related to POP presence in Spanish air coming from inner sites.

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## 1. Introduction

Persistent Organic Pollutants (POPs) are chemicals that persist in the environment, biomagnify at higher trophic levels, exhibit toxic effects that may threaten the health of the environment and undergo long-range atmospheric transport from their sources to remote regions (Stockholm Convention, 2011). International efforts have been implemented to reduce levels and emissions of POPs in the environment. Multilateral environmental agreements have been enacted to control release, production and use of POPs, including global conventions dealing with toxics and waste (the Basel and Rotterdam Conventions), the Stockholm Convention (SC) on POPs and the Convention on Long-Range Transboundary Air Pollution POPs Protocol of the United Nations Economic Commission for Europe.

The SC, created in 2001 and ratified in 2004 in Spain, is a global treaty to protect human health and the environment from POPs. This Convention requires Parties to take measures to eliminate or

reduce the release of POPs into the environment. In a first stage, the SC identified an initial group of twelve POP compounds – the “dirty dozen”, however, a process exists under the Convention to nominate and review candidate POPs and add them to the list if it is determined that they satisfy the criteria of persistence, bio-accumulation, toxicity and long-range transport potential. According to this possibility, nine new POPs were added at the fourth conference of the parties:  $\alpha$ -,  $\beta$ -,  $\gamma$ -hexachlorocyclohexanes (HCHs); tetra-, penta-, hexa- and heptabromodiphenyl ether (present in commercial penta- and octabromodiphenyl ether formulations); hexabromobiphenyl (HBB), perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F); penta-chlorobenzene (PeCB) and chlordecone, (UNEP, 2009); endosulfan was included at the fifth (UNEP, 2011); hexabromocyclododecane (HBCD) was joined on at the sixth (UNEP, 2013a), and finally, the list were incremented by hexachlorobutadiene, pentachlorophenol and its salts and polychlorinated naphthalenes, at the seventh (UNEP, 2015).

Under the leadership of its Ministry of Agriculture, Food and Environment, Spain was a pioneer in fulfilling its obligation of developing and carrying into effect a National Implementation Plan (NIP). Specifically, the Spanish NIP was initiated in 2007

\* Corresponding author.

E-mail address: [adrian.delatorre@ciemat.es](mailto:adrian.delatorre@ciemat.es) (A. Torre).

encompassing as core part of it a monitoring network to characterize the current status and temporal trends of POPs and to evaluate the effectiveness of practices adopted to reduce POP emissions. With that purpose, a comprehensive monitoring network was devised across Spain focusing on both remote and urban points. These sites were selected according to their geographical location in two different but rather homogeneous groups: inner and outer (or coastal) sampling points. Ever since its onset the work field of the Spanish monitoring program has been developed by the conjoint efforts of two leading research institutions: Centre for Energy, Environmental and Technological Research (CIEMAT) and Spanish National Research Council (CSIC). While CIEMAT was designated responsible of the maintenance and study of inner sites, CSIC was in charge of the mostly outer locations.

In 2008 this Spanish network began monitoring POPs in ambient air because it is the major route of long-range transport through the environment for many POPs. Air has also been recognized as a key of environmental medium in the Global Monitoring Plan (GMP) of the Stockholm Convention, which is intended to support evaluation of the effectiveness of the Convention. A guidance document for the GMP is also developed to provide comparable monitoring information on the presence of POPs (UNEP, 2013b). This document recommends the use of passive air samplers (PASs) for addressing data gaps on POP presence in air. PASs with polyurethane foam (PUF) disks have become increasingly popular over the past 10 years. PASs are cheaper than active samplers, easier to deploy and, thus, better-suited for remote air sampling or for developing a large monitoring network. They have been used successfully over a range of geographic scales including local (Ornellas et al., 2012; Pozo et al., 2012; Tombesi et al., 2014), national (Gevao et al., 2013; Moussaoui et al., 2012), continental (Bogdal et al., 2013; Li et al., 2014; Pribylova et al., 2012; Schuster et al., 2015) and global scale (Fiedler et al., 2013; Pozo et al., 2009). Consequently, they have been widely accepted to establish POP concentration levels in air.

The present study is framed in the Spanish NIP and shows the results of the Spanish air monitoring network obtained by CIEMAT in relation to mostly inner sampling points.

