PERSISTENT ORGANIC POLLUTANTS IN EUOPEAN DOMESTIC INDOOR AIR

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Introduction

Air results an ideal matrix in persistent organic pollutant (POPs) monitoring. First, it presents short response time to changes in atmospheric emission, being a highly effective tool in identifying POP sources. It is also a well mixed global transport medium, and therefore its study has been proposed to establish POP background levels[1.] For this reason, presence of POPs in outdoor environment has been studied in depth, however data regarding the extent of the indoor contamination and its significance in terms of overall chemicals exposure is limited. Until recently, indoor air studies have mainly focused in working places where processes involved were identified as potential POP sources. Nevertheless, data is scarce when it comes to domestic indoor air.

The aim of this study was to evaluate the presence of polybrominated diphenylethers (PBDEs), marker polychlorinated biphenyls (PCBs), hexachorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD), dichlorodiphenyldichloroethylene (DDE), and hexachlorocyclohexane isomers (α-, β-, γ-HCB) in domestic indoor air from four European Countries (Belgium, Italy, Portugal, and Spain). Considering this, passive air samplers (PASs) were used, since they are easy to handle, and more cost-effective than active samplers facilitating simultaneous monitoring in distinct locations[2]. In addition, PASs present relative low sampling rates necessitating long sampling periods at low air concentrations, and therefore they provide time weighted average concentrations, that are more appropriate with respect to exposure assessments[2].

Materials and methods

Chemicals
PCBs (including $^{12}C_{12}$ and $^{13}C_{12}$ CB-28, -52, -101, -118, -138, -153, -180, and -208), HCB ($^{12}C_6$ and $^{13}C_6$ HCB), DDTs ($^{12}C_{14}$ and $^{13}C_{14}$ o,p´-, and p,p´-DDT), DDD ($^{12}C_{14}$ o,p-DDD), DDEs ($^{12}C_{14}$ and $^{13}C_{14}$ p,p´-DDE, and $^{12}C_{14}$ o,p´-DDE), and HCHs ($^{12}C_6$ α-, β-, γ-HCH, and $^{13}C_6$ β-, γ-HCH) solutions were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). PBDEs solutions (containing $^{12}C_{12}$ BDE-17. -28, -47, -66, -77, -99, -100, -119, - 138, -153, -154, -156, -183, -184, -191, -196, -197, -206, -207, -209, and $^{13}C_{12}$ BDE-28, -47, -99, -138, -153, -154, -183, -197, -207, -209) were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada).

Sample preparation and deployment
Prior to deployment, PUF disks (14 cm diameter, 1.2 cm thickness, and 0.03 g/cm^3 density) were precleaned by soxhlet extraction with acetone and subsequently diethyl ether for 24 h each[3]. Precleaned PUFs were wrapped in aluminium foil and stored in polyethylene bags at -20ºC until shipment.

Passive air samplers (PASs), precleaned PUFs, and detailed instructions both for setting up the sampling kit (assembly and dismantlement), and choosing the sampling site inside the house, were sent in autumn 2010 to participants from Belgium, Italy, Portugal and Spain. Ten residential houses were evaluated in each country, resulting in a total of 40 air samples. In addition, three field/travel blanks were analyzed in each country. Participants were asked for installing the passive samplers 1.5 m above the ground in the room where the family stays more time (living room, study or bedroom), and trying to avoid windows and direct sunlight. After a sampling period of 3 months, participants returned samples to the laboratory for analysis. Additional details on the use of passive samplers in indoor environments can be obtained elsewhere[2,4,5]. Houses evaluated were selected based on their vicinity to potential sources of contamination such as: farming, car scrapping, and automotive or chemical industries. Presence of potential sources inside the houses were also considered. For this reason, participants completed a questionnaire on housing characteristics, including inhabitants habits (activities

performed at home), and details of the building and the room sampled (presence of textiles and/or electronic devices, type of heating system, frequency of ventilation, among others).

