



Investigating the presence of emerging and legacy POPs in European domestic air

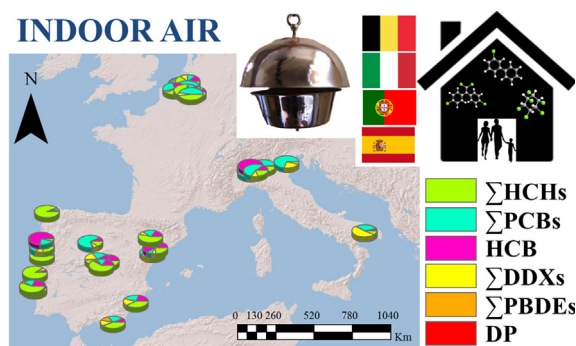
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HIGHLIGHTS

- Lower Σ PCBs and Σ DDXs levels were found at Portuguese homes.
- Italian samples presented lower Σ HCHs concentrations.
- Spanish homes revealed higher HCB and BDE-209 indoor air concentrations.
- Indoor air levels mirrored lindane, dicofol, PentaBDE and DecaBDE use.
- Calculated EDIs via inhalation were 2 to 6 orders of magnitude lower RfDs.

GRAPHICAL ABSTRACT



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ABSTRACT

Presence of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) were evaluated in indoor domestic air from four European countries (Belgium, Italy, Spain and Portugal). The main pollutants were hexachlorohexanes (sum of α -, β - and γ -HCH; Σ HCHs) and Σ PCBs (sum of PCB-28, 52, 101, 118, 138, 153 and 180), with median concentrations of 366 and 306 pg/m^3 , respectively. By decreasing order came hexachlorobenzene (HCB; 130 pg/m^3), Σ DDXs (sum of DDTs, DDEs and DDDs; 94.4 pg/m^3), Σ PBDEs (sum of BDE-17, 28, 47, 66, 99, 100, 153, 154, 183, 206, 207 and 209; 6.08 pg/m^3) and DP (0.30 pg/m^3). Lower Σ PCBs and Σ DDXs levels were found at Portuguese homes compared to Belgian, Italian and Spanish households. Italian samples presented also lower Σ HCHs concentrations while Spanish homes revealed higher HCB and BDE-209 indoor air concentrations than those obtained in the other countries. Σ HCHs, Σ DDXs and Σ PBDE levels mirrored lindane, dicofol and Penta-, DecaBDE use, respectively. The influence of building characteristics, surroundings and inhabitants habits on pollutant air concentrations was investigated. Data generated were used to conduct a human exposure assessment for toddlers and adults with median (P50) and upper (P95) concentrations. Results indicated that health risk posed by inhalation of Σ PCBs, Σ HCHs, Σ DDXs, HCB, Σ PBDEs and DP were 2 to 5 orders of magnitude lower than oral Reference Dose (RfD) values, and 90 (PCB-28) and 12 (γ -HCH) times lower than Minimal Risk Levels (MRLs) for toddlers at the worst case scenario.

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1. Introduction

Persistent Organic Pollutants (POPs) are a wide range of chemicals that possess toxic properties, resist degradation, bioaccumulate and are transported through air and water (UNEP, 2018). They include

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organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethanes (DDTs), hexachlorobenzene (HCB) and hexachlorocyclohexane isomers (α -, β -, γ -HCH), but also polychlorinated biphenyls (PCBs) or halogenated flame retardants (HFRs). Most of these chemicals have been subjected to regulatory directives on a worldwide scale but their intensive and widespread usage combined with environmental stability caused ubiquitous contamination even decades after restrictions that need to be addressed (Audy et al., 2018; Holt et al., 2017; Navarro et al., 2019; Pizzochero et al., 2019; Ricking and Schwarzbauer, 2012). The first studies that evaluated the human risk associated with the presence of POPs focused on working places where processes involved were identified as potential sources (e.i. dismantling plants, offices or even cars). Nevertheless, the population in industrialized countries spends most of the time at residences (toddlers and adults pass 86 and 64% of their time at home, respectively; Pawar et al., 2017), so interest should move to domestic environments. In this sense, the main strategies for pollution monitoring in homes are based on dust analyses due to the ease of sampling, but for volatile chemicals such as PCBs, HCHs, HCB or even some polybrominated diphenyl ethers (PBDEs) air monitoring is mandatory.

Considering all mentioned above, it is of great interest to achieve a better understanding related to the presence of OCPs including α -, β -, and γ -HCH, HCB, DDTs and its metabolites dichlorodiphenyldichloroethanes (DDD), dichlorodiphenyldichloroethylenes (DDEs), PCBs and HFRs (PBDEs and dechlorane plus (DP)) in domestic indoor air. Influence of building characteristics and inhabitant habits in indoor air levels were investigated in order to get evidence of chemical sources. In addition, outdoor sources were hypothesized and assessed due to their possible great importance in the indoor air levels. Finally, generated data were used to calculate inhalation risk assessments for toddlers and adults at central and worst case scenarios. Then, this study allows to extend the current scientific knowledge regarding domestic indoor environments. To reach these objectives, passive air samplers (PASs) were deployed in homes from Belgium, Italy, Portugal and Spain. PAS has made the quantification of pollution in indoor air easier. They are easy to handle and more cost-effective than actives and their small sampler footprint and silent operation are ideal for non-disruptive use indoors (Bidleman and Melymuk, 2019). In addition, PASs present relatively low sampling rates necessitating long sampling periods, and therefore they provide time weighted average concentrations, that are more appropriate with respect to exposure assessments (Audy et al., 2018; Demirtepe et al., 2019; Holt et al., 2017; Melymuk et al., 2016; Wang et al., 2019; Yadav et al., 2017).