## 2. Materials and methods

### 2.1. Sample collection

Data shown in the present study included 211 samples obtained during twenty one consecutive sampling campaigns (from summer 2008 to autumn 2013). Samples were collected from seven remote and four urban locations using European Monitoring and Evaluation Program (EMEP)/Global Atmospheric Watch (GAW)/Control Atmospheric Monitoring Program (CAMP) and State Meteorological Agency (AEMET) locations. Complete details related to sampling sites can be found in Table S1 (“S” indicating Supplementary data). Passive air samplers with PUF disks as the sorbent media were used. The principles of this kind of passive air sampling have been extensively explained elsewhere (Shoeb and Harner, 2002). Prior to deployment, PUF disks (14 cm diameter; 1.2 cm thickness, and 0.03 g cm<sup>-3</sup> density; TechnoSpec, Spain) were pre-cleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, wrapped in aluminium foil and stored in polyethylene bags at -20 °C until deployment. At each sampling point, four PASs were deployed for 3 months to correspond to the seasons. Three PUFs were used for dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs; including non-*ortho* PCBs (noPCBs: PCB 77, 81, 126 and 169); mono-*ortho* PCBs (moPCBs: PCB 105, 114, 118, 123, 156, 157, 167, 189) and indicator PCBs (i-PCBs or mPCBs: PCB 28, 52, 101,

138, 153 and 180)) and polybrominated diphenyl ethers (PBDEs: BDE 17, 28, 47, 66, 77, 100, 119, 99, 85, 153, 154, 138, 156, 184, 183, 191, 197, 196, 207, 206 and 209) determinations. The fourth one was used for organochlorine pesticides (OCPs) analysis including: 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT; *p,p'*- and *o,p'*-DDT), 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (DDE; *p,p'*- and *o,p'*-DDE), 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (DDD; *p,p'*-DDD and *o,p'*-DDD), hexachlorobenzene (HCB) and hexachlorocyclohexane (HCH;  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH). Field blanks were also collected at each station in each sampling period.

### 2.2. Chemical analysis

The analytical procedure followed the US EPA 1613B, 1668A and 1614 Methods for PCDD/Fs, PCBs and PBDEs, respectively analysis. Prior to Soxhlet extraction with toluene for 24 h, samples were spiked with a known amount of <sup>13</sup>C-labelled surrogate standards including PCDD/Fs, PCBs, PBDEs and OCPs congeners (Table S2). Extract obtained was solvent exchanged into hexane prior to cleanup step which was performed in an automated Power Prep™ System (FMS, Inc., USA) including silica, alumina and carbon columns. PCDD/Fs, PCBs, HCB, HCHs and DDT/E/Ds instrumental analysis were conducted on an Agilent GC 6890N, connected to a Micromass Ultima NT HRMS, at 10,000 resolving power (10% valley) and working in selected ion monitoring (SIM). GC column was a 60 m × 0.25 mm × 0.25 μm film thickness (DB-5MS, Agilent J&W). PBDE determinations were carried out by HRGC-q-MS on an Agilent 6890N Gas Chromatograph fitted with a short and narrow column (15 m × 0.25 mm × 0.10 μm film thickness; DB-5MS (Agilent J&W)) connected to an Agilent 5973MSD LRMS detector. Instrument operating conditions were described elsewhere (de la Torre et al., 2011; Dorneles et al., 2013). In all cases, quantification was carried out using isotopic dilution method.

### 2.3. Quality assurance and quality control (QA/QC)

Three criteria were used to ensure the correct identification and quantification of analytes: i) ± 3s retention time between the analyte and the standard, ii) the ratio of quantifier and qualifier ions had to be within ±15% of the theoretical values and iii) signal to noise ratio had to be greater than 3:1. The analytical procedures described above were checked for recoveries and reproducibility. Average recoveries of surrogates ranged from 40 to 105% for PCDD/Fs; 60–106% for PCBs; 57–108% for OCPs and 54–109% for PBDEs. In all cases, recoveries are in the ranges accepted in US EPA methods 1613B, 1668A and 1614. Blank levels were assessed from the field blanks consisted of the pre-extracted PUF disks that were taken to each sampling site at each sampling period. They were extracted and analyzed in the same conditions as the samples. Data were blank corrected. Method detection limits (MDL) were determined by assessing the amount that corresponded to a signal noise ratio ≥ 3. In case congener concentrations were below MDL a concentration equal to the detection limit was assumed.