Extraction, cleanup, and instrumental analysis
Prior to extraction, PUFs were spiked with $^{13}C_{12}$ labelled recovery standards ($^{13}C_{12}$-PCBs, $^{13}C_{12}$-PBDEs, $^{13}C_{14}$-DDTs, $^{13}C_{14}$-DDE, $^{13}C_6$-HCB, $^{13}C_6$-HCHs) and then soxhlet extracted with toluene for 24 h. Clean up was performed in an florisil column (6 g activated for 12h at 450ºC) topped with 1 g anhydrous sodium sulphate which was washed with 10 mL hexane and dichloromethane (1:1; v/v). Florisil column was eluted with 25 mL of hexane (first 7 mL were discarded) and subsequently with 60 mL of hexane:dichloromethane mixture (1:1; v/v). Obtained extracts were finally concentrated to incipient dryness under a flow of nitrogen, and re-dissolved in nonane spiked with the injection standards solutions (containing $^{13}C_{12}$-CB 208 and $^{13}C_{12}$-BDE 138). Instrumental analyses were carried out by high resolution mass spectrometry (MicroMass Autospec Ultima HRMS) coupled to an Agilent 6890 gas chromatograph. HRMS was operated in electron ionization mode at a resolution greater than 10,000 (10% valley). Chromatographic separations were carried out with DB5-MS (J&W Scientific) capillary columns. For PBDEs a 15 m column (0.25 mm i.d. x 0.10 μm film thickness) was selected while for PCB, HCB, HCH and DDT separations, a 60 m (0.25 mm i.d. x 0.25 μm film thickness) column was used.

Quality Assurance/Quality Control.
Criteria for quantification were: retention time and isotope ratio found within 2 s and 15 % of the standard, and a signal to noise ratio greater than 5. A total of 12 field/travel blank deployments were analyzed, 3 from each country. Laboratory blanks were also processed and injections of nonane, as instrumental blanks, were used to assess instrument contamination. No significant levels of analytes were found in laboratory blanks, however some field/travel blanks presented POP concentrations. In all cases, levels in these blanks were lower than 5% of those related to the samples. All data are blank corrected.

Results and discussion
Levels of PBDEs, PCBs, HCB, HCHs and DDTs in indoor air are shown in Figure 1. These concentrations (pg m^{-3}) were obtained dividing the mass quantified in each PUF by the number of deployment days, and the congener specific sampling rates (R, m^3 d^{-1}). Sampling rates obtained by Hazrati and Harrad 2007[2], and Abou-Elwafa and Harrad 2010[4], with the same sampler configuration in indoor air, were used. However, for those congeners with no data reported, the following approach was conducted: Octanol air coefficients (Koa)[6] were plotted against R, and the corresponding linear regression plots ($r^2 > 0.77$ for both PBDEs, and PCBs) were utilised to predict sampling rates. R values varied from 0.25 to 1.94 m^3 d^{-1} for BDE-14 and BDE-209, and from 0.7 to 1.27 m^3 d^{-1} for CB-28 and CB-180. For the rest of analytes (HCB, HCHs, DDTs, DDE, and DDDs) sampling rates were assumed to be similar to those obtained for PCBs with same number of chlorines. To compare pollutant levels and avoid the effect of outlier data, discussion of results was based on geometric mean concentrations.

Considering data obtained from the four countries, the major pollutants resulted the HCHs (∑HCH = 277.6 pg m^{-3}; geomean) and the PCBs (∑PCBs= 245.3 pg m^{-3}) following in decreasing order by HCB (107.4 pg m^{-3}) and DDTs (∑DDTs= 94.7 pg m^{-3}), and finally by PBDEs (∑PBDEs= 9.1 pg m^{-3}). Nevertheless, significant differences could be observed between countries when pollutants are evaluated by separate.