2. Materials and methods

2.1. Chemicals and materials

PCBs (including $^{12}\text{C}_{12}$ PCB-28, 52, 101, 118, 138, 153 and 180 and $^{13}\text{C}_{12}$ PCB-28, 32, 52, 70, 101, 118, 127, 128, 138, 153, 170, 180 and 208), HCB ($^{12}\text{C}_6$ and $^{13}\text{C}_6$ HCB), DDTs ($^{12}\text{C}_{14}$ and $^{13}\text{C}_{14}$ o,p'-, and p,p'-DDT), DDDs ($^{12}\text{C}_{14}$ and $^{13}\text{C}_{14}$ o,p'-, and p,p'-DDD), DDEs ($^{12}\text{C}_{14}$ and $^{13}\text{C}_{14}$ p,p'-DDE, and $^{12}\text{C}_{14}$ o,p'-DDE), HCHs ($^{12}\text{C}_6$ and $^{13}\text{C}_6$ α -, β -, and γ -HCH) and Dechlorane Plus (DP, $^{12}\text{C}_{14}$ and $^{13}\text{C}_{14}$ *syn*-DP and *anti*-DP) solutions were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). PBDE solutions (containing $^{12}\text{C}_{12}$ BDE-17, 28, 47, 66, 77, 85, 99, 100, 119, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209, and $^{13}\text{C}_{12}$ BDE-28, 47, 99, 138, 153, 154, 183, 197, 207, 209) were acquired from Wellington Laboratories Inc. (Guelph, ON, Canada). Passive sampler kits, comprising stainless steel bowls, rods and fixings were purchased from Lancaster University (United Kingdom). PUF disks were acquired from TechnoSpec (Spain).

2.2. Sample preparation and deployment

Prior to deployment, polyurethane foam (PUF) disks (14 cm diameter, 1.2 cm thickness, and 0.03 g/cm³ density) were precleaned by

Soxhlet extraction with acetone and subsequently diethyl ether for 24 h each. Precleaned PUFs were wrapped in aluminum foil and stored in polyethylene bags at -20 °C until shipment. Passive air samplers, 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 to participants from Belgium (B1 to B10 samples), Italy (I1 to I10), Portugal (P1 to P10) and Spain (S1 to S10). To minimize indoor temperature differences among countries (19 ± 3 °C; mean \pm SD), sampling was carried out from October 2010 to January 2011. Ten residential houses were evaluated in each country, resulting in a total of 40 air samples. Besides, three field blanks were collected in each country. Participants were asked for installing the passive samplers 1.5 m above the ground for resembling the breathing zone in the room where the family stays more time (living room, study or bedroom). After a sampling period of 3 months, all participants returned samples to CIEMAT laboratory where samples were stored at -20 until analysis. Houses were selected according to availability and distributed across the four countries (Fig. 1). The presence of both indoor and outdoor potential sources was evaluated using data collected by questionnaires (Table S1).

2.3. Extraction, clean up, and instrumental analysis

Prior to extraction, PUFs were spiked with ^{13}C labeled recovery standards ($^{13}\text{C}_{12}$ PCB-28, 52, 101, 118, 138, 153 and 180, $^{13}\text{C}_{12}$ BDE-28, 47, 99, 153, 154, 183, 197, 207 and 209, ^{13}C -DDT, DDE and DDD, ^{13}C -HCB, and ^{13}C -HCHs) and then Soxhlet extracted with toluene for 24 h. Clean up was performed in a florisil column (6 g activated for 12 h at 450 °C) topped with 1 g anhydrous sodium sulphate which was conditioned 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). Finally, extracts were concentrated to incipient dryness under a flow of nitrogen, and re-dissolved in nonane spiked with the injection standards solutions (containing $^{13}\text{C}_{12}$ -PCB-32, 70, 127, 128, 170, 208 and $^{13}\text{C}_{12}$ -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 and DP a 15 m column (0.25 mm i.d. \times 0.10 μm film thickness) was selected while for PCB, HCB, HCH and DDX separations, a 60 m (0.25 mm i.d. \times 0.25 μm film thickness) column was used.

2.4. Quality assurance and quality control

The mean recoveries of surrogates ranged from 69 to 93%, from 75 to 92% and from 83 to 104% for PCBs, OCPs and HFRs, respectively. Field blanks (3 per country), laboratory blanks and injections of nonane, as instrumental blanks, were analyzed. Only field blanks presented POP concentrations for some analytes, but never exceeded 10% of the quantities quantified in samples. All measured values were blank corrected by subtracting the mean value of field blanks at each country. Method detection limits (MDLs) were defined as the average field blank levels plus three times the standard deviation (Table S2). These were converted to concentrations by dividing by the average air volume. For those compounds not detected in field blanks, instrumental detection limits were used for MDL calculations.

2.5. Estimation of human intake via inhalation

Estimated Daily Intakes via inhalation ($\text{EDI}_{\text{inhalation}}$, pg/kg bw/day) were calculated for two different age classes, toddlers (12–35 months age) and adults (18–64 years age), as shown in Eq. (1) and described elsewhere (Barbas et al., 2018; Cequier et al., 2014; Johnson-Restrepo and Kannan, 2009; Yadav et al., 2017).