### 2.4. Data analysis

Statistical analyses were performed with SPSS 23.0 software. Principal component analysis (PCA), Pearson, and Mann–Whitney U test were conducted to evaluate correlations between pollutants and potential differences between urban and remote locations.

## 3. Results and discussion

Table 1 summarizes concentration (pg m<sup>-3</sup>) of PCDD/Fs, PBDEs, PCBs, HCB, HCHs and DDT/E/Ds in the different locations evaluated

**Table 1**  
Average  $\pm$  SD, (median) and range of concentrations ( $\text{pg m}^{-3}$ ) obtained for PCDDs/Fs, PBDEs, PCBs, HCHs, HCB and DDTs.

	$\sum_{17}\text{PCDD/Fs}^a$	$\sum_{21}\text{PBDEs}^b$	$\sum_{18}\text{PCBs}^c$	$\sum_3\text{HCHs}^d$	HCB	$\sum_6\text{DDTs}^e$
Total	0.07 $\pm$ 0.2 (0.04) 0.01–1.8	8.2 $\pm$ 18 (3.3) 0.08–211	49 $\pm$ 80 (20) 0.1–609	27 $\pm$ 23 (21) 0.13–154	57 $\pm$ 37 (49) 0.03–244	36 $\pm$ 68 (20) 0.35–561
Remote	0.08 $\pm$ 0.19 (0.03) 0.01–1.8	3.6 $\pm$ 5.2 (1.5) 0.08–26	38 $\pm$ 68 (18) 0.12–386	22 $\pm$ 19 (18) 0.13–100	61 $\pm$ 42 (50) 0.03–244	21 $\pm$ 18 (18) 0.35–110
Urban	0.06 $\pm$ 0.06 (0.05) 0.01–0.3	16 $\pm$ 27 (10) 0.08–211	68 $\pm$ 95 (37) 5.0–609	37 $\pm$ 27 (30) 5.0–154	51 $\pm$ 25 (48) 12–152	51 $\pm$ 69 (31) 6.0–561

<sup>a</sup>  $\sum_{17}\text{PCDD/Fs}$  = sum of 10 PCDFs and 7 PCDDs.

<sup>b</sup>  $\sum_{21}\text{PBDEs}$  = sum of BDE 17, 28, 47, 66, 77, 100, 119, 99, 85, 153, 154, 138, 156, 184, 183, 191, 197, 196, 207, 206 and 209).

<sup>c</sup>  $\sum_{18}\text{PCBs}$  = sum of PCB 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180 and, 189).

<sup>d</sup>  $\sum_3\text{HCHs}$  = sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH.

<sup>e</sup>  $\sum_6\text{DDTs}$  = sum of *p,p'*- and *o,p'*- DDTs, DDEs and DDDs.

in the present study. According to the literature (Harner et al., 2004; Jaward et al., 2004; Wilford et al., 2004) the sampling rate (R) remains linear over the first 100 days for chemicals with octanol-air partition coefficient ( $K_{OA}$ ) values higher than  $10^{8.5}$ , and it can vary from 3 to  $5 \text{ m}^3 \text{ d}^{-1}$ . Site- and seasonal-specific sample air volumes were calculated according to the Tom Harner Template (2015 v.1.1. PUF disk effective Air Volume Calculation or Target Chemicals: Harner, 2015) considering site specific seasonal average temperatures. Results shown small variations for all the analytes ( $3.7 \pm 0.4 \text{ m}^3 \text{ d}^{-1}$ ; average  $\pm$  SD), except for HCB, whose sampling rate range between  $1.5 \text{ m}^3 \text{ d}^{-1}$  in summer ( $26^\circ\text{C}$  maximum average temperature) to  $2.7 \text{ m}^3 \text{ d}^{-1}$  in winter ( $5^\circ\text{C}$  minimum average temperature). For consistency and comparability with other studies a sampling rate of  $4 \text{ m}^3 \text{ d}^{-1}$  was used to derive concentrations for all compounds analyzed except for the HCB, which site- and seasonal-specific sampling rates were used.