Geometric mean concentrations of PCBs (PCBs = sum of CB-28, -52, -101, -118, -138, -153, -180) ranked as follows: Italy (452.0 pg m^{-3}) ≈ Spain (447.8 pg m^{-3}) > Belgium (287.0 pg m^{-3}) > Portugal (62.32 pg m^{-3}). These concentrations are lower than those reported in indoor air from UK[7] (from 0.2 to 39.7 ng m^{-3}) and Canada[8] (from 0.8 to 130 ng m^{-3}). A similar PCB pattern was obtained in all cases, being the lower chlorinated PCBs (CB-25 and CB-52), those with the highest contribution to the total PCB content.
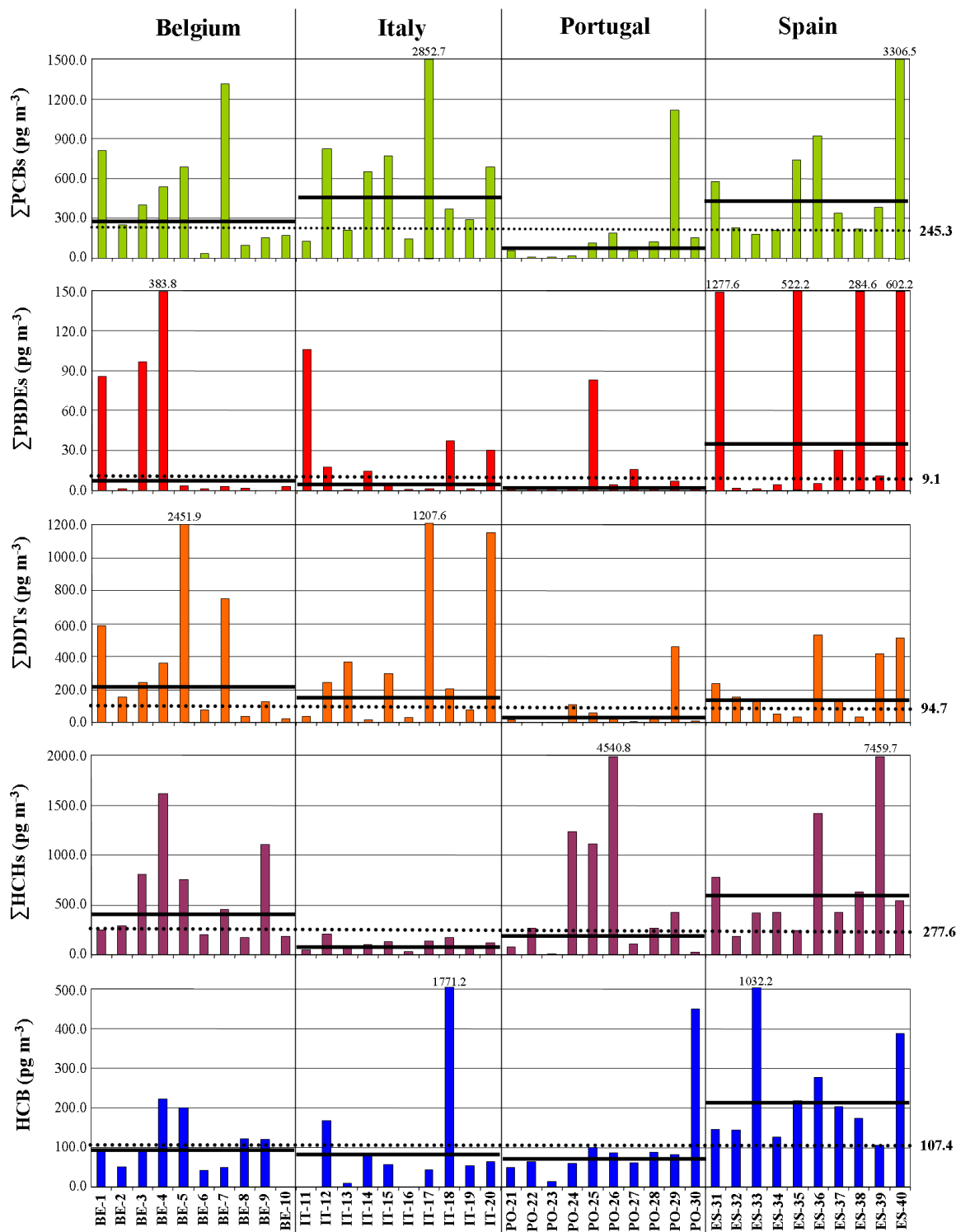
Figure 1.- Concentrations (pg m⁻³) of ∑PCBs (sum of CB-28, -52, -101, -118, -138, -153, -180), ∑PBDEs (sum of BDE-17, -28, -47, -66, -77, -99, -100, -119, - 138, -153, -154, -156, -183, -184, -191, -196, -197, -206, -207, - 209) , ∑DDTs (sum of o,p´-DDT, p,p´-DDT, o,p´-DDD, p,p´-DDE, and o,p´-DDE), ∑HCHs (sum of α-, β- and γ-HCH), and HCB obtained in domestic indoor air. Lines represent geometric means.