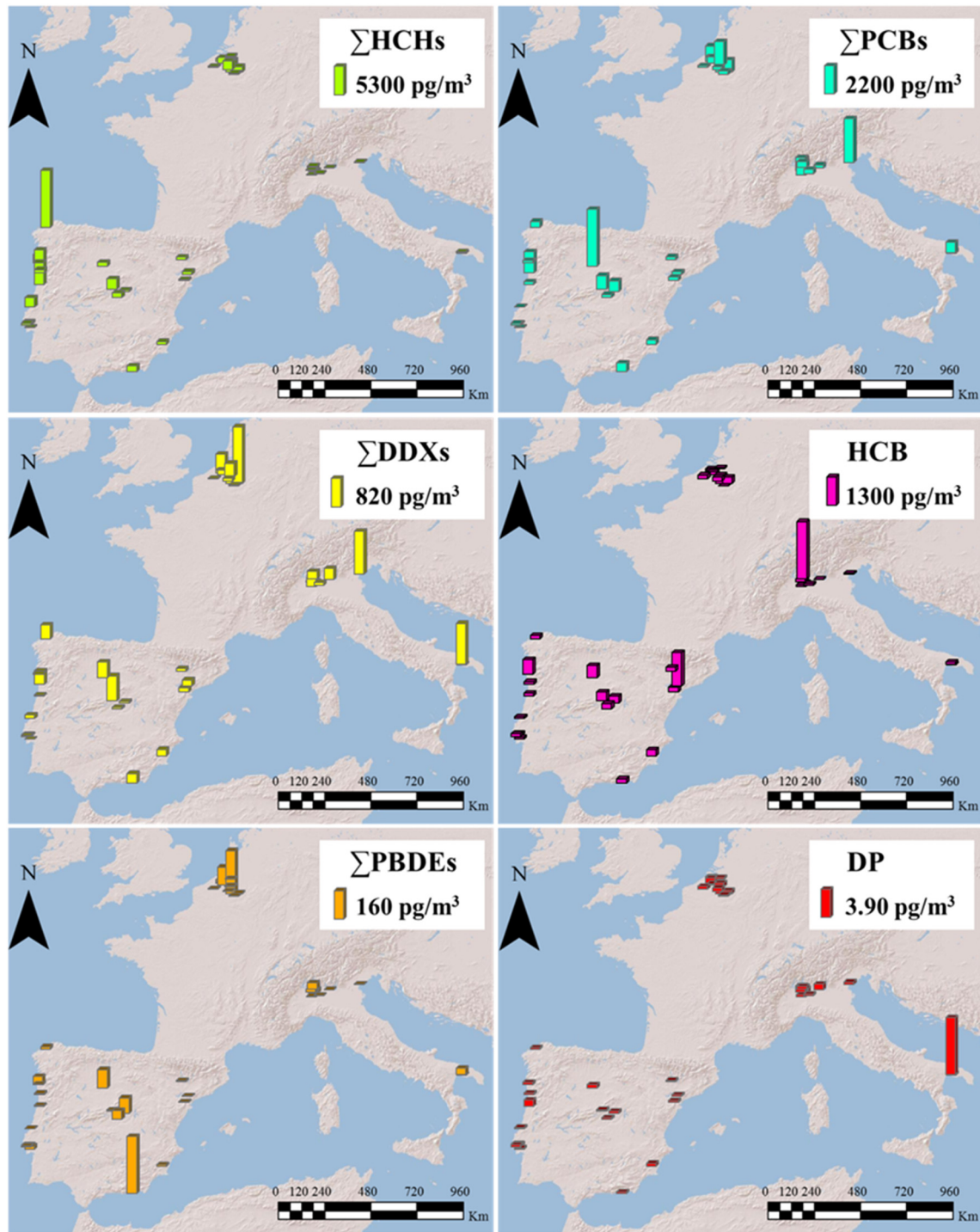


Fig. 1. Geographical distribution of indoor air concentrations (pg/m^3) of ΣHCHs , ΣPCBs , ΣDDXs , HCB, ΣPBDEs and DP.

$$EDI_{\text{inhalation}} = \frac{(C \times IR \times HEF)}{BW} \quad (1)$$

where C is the indoor air concentration (pg/m^3) at central (50th percentile; P50) and worst case scenario (95th percentile; P95), IR is the daily inhalation rate ($7.6 \text{ m}^3/\text{day}$ for toddlers and $13.3 \text{ m}^3/\text{day}$ for adults; US EPA, 2011), HEF is the indoor home exposure fraction (86% for toddlers and 64% for adults; Pawar et al., 2017) and BW is the body weight (13.8 kg for toddlers and 80 kg for adults; US EPA, 2011).

2.6. Statistical analysis

Statistical analyses were performed with IMB® SPSS® Statistics V26. Analyte concentrations were not normally distributed (Shapiro-Wilk W and Kolmogorov-Smirnov tests), hence Spearman rank correlation coefficient was derived to investigate bivariate relationship and H Kruskal-Wallis with Bonferroni post-hoc tests were used to evaluate differences between groups. Nondetects were replaced by MDLs divided by the square root of 2. For exploring bivariate associations (Spearman test)

values <MDLs were removed. A significant level of $p < 0.05$ (two sided) was accepted and only statistically significantly results were discussed.

3. Results and discussion

Levels of PCBs, HCHs, DDXs, HCB, PBDEs and DP in indoor air are shown in Fig. 1. Complementary, main statistics and geographical differences are listed in Table S3 and Fig. 2, S1–S6. Indoor air concentrations (pg/m^3) were obtained dividing the mass measured in each PUF by the number of deployment days, and the congener specific sampling rates (R_s , m^3/day). However, the main challenge using PUF-PAS lies in the determination of R_s . When using outdoor, these can be site-specific calculated based on the loss of depuration compounds, but for indoor monitoring, the addition of these chemicals is not allowed to avoid pollutants released at homes. In this case, practical assessments using field calibration with active samplers could be conducted. In the present study, sampling rates of $0.63 \text{ m}^3/\text{day}$ for PCBs and OPCs, including HCHs DDXs and HCB (Audy et al., 2018) and $1.56 \text{ m}^3/\text{day}$ for PBDEs (tri to decaBDE) and DP (Venier et al., 2016) were assumed. The adoption of these sampling rates seems appropriate since both works were conducted with the same sampler design (double-dome PASs) and placed in a similar way (sitting on a surface) as the present study.