Data were studied in a global (sum of remote and urban locations) way and also separately by remote and urban areas for all families analyzed. From the global data ( $n = 211$ ), it can be observed the following pattern of concentration:  $\text{HCB} (\text{pg m}^{-3}) > \sum_{18}\text{PCBs}$  (sum of non-ortho-, mono-ortho and i-PCBs;  $\text{pg m}^{-3}$ )  $\approx \sum_6\text{DDTs}$  (sum of *p,p'*- and *o,p'*- DDTs, DDEs and DDDs;  $\text{pg m}^{-3}$ )  $\approx \sum_3\text{HCHs}$  (sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH;  $\text{pg m}^{-3}$ )  $> \sum_{21}\text{PBDEs}$  (sum of tri- to decaBDE;  $\text{pg m}^{-3}$ )  $\gg \sum_{17}\text{PCDD/Fs}$  (sum of 7 PCDDs and 10 PCDFs;  $\text{fg m}^{-3}$ ). This pattern is also held when samples collected in urban areas are evaluated separately ( $n = 77$ ) of those associated with remote locations ( $n = 134$ ), see Fig. S1. The differences in the levels of pollutants analyzed between urban and remote areas have been evaluated by using a Mann–Whitney U test. Statistically significant differences ( $p < 0.05$ ) related to remote and urban areas have been found between the concentrations of all the pollutants studied, except for HCB. These differences are due to the higher levels that present urban areas compared to remote locations. This result is in agreement with data reported by the Global Atmospheric Passive Sampling Network (GAPS), (GAPS, 2009) that obtained lower values for PCBs, HCHs and DDTs in non urban (rural, polar, agricultural and remote locations) compared to urban ones, and suggests urban areas as source of these pollutants in the air. This hypothesis will be discussed in depth latter.

Average PCDD/F profile has been calculated for each sampling point and for the sum of remote and urban locations (Fig S2a). It can be observed that the profiles obtained in all sampling points are very similar. The contribution to total PCDD/Fs increases with the degree of chlorination, being the most abundant congener the OCDD (26%), followed by OCDF (11%), 1234678-HpCDD (8%), 1234789-HpCDF (6%) and 1234678-HpCDF (6%). This agrees with the general pattern reported for 2378-substituted PCDD/Fs in air (Mari et al., 2008; Schuster et al., 2015). Interestingly, when urban and remote locations were compared results shown higher contribution for OCDD (33% urban) in the former compare to the

latter (22% remote), which evidences anthropogenic activities occurring in urban areas as potential source for the major PCDD/F congener.

PCB concentrations were dominated by i-PCBs contribution ( $\sum_6\text{mPCBs}$ , 86%), followed by mono-ortho PCBs ( $\sum_8\text{moPCBs}$ , 13%) and non-ortho PCBs ( $\sum_4\text{noPCBs}$ , < 1%). The congener profile of PCBs remained fairly constant for all samples analyzed.  $\sum_6\text{mPCBs}$  concentrations ranged from 0.02 to  $566 \text{ pg m}^{-3}$ , with a median of  $16.6 \text{ pg m}^{-3}$ . PCB 101 dominated the profile, representing 24% of the total mass of PCBs analyzed, followed by PCB 52 (17%), PCB 153 (16%) and PCB 138 (15%), (see Fig. S3a). PCB 28 and/or PCB 52 have been also reported as the most abundant congener in literature (Bogdal et al., 2013; Tombesi et al., 2014; Diefenbacher et al., 2015). Contribution of the  $\sum_8\text{moPCBs}$  to total dioxin like PCBs (dl-PCBs) content (sum  $\sum_8\text{moPCBs}$  and  $\sum_4\text{noPCBs}$ ) was over 97% being PCB 118 the major congener (63%) followed by PCB 105 (20%), see Fig. S2c. PCB 126 was the dominant contributor to the PCB WHO<sub>98</sub>-TEQ providing a mean value of 69%, see Fig. S2d. These results are in good agreement with those from previous studies (Cortés et al., 2014; Yoonki et al., 2014).

Toxic equivalents (TEQs) were calculated for PCDD/Fs and dl-PCBs using the international toxic equivalency factors published in 1998 by the World Health Organization (WHO<sub>98</sub>-TEFs). Average values for PCDD/Fs ( $\text{TEQ}_{\text{PCDDs/PCDFs}}$ ), dl-PCBs ( $\text{TEQ}_{\text{dl-PCBs}}$ ) as well as the sum of these TEQs ( $\text{TEQ}_{\text{total}}$ ) are provided in Table S3. With respect to total TEQ (see Fig. S4), the contribution of PCDDs (44%) was found higher than that of PCDFs (30%), and followed by dl-PCBs (26%). Congener 12378-PeCDD (35%) was the dominant contributor to the  $\text{TEQ}_{\text{PCDDs/PCDFs}}$ , followed by 23478-PeCDF (25%), see (Fig S2b). Congener 23478-PeCDF was also observed as the main contributor to  $\sum\text{WHO-TEQ}$  in studies performed in urban-residential and industrial areas (Gao et al., 2014; Heo and Lee, 2014). Toxic concentrations for PCDD/F and dl-PCBs obtained in this study are the same range that those reported worldwide in studies conducted with both passive and active samplers (Table S4).

