

PCDD/Fs, PCBs, PBDEs, HCHs and DDTs IN AIR: RESULTS OF THE SPANISH MONITORING PROGRAMME ON POPs IN THE PERIOD 2008-2012

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) that entered into force in 2004 in Spain, is a global treaty to protect human health and the environment from POPs¹. This Convention requires Parties to take measures to eliminate or reduce the release of POPs into the environment.

The present study is framed in the Spanish Implementation Plan (SIP) of the Stockholm Convention, managed by the Ministry of the Agriculture, Food and Environment since 2007 to date. The main objective of the SIP is to establish a national monitoring network to characterize the current status and temporal trends of POPs and to evaluate the effectiveness of practices adopted to reduce POP emissions. In 2008 this network began monitoring POPs in air but, afterwards, it has been extended to other matrices such as soil and water.

This work has been focused on investigating POP levels in Spanish air, to elucidate background concentrations and their potential sources. Target analytes were PCDDs, PCDFs, non-ortho PCBs (TnoPCB), mono-ortho PCBs (TmoPCB), i-PCBs (TmPCB), DDTs, HCB, HCHs and PBDEs.

Materials and methods

Sampling

Since summer 2008 a total of 23 sampling campaigns have been conducted. Data shown in the present study correspond to the first seventeen campaigns, including 167 samples. Seven remote locations from an existing sampling network in Spain (European Monitoring and Evaluation Program (EMEP) / Global Atmospheric Watch (GAW) / Control Atmospheric Monitoring Program (CAMP)), and four urban sites close to the remote locations, were chosen as sampling points (Figure 1). Passive air samplers (PASs) with polyurethane foam disks (PUF disks) as the sorbent media were used. These PASs are advantageous because of their low cost, simple construction, and electricity-free operation². At each sampling point, four PUFs were deployed for 3 months, corresponding with each season, and then, collected after exposure. Three of them were used for 2,3,7,8-PCDD/Fs, TnoPCBs (PCB 77, 81, 126 and 169); TmoPCBs (PCB 105, 114, 118, 123, 156, 157, 167, 189); i-PCBs (PCB 28, 52, 101, 138, 153 and 180) and PBDEs determinations (BDE 17, 28, 47, 66, 77, 100, 119, 99, 85, 153, 154, 138, 156, 184, 183, 191, 197, 196, 207, 206 and 209). The fourth one was used for analysis of organochlorine pesticides: TDDT (sum of op '-DDE, pp'-DDE, op '-DDD, pp'-DDD, op'-DDT and pp'-DDT); THCH (sum of α -, β - and γ -HCH) and HCB. A field blank at each station and each sampling period was also deployed.

Prior to deployment, PUF disks (14 cm diameter, 1.2 cm thickness, and 0.03 g/cm³ density) were precleaned by Soxhlet extraction with acetone and diethyl ether, wrapped in aluminum foil and stored in polyethylene bags at -20°C until deployment.³

Samples analysis

Samples were spiked with ¹³C labeled internal standards before Soxhlet extraction in toluene for 24 h. Purification and fractionation stages were performed in an automated Power PrepTM System (FMS, Inc., USA) including multilayer silica, basic alumina and carbon columns.

PCDD/Fs, PCBs, HCB, HCHs and DDTs were analyzed on an Agilent GC 6890, 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 60m x 0.25 mm x 0.25 μ m film thickness (DB-5MS from J&W). PBDEs were determined by GC-qEI-MS on an Agilent 6890 Gas Chromatograph connected to an Agilent 5973 LRMS detector. A 15 m x 0.25 mm x 0.10 μ m film thickness chromatographic capillary column (DB-5MS from J&W) was used for congener

separation. Identification and quantification were carried out using isotopic dilution. All data are blank corrected. Final results are expressed as concentration, considering 4 m³/day as the volume sampled by each PUF disk^{2,4}.

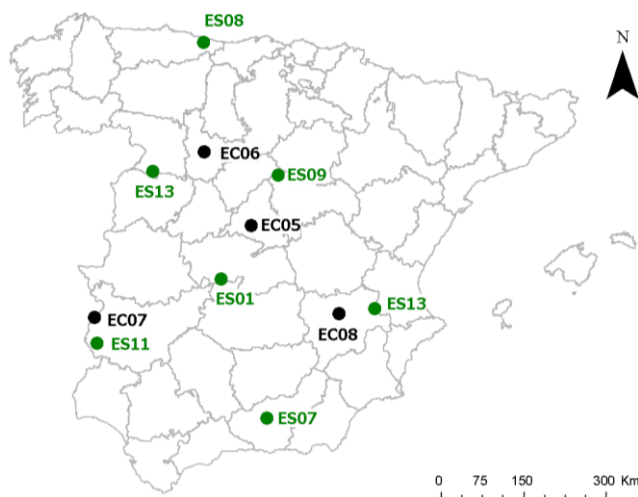


Figure 1. Geographical location of sampling points evaluated: Remote points (ES; Green) corresponding with stations of the EMEP/GAW/CAMP network and urban points (EC; Black).