Collectively, the major pollutants resulted the ΣHCHs (sum of α -, β - and γ -HCH; $366 \text{ pg}/\text{m}^3$ median) and the ΣPCBs (sum of PCB-28, 52, 101, 118, 138, 153 and 180; $306 \text{ pg}/\text{m}^3$) following in decreasing order by HCB ($130 \text{ pg}/\text{m}^3$) and ΣDDXs (sum of o,p' -DDT, p,p' -DDT, o,p' -DDD, p,p' -DDD, o,p' -DDE and p,p' -DDE; $94.4 \text{ pg}/\text{m}^3$), and finally by ΣPBDEs (sum of BDE-17, 28, 47, 66, 99, 100, 153, 154, 183, 206, 207 and 209; $6.08 \text{ pg}/\text{m}^3$) and DP (sum of *syn*-DP and *anti*-DP; $0.30 \text{ pg}/\text{m}^3$).

3.1. PCBs

Mixtures of PCBs were used in several industrial and commercial applications since the 1920s, peaked in the 1960s and 1970s, and ceased in most countries by the end of the 1970s and early 1980s (IARC, 2016). Therefore, concentrations of ΣPCBs in the four countries ranging from 7.27 to $4348 \text{ pg}/\text{m}^3$ evidenced that four decades after most countries banned their production and use (Directive 85/467/CEE) PCBs remain at high concentrations in indoor environments. Interesting differences were found among countries (Table S3 and Fig. S1). Samples from Portugal presented statistically significantly lower ΣPCB air levels ($97.8 \text{ pg}/\text{m}^3$; median) compared to the other countries (427, 616 and $413 \text{ pg}/\text{m}^3$; Belgium, Italy and Spain). Demirtepe et al., 2019 detected a significant relationship between PCB use per capita and median air concentrations. A similar approach was conducted with data raised

in the present study. Country specific default estimated for ΣPCB consumption from 1930 to 2000 (Breivik et al., 2002) were divided by population in 1975 (maximum PCB use) as shown in Table S4. Results of global PCB use per capita (172, 158, 89.7 and $14.5 \text{ g}/\text{cap}$, Belgium, Spain, Italy and Portugal) were in agreement with quantified indoor air concentrations and would imply less PCB contamination in Portuguese environment. To the best of our knowledge, there are no previous studies on PCBs from Belgian, Portuguese or Spanish residential indoor air. Nonetheless, Italian levels were in the low end of those reported by Menichini et al., 2007 (1.9 to $8.3 \text{ ng}/\text{m}^3$; Table S5) in samples collected by active sampling from buildings in Rome. Unfortunately, this city was not covered in our study. PCB levels measured here were comparable with those described for homes from France, United Kingdom, Czech Republic, Slovakia, Sweden, Mexico, Canada, USA, or Australia (Alliot et al., 2014; Audy et al., 2018; Bohlin et al., 2008; Demirtepe et al., 2019; Harrad et al., 2006; Melymuk et al., 2016; Moreau-Guigon et al., 2016; Wang et al., 2019; Zhang et al., 2011; Table S5).

As could be expected PCB composition in air from the four countries was dominated by the less chlorinated congeners PCB-28 (39% contribution to ΣPCBs ; Fig. S1), PCB-52 (31%) and PCB-101 (16%) since these have higher vapor pressure than the more highly chlorinated ones (Table S2). Congener profile evaluation can be a useful tool when identifying POP sources. However, in PCB case it is difficult because commercial products were marketed under more than one hundred different trade names (Aroclor, Apirolo, Blacol, Clophen, Chlorophen, Delor, Frenchlor, Phenochlor, Kanechlor, Pyralene, Pyrochlor or Tarnol among others), with great congener composition variation depending on the place of manufacture, production process, and batches (BIPRO, 2005; IARC, 2016). Once formulated, the composition could be altered by weathering, released to the environment, transport, partitioning or chemical transformation, making it very difficult to identify the commercial mixture used 40 years ago. Assuming these pitfalls, findings in the present study could reflect the major use of technical mixtures of low chlorine content (Aroclor 1232, 1016, 1242 1248 and Clophen A30, A40, Delor 103; Breivik et al., 2002). Nevertheless, Spearman correlation matrix (Table S6) differentiated two groups for PCBs, indicating a different origin for congeners with a great chlorinate degree. This is the case of samples I4 and P9, which presented low values for PCB-28, -52 and -101 (<35% of ΣPCB content) and high levels of PCB-180 (174 and $145 \text{ pg}/\text{m}^3$; samples I4 and P9), PCB-153 (358 and $552 \text{ pg}/\text{m}^3$) and PCB-138 (132 and $297 \text{ pg}/\text{m}^3$) compared to median European values (2.46 , 17.5 and $10.2 \text{ pg}/\text{m}^3$; PCB-180, -153 and -138; Table S3) suggesting the use of PCB mixtures with a high contribution of hexa- and heptachlorinated homologs (Aroclor 1260, 1262, Clophen A60; Breivik et al., 2002). Data from questionnaires collected from homes I4 and P9

