Cod: 8.3001

PASSIVE AIR SAMPLING TO ASSESS POP AIR CONCENTRATIONS IN SPAIN

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INTRODUCTION

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 encompassing as core part of it a monitoring network to characterize the current status and temporal trends of persistent organic pollutants (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 locations. Sites were selected according to their geographical location in two different but rather homogeneous groups: inner and outer (or coastal) sampling points.

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.

MATERIALS AND METHODS

Sampling:
Data shown in the present study included 211 samples obtained during 21 consecutive sampling campaigns (from summer 2008 to autumn 2013). Seven remote locations from an existing sampling network in Spain (European Monitoring and Evaluation Program/Global Atmospheric Watch/ Control Atmospheric Monitoring Program), and four urban sites close to the remote locations, were chosen as sampling points. Passive air samplers with polyurethane foam (PUF) disks as the sorbent media were used. 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 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) determinations. The fourth one was used for analysis of organochlorine pesticides: 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDTs) and their metabolites (1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (DDEs) and 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (DDDs), hexachlorocyclohexanes (HCHs) and hexaclorobenzene (HCB). A field blank at each station and each sampling period was also deployed.

Chemical 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 60 m x 0.25 mm x 0.25 µm 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 µm 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[1].

RESULTS AND DISCUSSION

Concentration of PCDD/Fs, PBDEs, PCBs, HCB, HCHs and DDT/E/Ds in the different locations were evaluated in the present study, see Figure 1. From the global data (n=211), it can be observed the following pattern of concentration: HCB (pg m^{-3}) > Σ_{18}PCBs (pg m^{-3}) ~ Σ_6DDTs (pg m^{-3}) ~ Σ_3HCHs (sum of α-, β- and γ-HCH; pg m^{-3}) > Σ_{21}PBDE (pg m-3) >> Σ_{17}PCDD/F (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).

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 levels remain similar in both locations probably reflecting background concentrations. This result is in agreement with data reported by the Global Atmospheric Passive Sampling Network (GAPS)[2].

Average congener patterns were obtained independently for each sampling point and also by considering remote and urban locations. In all cases it has been found a common pattern[3]:

• PCDD/Fs: OCDD/Fs > HpCDD/Fs > HxCDD/Fs.
• PCBs: m-PCBs > mono-ortho-PCBs >> non-ortho-PCBs.
• PBDEs: BDE 209 >> BDE 47 ~ BDE 99. Nonabrominated congeners (BDE 207 and BDE 206), presented a relative high contribution to total PBDE content, correlating well with the pattern described by La Guardia et al.[4] for two DecaBDE commercial mixtures (Saytex 102E and Bromkal 82-0DE).
• HCHs: γ-HCH > α-HCH >> β-HCH.
• DDTs: DDEs > DDTs >> DDDs. This DDT pattern could be related to historical use and/or production of dicofol in Spain[5].

These data 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.

ACKNOWLEDGEMENTS
This work has been supported by the Spanish Ministry of Agriculture, Food and Environment under the project "POP monitoring in some matrices and areas of interest". The authors thank The State Meteorological Agency for the permission for the sampling stations and AFC Ingenieros, S.A. and Ingenieros Asesores, S.A. for the diligence and willingness to establish the sampling dates. The authors also wish to thank the GAPS network the availability of the template to determine air sampling rates of POPs sampled using PUF disks.

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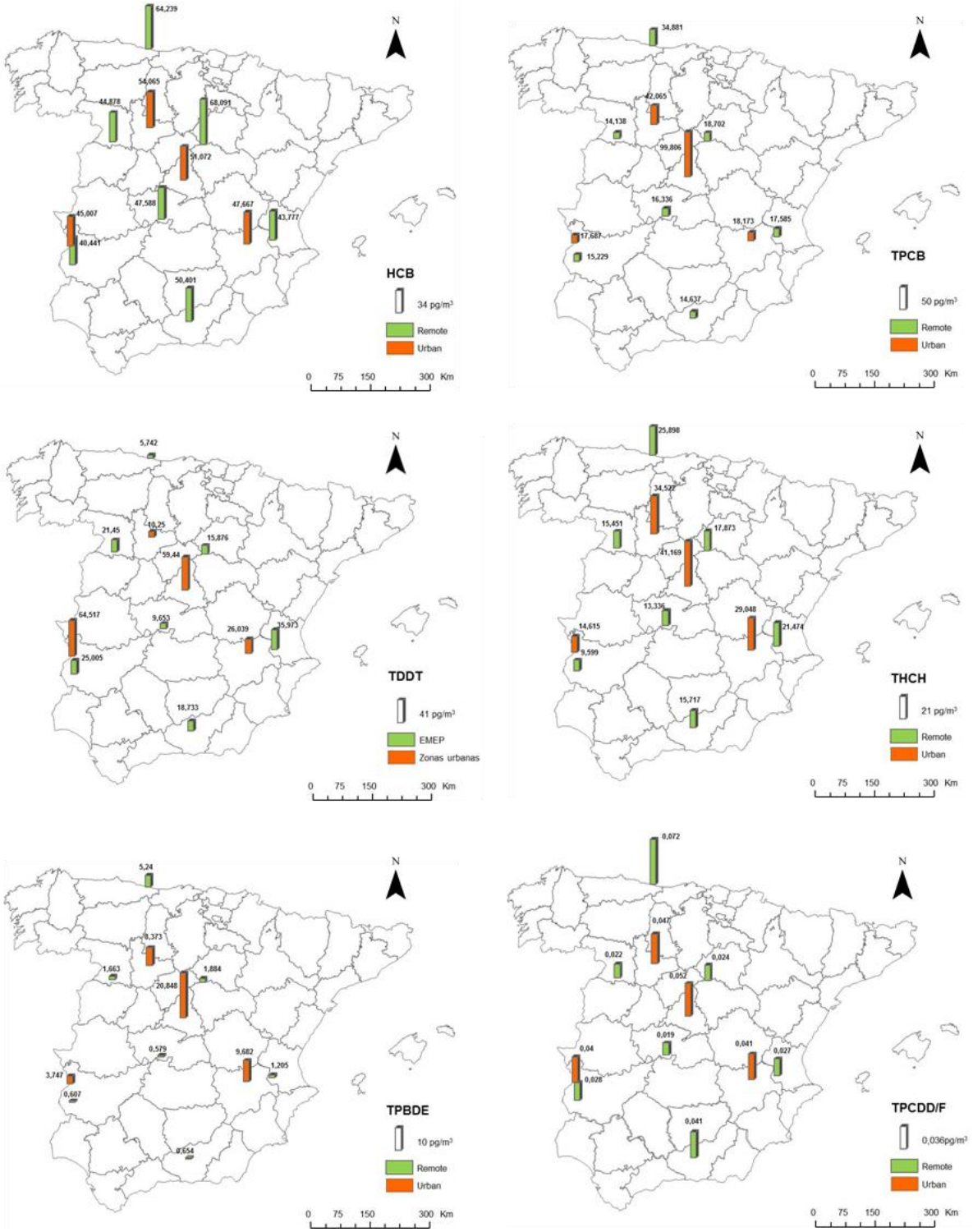

Figure 1. Median concentrations of POPs in remote (green) and urban (orange) sampling sites.