Data analysis

All statistical analyses were performed with SPSS 17.0 software. In order to represent together the levels of the different pollutant families, data were logarithmically transformed ($1 + \log [X + 1]$, where X is the concentration measured). Information has been obtained both overall and related to remote and urban locations independently.

Results and discussion

Table 1 summarizes concentration (pg/m³) of PCDD/Fs, PBDEs, PCBs, HCB, HCHs and DDTs in the different locations evaluated in the present study. From the global data (n=167), it can be observed the following pattern of concentration: HCB (pg/m³) \approx TDDT (pg/m³) \approx THCH (pg/m³) > TPCB (pg/m³) > TPBDE (pg/m³) \gg TPCDD/F (fg/m³). However, this pattern varies when samples collected in urban areas (TDDT (pg/m³) > TPCB (pg/m³) \approx THCH (pg/m³) > HCB (pg/m³) > TPBDE (pg/m³) \gg TPCDD/F (fg/m³)), are evaluated separately of those associated with remote locations (HCB (pg/m³) \approx TDDT (pg/m³) > TPCB (pg/m³) > THCH (pg/m³) > TPBDE (pg/m³) \gg TPCDD / F (fg/m³)).

Table 1. Average \pm SD, median and range (min-max) concentrations (pg/m³) of PCDD/Fs, PBDEs, PCBs, HCB, HCHs and DDTs obtained in this study.

	Total	Remote	Urban		Total	Remote	Urban
TPCDD/F	0.08 \pm 0.17	0.09 \pm 0.21	0.07 \pm 0.07	THCH	23.98 \pm 16.09	18.31 \pm 10.73	33.81 \pm 18.96
	(0.034)	(0.03)	(0.04)		(20.84)	(17.55)	(30.58)
	0.006-1.78	0.06-0.78	0.006-0.38		0.13-99.24	0.13-58.59	8.04-99.24
TPBDE	9.30 \pm 19.25	4.35 \pm 5.55	17.90 \pm 29.20	HCB	25.72 \pm 16.37	26.38 \pm 17.67	24.57 \pm 13.90
	(3.86)	(2.17)	(10.09)		(23.09)	(23.04)	(23.69)
	0.001-210.64	0.00-26.31	0.00-210.64		0.001-81.44	0.001-81.44	6.68-69.98
TPCB	28.54 \pm 51.55	19.37 \pm 47.17	44.48 \pm 55.25	TDDT	39.12 \pm 75.73	22.64 \pm 19.04	67.23 \pm 117.39
	(11.58)	(9.82)	(30.90)		(20.86)	(18.76)	(38.49)
	0.12-359.26	0.12-359.26	1.28-328.79		0.35-756.80	0.35-109.62	6.05-756.80

Statistically significant differences ($p < 0.05$, Mann-Whitney U test) have been found between the concentrations of TPCDD, TPCDD/F, TnoPCB, TmoPCB, TmPCB, TPCB, TPBDE, THCH and TDDT related to remote and urban areas. These differences are due to the higher levels that present urban areas compared to remote locations.

Furthermore, it has been evaluated the possible variations in the profiles and patterns of the compounds analyzed, between different locations. Average profile and patterns have been also calculated for each sampling point independently and additionally for remote and urban locations. In all cases it has been found a common pattern of congeners: OCDD/F > HpCDD/F > HxCDD/F, TmPCB > TmoPCB >> TnoPCB, BDE 209 >> BDE 47 \approx BDE 99, γ -HCH > α -HCH >> β -HCH, DDE > DDD >> DDT.

POP levels reported in this study has been compared with those from the Global Atmospheric Passive Sampling Network (GAPS)⁵ (Table 2). This comparison is feasible because the GAPS Network uses similar passive sampling systems and performs sampling campaigns also every three months, although PCDD/Fs have not been measured. As can be seen, the levels of Σ PBDE (sum of BDE 47, 99 and 100), Σ HCH and Σ DDE/T evaluated in this study are in the same order of magnitude as those obtained in the GAPS Network.

Table 2. Comparison of concentrations (pg/m^3) of Σ BDEs, Σ PCBs, Σ HCHs and Σ DDTs in the GAPS Network and those obtained in this study. Mean \pm SD, (median) and range.

