Environmental Pollution 217 (2016) 26-32

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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 ______

ARTICLE INFO

Article history: Received 30 September 2015 Received in revised form 14 January 2016 Accepted 14 January 2016 Available online 1 February 2016

Keywords: Air Persistent organic pollutant Passive sampler Polyurethane foam disks Spanish national implementation plan of stockholm convention

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)), hexaclorobenzene (HCB) and hexachlorocyclohexanes (HCHs), in the Spanish ambient air. Results revealed HCB (49 pg m⁻³; median) as the major pollutant, followed in decreasing order by HCHs (21 pg m⁻³), \sum DDT/E/Ds (20 pg m⁻³), PCBs (20 pg m⁻³), PBDEs (3.3 pg m⁻³) and PCDD/Fs (0.04 pg m⁻³), 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.

© 2016 Elsevier Ltd. All rights reserved.

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), 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

* Corresponding author. E-mail address: adrian.delatorre@ciemat.es (A. Torre). 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, bioaccumulation, toxicity and long-range transport potential. According to this possibility, nine new POPs were added at the fourth conference of the parties: α -, β -, γ -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); pentachlorobenzene (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 napthalenes, 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









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 (Shoeib and Harner, 2002). Prior to deployment, PUF disks (14 cm diameter; 1.2 cm thickness, and 0.03 g cm^{-3} density; TechnoSpec, Spain) were precleaned 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), hexaclorobenzene (HCB) and hexachlorocyclohexane (HCH; *α*-, β- and γ-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 ¹³C-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 $60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{m}$ 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 \times 0.25 mm \times 0.10 um 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) \pm 3s retention time between the analyte and the standard, ii) the ratio of quantifier and qualifier ions had to be within $\pm 15\%$ 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^{-3}) of PCDD/Fs, PBDEs, PCBs, HCB, HCHs and DDT/E/Ds in the different locations evaluated

Download English Version:

https://daneshyari.com/en/article/6314768

Download Persian Version:

https://daneshyari.com/article/6314768

Daneshyari.com