PBDE congener profile is shown in Fig. S3c. In this graph, only the congeners whose contribution to the total concentration was higher than 2% are represented. In all cases BDE 209 was the major congener, accounting 68%, followed by BDE 47 (10%) and BDE 99 (6%). In addition, relative high contribution (~3%) to total PBDE content was found for nonabrominated congeners (BDE 207 and BDE 206), which correlates well with the pattern described by La Guardia et al., 2006 for two DecaBDE commercial mixtures (Saytex 102E and Bromkal 82-ODE). As mentioned before, higher levels of  $\sum_{21}\text{PBDEs}$  were found in urban locations compared to the remote ones, but also the contribution of BDE 209 in the former ones is higher (83%) than in the latter ones (63%). As happened for OCDD, these results not only evidence urban zones as potential PBDEs sources but also highlight that BDE 209 degradation processes (photolysis) may occur once pollutant is released to the air.

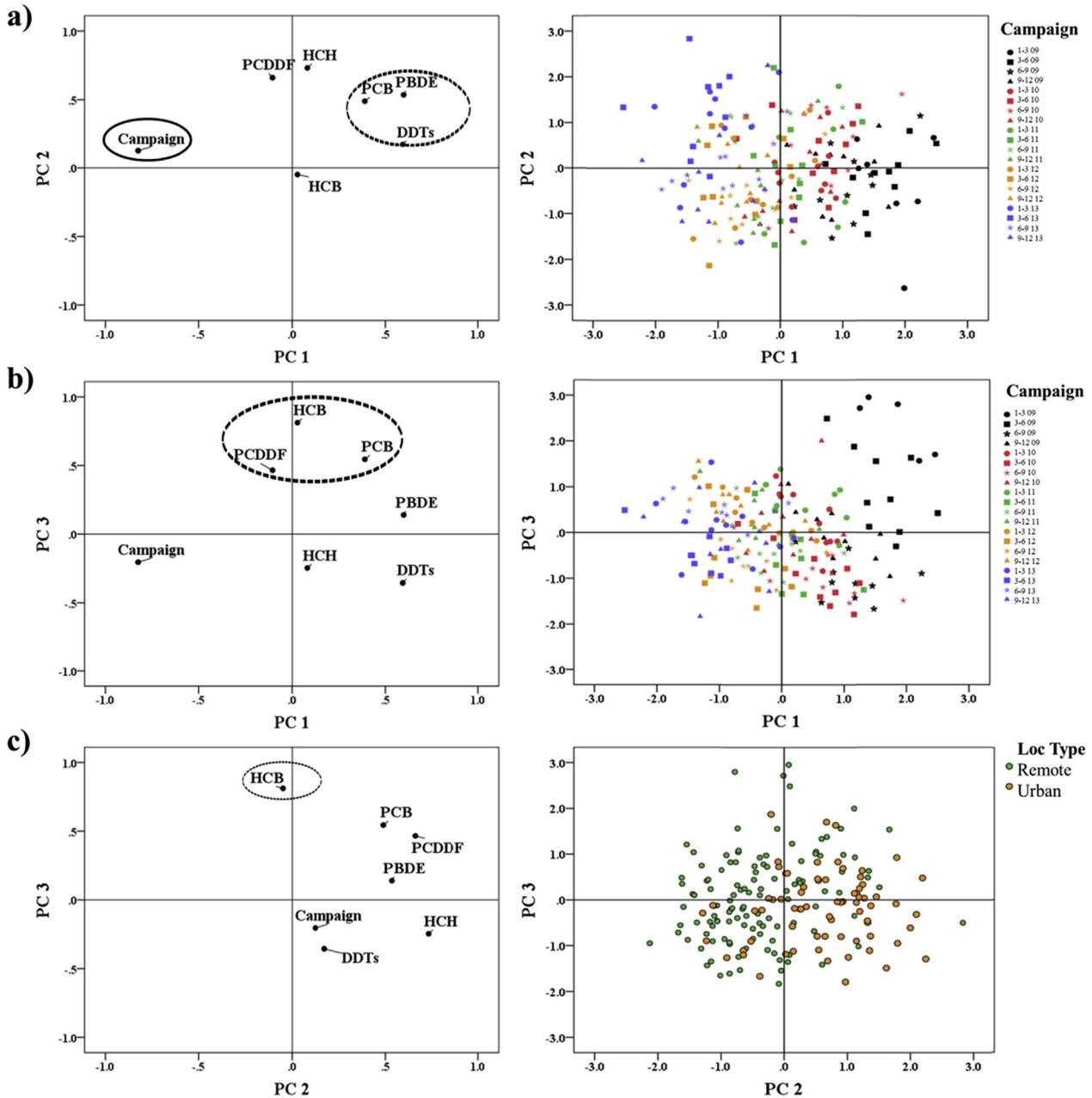
HCH isomers profile is dominated by the  $\gamma$ -HCH (62%), followed by  $\alpha$ - (26%) and  $\beta$ -HCH (5%) isomers. As shown in Fig S3b no differences were found between urban and remote locations in terms of isomer pattern. HCH was used as a commercial insecticide in two formulations: technical HCH and Lindane. Both products were rapidly introduced on a large scale due to their universal insecticidal properties and promising market opportunities in the search for alternatives to DDT (Vijgen, 2006). Technical HCH is produced by benzene chlorination under free radical conditions, and resulting in a mixture of multiple HCH stereoisomers:  $\alpha$  (55–80%);  $\beta$  (5–14%),  $\gamma$  (8–15%),  $\delta$  (2–16%) and  $\epsilon$  (3–5%) (Qiu et al., 2004). Lindane is then extracted from technical HCH with methanol at 15–25 °C, filtered, distilled, crystallized cooling, and finally purified to achieve a purity of more than 90% of  $\gamma$ -HCH isomer. Therefore, differences in  $\alpha$ -/ $\gamma$ -HCH ratios could be used to identify