	GAPS Network, 4 sampling campaigns (January- December 2005)			CIEMAT, 17 sampling campaigns (June 2008- December 2012)		
	TOTAL	No urban ^a	Urban	TOTAL	Remote	Urban
Σ PBDE ^b	5.5 \pm 6.2 (3.9) 0.02-24	5.9 \pm 6.7 (3.9) 0.3-24	4.1 \pm 3.4 (4.1) 0.02-10	1.1 \pm 1.5 (0.5) 0.02 – 10.3	0.7 \pm 1.2 (0.3) 0.03 – 8.8	1.7 \pm 1.8 (1.2) 0.02 – 10.3
Σ PCB ^c	203.8 \pm 610.2 (39) 2-4052	62.2 \pm 109.3 (29.5) 2-702	720.2 \pm 1186.9 (196) 18-4052	28.5 \pm 51.6 (11.6) 0.12 – 359.3	19.4 \pm 47.2 (9.8) 0.12 – 359.3	44.5 \pm 55.2 (30.9) 1.3 – 328.8
Σ HCH ^d	53.8 \pm 110.9 (28) 1-710	29.7 \pm 24.7 (22) 1-119	140 \pm 215.9 (43.5) 12.1-710	22.5 \pm 15.0 (19.7) 0.06 – 85.0	17.2 \pm 10.3 (16.1) 0.06 – 56.6	31.7 \pm 17.3 (29.2) 7.5 – 85.0
Σ DDE/T ^e	72.1 \pm 114.5 (21.2) 0.8-536	62.4 \pm 123.9 (11) 0.8-536	97.3 \pm 83.6 (60) 11-260	24.9 \pm 48.8 (15.4) 0.15 – 589.3	15.4 \pm 12.1 (13.0) 0.15 – 50.1	41.1 \pm 76.3 (22.9) 3.7 – 589.3

^a Rural, polar, agricultural and remote locations. ^b Σ PBDE = sum of BDE 47, 99 and 100. ^c Σ PCB = sum of 48 congeners not specified by GAPS and 22 by CIEMAT. ^d Σ HCH = sum of α - and γ -HCH. ^e Σ DDE/ = sum of pp'-DDE and pp'-DDT.

Although the representativeness of temporal series is low due to the number of sampling campaigns performed (n=17), it can be observed a cyclical trend in the HCB concentrations. As shown in Figure 2, concentrations of this pollutant increase in autumn and winter, decreasing in spring and summer. Similarly to TPCDD/F, there are no differences in the levels of concentration of HCB between urban and remote locations, while levels of TPCB, TPBDE, THCH and TDDT in urban areas are higher than those corresponding to remote ones.

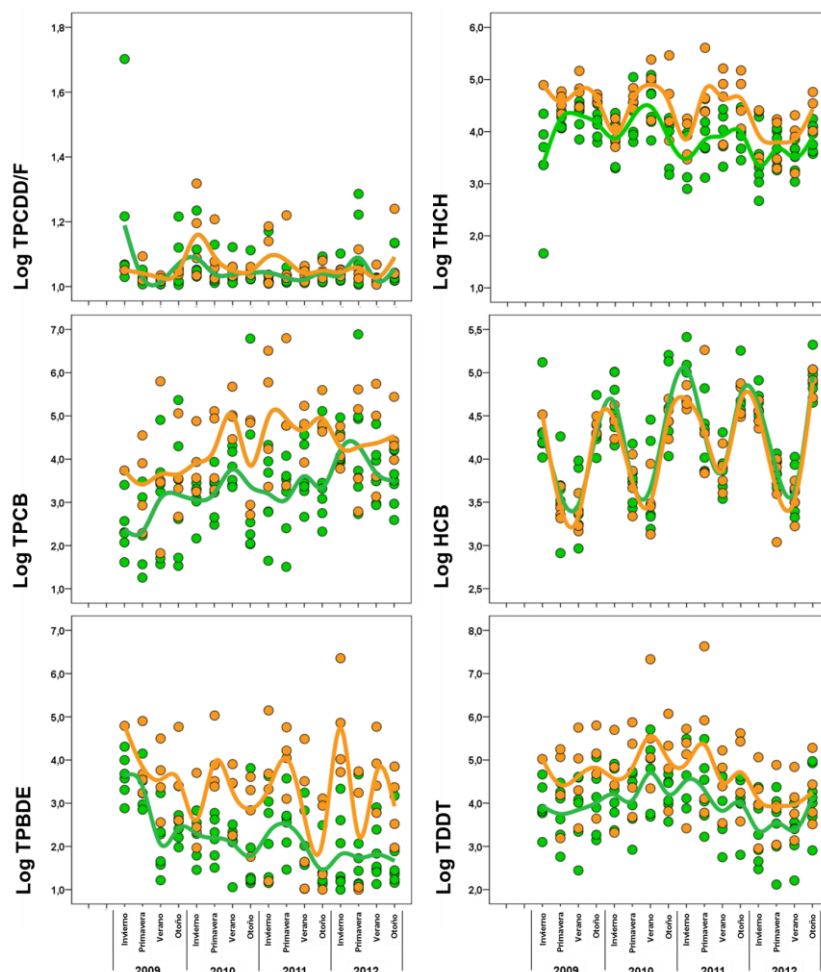


Figure 2. Seasonal trends ($\text{Log}_X = 1 + \log(1 + X)$, where X is the concentration in pg/m^3). Remote (green) and urban locations (orange). The lines represent the average trend.

In order to reach definitive conclusions, including spatial and temporal trends, the maintenance of this POP monitoring plan, involving periodic air samplings throughout the Spanish territory, is estimated mandatory. Only in this way, it will be possible a proper evaluation of the measures taken to reduce the POP levels.

Acknowledgements

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