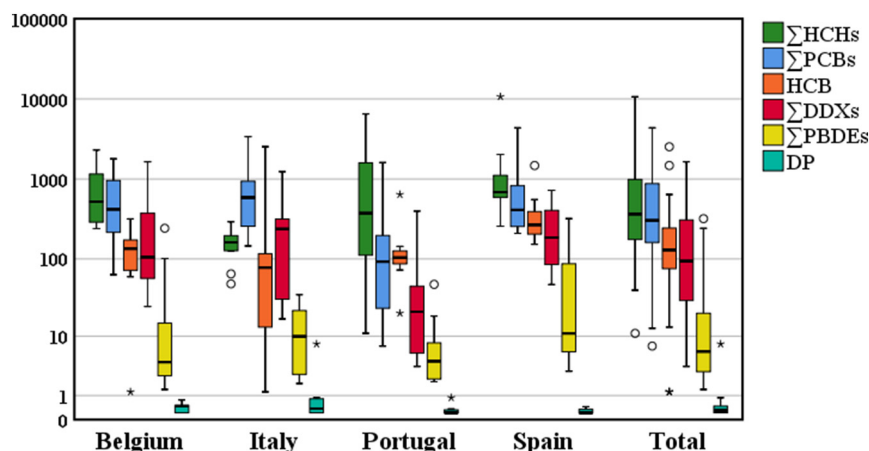


Fig. 2. Box plot of air concentrations (pg/m^3) of the ΣHCHs , ΣPCBs , HCB, ΣDDXs , ΣPBDEs and DP in homes.

were investigated. Unfortunately, no unequivocal source could be identified to explain such findings and only the presence of an electrical power station close to P9 could be hypothesized. Until 1986, mixtures of PCBs were widely used as dielectric fluids in electrical equipment such as oil-cooled transformers and capacitors (Directive 85/467/CEE). Thereafter, only articles in service may be used and maintained according to the provisions of Directive 1996/59/EC; phase out of all equipment >500 ppm until 2010 and equipment 50–500 at end of lifetime. Contribution from these so-called “closed” systems could not be dismissed since it has been estimated that 48% of the PCB production had been used in transformer oil, 21% for small capacitors, 10% for other closed systems and finally 21% for open uses (BIPRO, 2005; UNEP, 2016). Nonetheless, when indoor environments were investigated major sources are associated with the latter, including plasticizers, paints, varnishes, adhesives, waxes, additives in cement and plaster, sealants, fire retardants, wood treatment preparations, surface coatings, wire insulators, and metal coating (BIPRO, 2005; de Voogt and Brinkman, 1989; IARC, 2016). Influence of building characteristics, surroundings or inhabitants habits on PCB air levels was evaluated (Tables S6 and S7), but sources were not identified. Similar results were reported by Hazrati and Harrad, 2006, which authors considered to reflect the complexity of relationships between indoor air contamination and microenvironment characteristics. A positive correlation was obtained for PCB-52 and indoor temperature ($r_s = 0.419$; $p < 0.01$; Table S6), which is in agreement with previous studies (Hazrati and Harrad, 2006; Lyng et al., 2016). PCBs were also used as carrier substances of pesticide (BIPRO, 2005; de Voogt and Brinkman, 1989; IARC, 2016), which could be responsible for the positive intercorrelations found for PCBs and some OPCs (HCHs, DDXs, and HCB; Table S6). Such findings will be discussed later.

As shown in Fig. 1 and S1, from the forty samples evaluated in this study, two clearly stood out ($\Sigma\text{PCBs} = 4.35$ and 3.38 ng/m³; S10 and I7). In neither case, evaluation of data gathered in the questionnaires revealed an indoor source. The Italian home was located in the city of Venice, which is a well-known PCB polluted area owing to the proximity to Marguera Harbour an important industrial district (Manodori et al., 2006). The Spanish home S10 was sited in Valladolid, near an industrial park (<1 km) and a car factory (<3 km). Both outdoor activities could be considered as PCB sources. To delve into the outdoor influence on indoor PCB levels, two households located near PCB historical manufacturing facilities were selected. Home I3 is sited in Brescia (Italy) where the chemical industry Caffaro produced 31,092 t of PCBs from 1958 to 1983. Sample S3 was located in Flix (Spain) where 29,012 t of PCBs were manufactured by Ercros SA between 1955 and 1984 (de Voogt and Brinkman, 1989). Both industries were responsible for PCB contamination in surrounding areas (Colombo et al., 2013; Garí et al., 2014). On contrary to what could be expected, ΣPCB concentrations quantified in these homes (257 and 209 pg/m³; I3 and S3) were well below Italian (616 pg/m³) and Spanish (413 pg/m³) median values, suggesting that these historical PCB production facilities may not represent a major pollution source. A similar scenario was reported by Demirtepe et al., 2019 for the Chemko Strážske plant located in Slovakia. Nevertheless, considering the strong influence of temperature on atmospheric PCB concentrations (Currado and Harrad, 2000), results must be viewed with caution since indoor sampling was conducted during autumn and winter, when low outdoor temperatures may not contribute to the PCB re-volatilization from local polluted areas.

3.2. HCHs

Concentrations of ΣHCHs ranging from 10.9 to 10,657 pg/m³; Table S3) are in the same range with those recorded in homes from the Czech Republic, Slovakia, Sweden, United Kingdom, Mexico, Canada and USA (Audy et al., 2018; Bohlin et al., 2008; Demirtepe et al., 2019; Table S8). Samples from the four countries presented a similar HCH isomer pattern (Fig. S2), which was clearly dominated by γ -HCH (91%)