HCH origin. If the source of HCH in the atmosphere comes from fresh input of technical HCH, the  $\alpha$ -/ $\gamma$ -HCH ratio ranges between 4 and 7 (Shen et al., 2004) while coming from Lindane usage drops to values below or equal to 1. In addition, it has been described that  $\alpha$ -HCH isomer has a longer atmospheric lifetime than  $\gamma$  isomer (Willett et al., 1998) and photochemical transformation of  $\gamma$ -to  $\alpha$ -HCH in the atmosphere could happen during long-range transport (Barrie et al., 1992). Thus,  $\alpha$ -/ $\gamma$ -HCH ratios above 7 have been identified as a result of long range transport or recycling of technical HCH. Levels of HCH were quantified in 206 samples, and  $\alpha$ -/ $\gamma$ -HCH ratios were below 1 in 169 samples (82%), between 4 and 7 in 2 rural samples (1%), and above 7 in 2 cases (1%). This result implies that the contribution related to the use and long range transport of technical HCH is low, while the historical use of Lindane is highlighted as the major source for the presence of this pollutant in the air. Lindane has been used in specific applications: to enhance durability of materials like wood, leather, wool and cotton in industrial and indoor domestic applications (up to September 1, 2006), and as a topical insecticide in veterinary and public health (with a  $\gamma$ -HCH purity >99%; up to December 31, 2007). However, all uses of HCH, including Lindane as agricultural pesticide, as biocide, as well as pharmaceutical are banned in the EU (Regulation (EC) 850/2004) from 2008. Lindane use for agricultural purpose in Europe has been estimated around 287,000 tonnes for the period 1950 to 2000, representing 63% of global demand (Vijgen, 2006). In addition, for more than forty years (starting in 1953) technical HCH and Lindane were produced in Spain. As mentioned before Lindane was extracted from the technical HCH mixture, leaving behind huge amounts of waste HCH isomers, that unfortunately have been dumped to the environment that could contribute to the presence of HCH in the air.