Samples from Spain presented higher PBDE levels (∑PBDEs = sum of tri to deca-BDE) than the corresponding to the other evaluated countries: Spain (34.59 pg m^{-3}) > Belgium (8.55 pg m^{-3}) ≈ Italy (6.00 pg m^{-3}) ≈ Portugal (3.78 pg m^{-3}). But in this case, the result is clearly influenced by the high presence of congeners from DecaBDE commercial mixtures (BDE-209, BDE-207, and BDE-206). Excluding these samples, major congeners were BDE-47, -99, and 28. Concentrations found in Spain are similar to those reported in Birmingham (47 pg m^{-3})[7], Ottawa (100 pg m^{-3})[9], and Toronto (74 pg m^{-3})[8] indoor air samples, while levels quantified in Belgium, Italy and Portugal, are in the same range than the ones described in Kuwait (8 pg m^{-3})[10].

Similarly, samples from Spain also revealed higher HCB and HCH (∑HCH = sum of α-, β-, γ-HCH) levels than those obtained in the other countries: Spain (217.3 pg m^{-3}) > Belgium (95.04 pg m^{-3}) ≈ Italy (81.28 pg m^{-3}) ≈ Portugal (73.97 pg m^{-3}) for HCB, and Spain (624.7 pg m^{-3}) > Belgium (431.9 pg m^{-3}) > Portugal (221.35) > Italy (99.41 pg m^{-3}) for HCHs. In all cases, γ-HCH was the major isomer, accounting around 90% to the total HCH content.

Total DDTs (∑DDTs = sum of o,p´-DDT, p,p´-DDT, o,p-DDD, p,p´-DDE, and o,p´-DDE) found in the four countries ranked as follows: Belgium (205.8 pg m^{-3}) ≈ Italy (158.2 pg m^{-3}) ≈ Spain (149.7 pg m^{-3}) > Portugal (16.52 pg m^{-3}). However, there are interesting differences in the DDT pattern between countries. Samples from Italy, Spain, and Portugal presented a high contribution of p,p´-DDE, and o,p´-DDE, while in Belgian samples o,p-DDD was the major isomer.

Outdoor PCB and PBDE concentrations reported in a previous study[11] from Spain were used to calculate indoor to outdoor (I/O) concentration ratios. The I/O calculated with the geometric means was 3 and 15 for PBDEs and PCBs, respectively. This result is consistent with other studies carried out for both PBDEs[7, 8], and PCBs[8, 12], where higher indoor levels were proven.

In summary, this study reports the occurrence of PBDEs, marker PCBs, and pesticides (HCB, HCHs, DDTs, DDE, DDDs) in domestic indoor air from four European countries. To the best of our knowledge, this is the first time DDTs, HCHs, and HCB have been detected in this matrix. Interestingly, levels found in samples from Portugal presented lower values for PCBs and DDTs than those obtained in the other countries. On the other hand, concentrations of PBDEs, HCB and DDTs in samples from Spain reached maximum levels.

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