compared to α -HCH (6%) and β -HCH (3%). HCH is an insecticide produced by chlorination of benzene which has been extensively used worldwide since the 1940s (Breivik et al., 1999). HCH was available in two formulations: technical HCH, where α -HCH was the dominating isomer (55–80%; Breivik et al., 1999) followed by β -HCH (5–14%), γ -HCH (8–15%), δ -HCH (2–16%) and ϵ -HCH (1–5%), and lindane (purified γ -HCH, $\approx 100\%$), the isomer with the highest insecticidal activity. Considering this, the ratio of α/γ -HCH could be used to identify emission sources by distinguishing the application of technical HCH (α/γ -HCH around 4–5) from the use of lindane (α/γ -HCH far below 1; Bohlin et al., 2008; Navarro et al., 2019). When this evaluation is carried out from air samples it must be taken into account that the subcooled vapor pressure of α -HCH is an order of magnitude higher than γ -HCH (Table S2). This difference would imply a higher α/γ -HCH ratio in air compared to marketed formulations. Therefore, α/γ -HCH ratios ranging from 0.01 to 0.44 (Table S3), clearly suggested the past use and/or air transport from other regions of lindane. This result was not strange since the European Union Directive 79/117/EEC caused a ban of technical HCH in 1979 within the EU Member States, and thereafter lindane became the dominating HCH source in Europe. However, it should be noted that while the four countries in the present study revealed a clear lindane origin, ΣHCHs quantified in Italian homes (162 pg/m³; median) were lower ($p < 0.05$; Table S3 and Fig. S3) compared to Belgian (536 pg/m³), Portuguese (375 pg/m³) and Spanish (693 pg/m³) households. HCH use was banned in Portugal since 1974 and Belgium severely restricted the use of lindane to veterinary use and wood protection since 1989 (Breivik et al., 1999). In contrast, Spain and Italy were among the top 10 countries with the highest lindane usage in Europe between 1950 and 2000 (Vijgen, 2006), but reasons for the lower levels measured in indoor air from Italy are unclear. After technical HCH ban, the EU decided a complete phase-out of lindane by the EC regulation on POPs (EC 850/2004) restricting its use to the professional remedial and industrial treatment of lumber, timber and logs and indoor industrial and residential applications until 1.9.2006, and as an intermediate in chemical manufacturing (technical HCH) and for use as public health and veterinary topical insecticide (lindane with γ -HCH purity > 99%) until 31.12.2007. Detached residences presented higher HCH levels than flats (Table S7) but home characteristics and inhabitant habits did not shed light on this difference. The same happened for sample S9, which went up to the maximum level of HCH (Fig. 1 and S2), but unfortunately, no indoor or outdoor sources could be identified. ΣHCH concentration (10.7 ng/m³) quantified in this home exceeded the maximum residential indoor level reported to date (7.82 ng/m³; Audy et al., 2018). This home was sited in A Coruña (Fig. 1), one of the biggest Spanish marine ports (unloading of goods). A Coruña is around 150 km from O Porriño, where the pharmaceutical company Zeltia dumped 1000 t of lindane production waste from 1947 to 1964 (Vega et al., 2016). The waste was dispersed during the years due to road construction and urban development. Nonetheless, the O Porriño influence in house S9 should be considered low, since other houses located closer to this hotspot showed much lower HCH concentrations (1592, 606 and 40 pg/m³; P5, P9 and P10).

Organochlorine pesticides indoor uses included the treatment of different kinds of wood, construction materials, furniture, floors and roofs against insects, fungi and mold. To meet these demands, both pure products and mixtures of several chemicals were marketed and used. For example, Pentalidol (Holt et al., 2017) and Hylotox® (Schieweck et al., 2007) were commercial formulations combining HCHs and DDTs among other chemicals. Moreover, as stated early, PCBs were used as pesticide extenders and there are evidence of PCBs and DDTs combined use as a wood preservative for indoor applications (Audy et al., 2018). Considering all mentioned above, it is not strange to find positive intercorrelations among different OCPs or even PCBs in indoor air (Table S6). As expected quantified α -, β - and γ -HCH air concentrations were positive correlated ($r_s > 0.625$; $p < 0.01$). Nevertheless, while α - and β -HCH levels were also associated with the more volatile

PCBs (PCB-28 and 52; $r_s > 0.568$, $p < 0.01$) and some DDEs and DDDs, γ -HCH did not. Therefore it is plausible to believe that α - and β -HCH indoor levels may partially originate from their presence in OCP combined formulations.

3.3. DDXs

Levels of Σ DDXs in indoor air ranging from <MDL to 1645 pg/m^3 (Table S3) could be associated to the historical production and/or use of technical DDT and dicofol, an organochlorine pesticide manufactured from DDT by hydroxylation resulting in the presence of DDT or DDT related compounds as impurities. Differentiation of technical DDT and dicofol emission used intensively o,p' -DDT/ p,p' -DDT ratios, assuming that technical DDT contains less o,p' -DDT than p,p' -DDT, while o,p' -DDT has a higher portion than p,p' -DDT in dicofol case (Qiu et al., 2005). Different values of o,p' -DDT/ p,p' -DDT ratios have been reported for both technical DDT and dicofol formulations (Table S9), but in general, they were lower than 0.25 for technical DDT. This approach can be somewhat simplistic since DDT isomeric composition in the air can be influenced by environmental processes (Ricking and Schwarzbauer, 2012) and isomeric specific physical-chemical properties, especially higher subcooled vapor pressure of o,p' -DDT isomer compared to p,p' -DDT (Table S2) may result in higher o,p' -DDT/ p,p' -DDT ratios in the air than those expected from commercial formulations. It cannot be ruled out that the high o,p' -DDT/ p,p' -DDT ratios calculated here (from 0.51 to 4.90, Table S3 and Fig. S7) indicating dicofol-based contamination, may be influenced by preferential mobilization of o,p' -DDT from contaminated soils to air. However, a dicofol origin will be also in agreement with the fact that while DDT production and application were banned in Europe in the early 1970s and 1980s (Pacyna et al., 2003), dicofol use continued until 2009 (Directive 2008/764/EC) in some countries. Dicofol was used as a plant protection product used on a wide variety of fruits, vegetables, ornamentals and field crops (OSPAR Commission, 2008). The presence of DDT and DDT related compounds in dicofol formulations was restricted to 0.1% since 1978 (European Community Directive 79/117/EEC, amended by Council Directive 90/533/EEC). Nevertheless, this percentage was exceeded in products marketed before (up to 23% in old dicofol from Italy; Muccio et al., 1988) and after (up to 14% in Turkey; Turgut et al., 2009) this date, which could represent an important DDXs source.