It is of great interest the fact that similar HCB concentrations were quantified in remote (61 pg m<sup>-3</sup>; average) and urban (51 pg m<sup>-3</sup>) sampling points (Table 1). These values closely resemble the average (49 pg m<sup>-3</sup>) concentration reported by Halse et al., 2011 for European background sites, and could be interpreted as evidence of HCB atmospheric persistence and high degree of mixing in air. A remarkable result was found when seasonal variations were explored for HCB. As shown in Fig S5 a cyclical trend for HCB, whose concentrations increase in autumn and winter and decrease in spring and summer, is observed. This behaviour was found in both urban and remote locations, while no seasonal variations were found for the rest of the analytes.

Considering the DDTs ( $\sum_6$ DDT/E/Ds as the sum of  $o,p'$ - and  $p,p'$ -DDT, DDE, and DDD isomers),  $\sum_2$ DDE presented the highest contribution (66%) followed by  $\sum_2$ DDT (25%) and  $\sum_2$ DDD (9%), (Fig. S3d). As for HCH and PCB pattern, no differences in terms in DDT pattern were found between samples from urban and remote locations. Presence of these chemicals in the air could be due to the historic use of technical DDT formulation and/or dicofol, an

acaricide manufactured from technical DDT that can be contaminated by  $o,p'$ - and  $p,p'$ -DDT isomers. Technical DDT formulations are mainly comprised of  $p,p'$ -DDT (85%) and  $o,p'$ -DDT (15%) isomers giving a  $o,p'$ -/ $p,p'$ -DDT ( $R_{o,p'/p,p'}$ ) ratio typically around ~0.18 (Qiu et al., 2005; Wong et al., 2009), while  $o,p'$ -DDT has a higher proportion than  $p,p'$ - isomer in technical dicofol. Considering also that  $o,p'$ -DDT shows a shorter half-life than  $p,p'$ -DDT in the environment (Li et al., 2006), it seems reasonable to assume a technical DDT origin when encountering  $R_{o,p'/p,p'} < 0.18$ , or dicofol sources for  $R_{o,p'/p,p'} > 0.18$ . In all air samples the average ratio of  $o,p'$ -/ $p,p'$ -DDT was 1.1, only in 3 samples it drops to values below 0.18, suggesting the presence of DDT impurities in the dicofol product as the main source for DDT/E/D in the air. In the environment,  $p,p'$ -DDT is converted to  $p,p'$ -DDE and  $p,p'$ -DDD. Therefore, the relative abundance of parent and metabolite is used to distinguish relatively recent use ( $p,p'$ -DDT/ $p,p'$ -DDE > 1) from an aged signature ( $p,p'$ -DDT/ $p,p'$ -DDE < 1) (Harner et al., 2004). In this study, the average ratio DDT/DDE was 0.30, which means mainly an aged signature dicofol. Dicofol is used as an acaricide in many countries around the world on a wide range of crops, including fruits, vines, vegetables, ornamentals, cotton and field crop. In the European Union (EU), dicofol was produced in Spain until 2008 in amounts of about 1500–1800 tonnes year<sup>-1</sup> (UNECE, 2010), and worldwide production takes place in China, India and possibly in Brazil and Israel. The use of dicofol is mainly registered in Southern European countries, with an estimate value of 290 tonnes year<sup>-1</sup> for the year 2000 (OSPAR, 2002), which represents the 50% for the total use in the UN-ECE region (UNECE, 2010). Therefore, conclusions from results obtained in this study, linking DDTs air content with historical use and/or production of dicofol in Spain, could be plausible.