Portugal's homes revealed lower Σ DDX levels (21.7 pg/m^3 , median Table S3 and Fig. S3) compared to the other countries (109, 239 and 185 pg/m^3 ; Belgium, Italy and Spain). Again, this result reinforced a dicofol origin because the use of dicofol in Europe was banned in 2009 by Directive 2008/764/EC, but Portugal limited the target crops (citrus fruits, wine grapes and cucurbits with inedible peels) for dicofol and thereby the use of it 8 years early (OSPAR Commission, 2008). Contrarily to what could be expected, Σ DDX levels in Belgian, Italian and Spanish households showed homogeneous data. Spain and Italy were the only places where European production and formulation of dicofol have taken place until 2009, while six years early (2003) Belgium declared dicofol end of use (UNECE, 2010). Besides, a lower dicofol Belgian usage (Pacyna et al., 2003) and calculated emission inventories (20 kg/year ; Denier van der Gon et al., 2007) compared to those for Spain (12,500 kg/year), Italy (9500 kg/year) or even Portugal (486 kg/year) have been documented. Once in the environment, DDT undergoes degradation to DDD and DDE (Ricking and Schwarzbauer, 2012) being the ratio of p,p' -DDE to p,p' -DDT a good indicator for DDT resident time in the environment. Interestingly, Belgian indoor air levels presented lower p,p' -DDE/ p,p' -DDT ratios (Table S3 and Fig. S7) and higher DDT contribution to Σ DDT content (Fig. S3) compared to the other countries, which may denote fresher DDT input.

Around 1500 t/year of dicofol were produced until 2009 in a chemical facility in Monzón (Spain) operated by Montecinca S.A (UNECE, 2010). Considering this, a home (S4) located close (<2 km) to this facility was included in the present study. Concentration obtained for the

Σ DDXs in this sample (85.2 pg/m^3) was below the Spanish median (185 pg/m^3), suggesting that the presence of the factory did not represent a DDX pollution source. Dicofol is produced by hydroxylation of DDT, but the producer could purchase DDT and use it as a feedstock or make DDT as intermediate in house. Montecinca S. A. manufactured dicofol following the later procedure and produced DDT in house from chloral, monochlorobenzene and oleum (OSPAR Commission, 2008), eliminating the need to transport and store DDT itself, which reduced the possibility of dispersion of this contaminant. Another well-known DDT potential pollution source in Spain is the chloro-alkali plant located in Flix (sample S3). This facility produced 31,750 t of DDT between 1945 and 1971 and there is evidence that the manufacture of this chemical caused high pollution in the area including DDT mobilization to the atmosphere (Garí et al., 2014). Nevertheless, relatively low Σ DDX concentration (176 pg/m^3), together with o,p' -DDT/ p,p' -DDT (1.74) and p,p' -DDE/ p,p' -DDT (44.4) ratios in home S3, did not suggest DDX contamination coming from this source. The maximum Σ DDX concentration was found in a home (B5, 1645 pg/m^3 ; Fig. S3) located in Namur (Belgium). To the best of our knowledge, there was no clear DDT outdoor source in the surroundings and only the inhabitants gardening habits described in the questionnaires could be a DDX source. In this sample, o,p' -DDT/ p,p' -DDT (1.89) and p,p' -DDE/ p,p' -DDT (1.0) ratios, suggested a not very old dicofol usage.

3.4. HCB

Levels of HCB ranging from <MDL to 2531 pg/m^3 were comparable to those determined in other world areas (Table S8). Spanish samples presented higher ($p < 0.01$) HCB levels (268 pg/m^3 ; median) compared to Belgium (135 pg/m^3), Italy (77.5 pg/m^3) and Portugal (105 pg/m^3). This geographic pattern was consistent with the higher HCB historical usage and emission inventories made for the period 1970–2000 (Denier van der Gon et al., 2007; Pacyna et al., 2003). HCB was first introduced in 1933 as a fungicide for seed treatment and crops in agriculture and gardening, with an estimated global production between 10,000 and 30,000 t/year in the late 1970s (Pacyna et al., 2003). Nonetheless, HCB fungicide use was banned in the European Union 40 years ago. HCB is still being generated as a by-product and/or impurity in several chemical processing, such as the manufactured of chlorinated pesticides, chlorine and chlorinated solvents, and combustion processes like waste incineration, coal and wood combustion and the production and processing of metals or even fireworks (Audy et al., 2018; Bailey, 2001; Barber et al., 2005; Navarro et al., 2019), which represent 83% of total HCB emission in UNECE-Europe countries (Denier van der Gon et al., 2007). Results from the present study gave a hint to these secondary sources, especially for the maximum HCB values assessed in Italy and Spain (Fig. S4). To the best of our knowledge, the highest concentration of HCB in residential air described to date (1.5 ng/m^3) was measured by Audy et al., 2018 in a home from the Czech Republic. This value was similar to the concentration recorded at S3 and clearly exceeded by sample I8 (2531 pg/m^3). Home I8 was sited in Seveso (Italy), a location known worldwide for the accident that occurred in ICMESSA chemical plant in 1976. There are evidences that the accident caused the emission of 2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-TCDD), ethylene glycol, trichlorophenol, sodium chloride and sodium hydroxide (Fattore et al., 2003), but to the best of our knowledge, no data regarding HCB have been reported. Studies conducted by Fattore et al., 2003 to assess whether dioxins released during the accident and still present in soils could pollute the air, identified emissions from the combustion of wood residues from furniture factories as a source of dioxin and furans. Thus, considering HCB has been used as a wood-preserving agent, and it is also released to the environment by incomplete combustion (Audy et al., 2018; Bailey, 2001; Barber et al., 2005; Pacyna et al., 2003) these potential sources could not be disregarded. The other maximum value (S3; 1.48 ng/m^3) was obtained in a home located in Flix (Spain), whereas previously mentioned, a

chlorine related industry produced PCBs and DDT between 1959 and 1987. As discussed for PCBs and DDXs in contrast to what would be expected, sample S3 did not reach high values for DDT or PCBs, however, HCB air concentration was in agreement with high HCB outdoor atmospheric levels (mean 35 ng/m³) reported in the area (Grimalt et al., 1994), highlighting the emission of HCB as a by-product in the synthesis of organochlorine products.