Principal component analysis (PCA) was performed with PCDD/F ( $\sum_{17}$ PCDD/Fs), PBDE ( $\sum_{21}$ PBDEs), PCB ( $\sum_{18}$ PCBs), HCH ( $\sum_3$ HCHs), DDT ( $\sum_6$ DDT/E/Ds) and HCB concentrations, but also the sampling campaign (from winter 2009 to winter 2013) was included to evaluate potential interannual influence in the pollutant content. All variables were log transformed prior to analysis, and scores and loading plots are shown in Fig 1. Models depicted in three principal components (PC) 65% of the variance. The first component is mainly influenced by the sampling campaign and explained 32% of the variance. Second component depicted 18% of the variance and included all pollutants (HCHs, PCDD/Fs, PBDEs, PCBs and DDTs) excluding HCB, which is clearly influencing the third component (15% of the variance). The first component revealed that the sampling campaign (solid line in Fig 1a) is negative correlated to the PCB, PBDE and DDT content (broken line Fig 1a). The scores plots in Fig. 1 a. (right) shows that pollutant concentrations have undergone a decreasing trend from January 2009 to December 2013, although in this sense, results from Pearson tests reveal that important differences could be found between remote and urban samples. Pearson correlation coefficients refute a decreasing trend for PBDEs ( $r = -0.50$ ,  $p < 0.01$ ), PCBs ( $r = -0.30$ ,  $p < 0.01$ ) and DDTs ( $r = -0.20$ ,  $p < 0.05$ ) levels in samples obtained from remote locations (see Table S7). However, this trend is only statistically significant for PCBs ( $r = -0.30$ ,  $p < 0.01$ ) if we move to urban samples (see Table S8). In addition it could be also observed that PCDD/F, HCH and HCB levels are not influenced by the first component which means that their concentrations in Spanish air have not undergone important changes during sampling period (2009–2013). Studies conducted by Schuster et al., 2010, have reported that trends in European background air reflect reduction in primary emissions of PCBs and PBDEs, and similar results could be also observed when data reported by the GAPS Network in 2005 are compared to the values presented here (2009–2013), in which  $\sum_3$ PBDEs and  $\sum_{48/22}$ PCBs are significant lower, while  $\sum_2$ HCHs and HCB concentration remains



**Fig. 1.** Diagrams of dispersion related to the three components resulting from a principal components analysis (PCA): a) PC1 and PC2, b) PC1 and PC3, and c) PC2 and PC3. Loadings plots (left) contribution of each variable to each component. Scores plots (right), markers set by sampling campaign (a and b) and sampling type (c), of all samples on each component.

in the same order of magnitude during time period covered by both studies (see Table S5).

Results from Pearson test, also shown that PCBs, HCB and PCDD/Fs are positive correlated ( $p < 0.01$ ) when total samples (urban and remotes) were studied (see Table S6), and this significance is not only maintained but also includes PBDEs when only remote samples are analyzed (Table S7). This result reveals a common origin for PCBs, PCDD/Fs, PBDEs and HCB in remote locations which could be easily associated transport phenomena from urban areas. However, in the urban samples only PCB and HCB content are positive correlated ( $r = 0.38$ ,  $p < 0.01$ , Table S8) evidencing difference urban sources in the case of PBDE (use of consumer products containing these flame retardants) and PCDD/F (produced unintentionally due

to incomplete combustion processes such as burning of hospital, municipal and hazardous waste, and also from automobile emissions, peat, coal, and wood). As mentioned before the second component included all pollutants except HCB. Interestingly, when in the scores plot of PC2 and PC3 markers were set by location type (Fig 1c, right), it could be observed that urban samples are mainly located in the positive side of PC2 while remote places are situated in negative side, which corroborated previous results from Mann Whitney U Test that reflect higher levels for all families studied, except for HCB, in urban locations compared to samples obtained from remote ones. In contrast, similar HCB concentrations were found between both types of locations which as commented before, implies that pollutant concentration could reflect background

levels. Nevertheless, HCB levels do not seem to diminish with time, which results from the fact that samples are distributed in the negative and positive side of PC3 when scores plots of PC1 and PC3 (Fig 1b, right) are labelled according to sampling campaign.

#### 4. Conclusions

The current study evaluates the data produced during 5 years sampling campaigns (21 consecutive sampling periods of 3 months between June 2008 and December 2013) using PASSES to monitor POPs in 11 locations across Spain. This sampling size ( $n = 211$ ) is considered enough representative to offer results that demonstrate the presence of these pollutants in the air. Important differences were obtained between urban and remote locations, being PCBs, DDTs, HCHs, PBDEs and PCDD/F levels obtained in the former higher than those calculated in the latter. This result revealed anthropogenic activities as potential sources for these chemicals. On the contrary, similar HCB concentrations were obtained in both types of sampling points, which could suggest that these levels reflect background concentrations. Temporal trends were evaluated, and although results should be considered carefully because of the reduced time series (5 years), results revealed that concentrations of PBDEs, PCBs and DDTs decrease during study sampling period in remote areas but this trend could be only evidenced for PCBs in urban samples case. This work is framed in the Spanish NIP, managed by the Ministry of the Agriculture, Food and Environment since 2007 and all data presented here, represent the first complete analysis related to POP presence in Spanish air coming from inner sites. In consequence, these results could be easily used for a proper evaluation of measures taken to reduce POP levels in the environment under the Stockholm Convention.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.01.040>.

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