HCB air levels were positive associated with PCB-28, α - and β -HCH ($r_s > 0.445$; $p < 0.01$, Table S6) and on a lesser extent with γ -HCH ($r_s = 0.361$; $p < 0.05$). Again, associations within OCPs in indoor air would imply a similar source that could be related to building characteristics or inhabitant habits but this was not demonstrated here. There were no significant differences when building or room type, surroundings, nor activities performed at home comparison was carried out (Table S7). Nevertheless, it is important to note that these chemicals (HCB, PCB-28 and HCHs) present higher vapor pressures compared to the rest of the analytes (Table S2). In fact, HCB air concentrations revealing a positive relationship with the indoor temperature ($r_s = 0.443$; $p < 0.01$; Table S6) suggested the volatilization of previously deposited HCB as a potential source. It is worth to mention that, HCB air concentrations were correlated with Σ PBDEs ($r_s = 0.524$; $p < 0.01$) but also with the number of electric and electronic devices (EEDs) in the room where PAS was located ($r_s = 0.402$; $p < 0.05$) and the total EED use at home ($r_s = 0.440$; $p < 0.01$). For some time HCB was also used as a fire retardant in plastics and as softener especially for PVC (Pacyna et al., 2003), which could explain these results.

3.5. Halogenated flame retardants

Σ PBDE indoor air concentrations ranged from <MDL to 320 pg/m³. Levels in the four countries were statistically indistinguishable (Table S3) and in the same range as those described worldwide (Table S10). Only 12 out of the 21 measured PBDEs were above MDL in the PUFs. As expected, higher quantification frequencies were obtained for the lower brominated and more volatile congeners BDE-47 (95%), BDE-28 (60%) and BDE-99 (55%) compared to BDE-209, 206 and 207 (23%). Nonetheless, the presence of nonaBDEs and BDE-209 in the PUF evidence the appropriateness of the use of PASs to provide also reliable data for higher molecular weight compounds. Differences in quantification frequencies made it difficult to evaluate PBDE congener patterns (Fig. S5). However, it could be observed that in Belgian, Italian and Portuguese households the predominant congener was BDE-47 (55%; mean). Similar results were described in homes from Norway (Cequier et al., 2014), Slovakia (Demirtepe et al., 2019), Kuwait (Gevao et al., 2006), Canada, Czech Republic and USA (Johnson-Restrepo and Kannan, 2009; Venier et al., 2016). On the contrary, samples from Spain presenting higher BDE-209 levels and contribution (34%) to Σ PBDEs, are in line with studies conducted in France (Moreau-Guigon et al., 2016), UK (Tao et al., 2016), Sweden (Thuresson et al., 2012) or Nepal (Yadav et al., 2017). Although the use of PentaBDE and DecaBDE commercial mixtures is currently prohibited worldwide (UNEP, 2018), Spearman's correlation matrix corroborates the historical use of both formulations in Europe. It is also noteworthy that associations were found among PentaBDE (BDE-47, 99 and 100; $r_s > 0.812$, $p < 0.05$; Table S6) and DecaBDE (BDE-209, 206 and 207; $r_s > 0.900$, $p < 0.01$) congeners separately. At first, this result may suggest different application areas, but it could be highly influenced by the different volatility of congeners. The presence of DecaBDE in the PUF is associated with particulate matter while PentaBDE congeners are mainly in the gas phase (de la Torre et al., 2018). Spearman tests showed a moderate positive relationship for some of the more volatile congeners (BDE-28, 47 and 99, $r_s > 0.398$, $p < 0.05$) and indoor temperature but only DecaBDE congeners were influenced by the room where the PAS was placed (Bedroom > living room, kitchen or office; Table S7). These results reflect the high spatial variability that the PBDEs could present within the home. Reason for Σ PBDE maximum level (320 pg/m³; sample S1) was unclear.

Nevertheless, it was particularly interesting the high contribution of nonaBDEs (sum of BDE 206 and 207; 27%) to total PBDE content in this sample. Home S1 was located in Almeria, a Spanish province with the largest concentration (30,000 ha) in the world of plastic greenhouses. Previous studies have evidenced photodegradation of BDE-209 as a source of nona- and octaBDEs (Bezares-Cruz et al., 2004; Shih and Wang, 2009). Therefore considering that Almeria is subjected to a high solar irradiance (>5 kWh/m²/day; annual mean; CIEMAT, 2020) it could be speculated that exposition of greenhouse plastics to direct sunlight could be responsible for this PBDE congener pattern. Further research is needed to confirm this hypothesis in the future.

Although DP made up a small fraction of total HFRs, its presence in indoor air samples is of major importance. Quantification frequency (55%) and indoor air concentrations (<MDL-7.79 pg/m³; min-max) for DP decreased in great extent compared to PBDEs, which is not strange considering that sampling was conducted in 2010–2011 when the flame retardant market was still heavily dominated by PBDEs (Venier et al., 2016). DP concentrations in the four countries did not reveal significant differences and were in the same range to those reported with passive and active samplers in homes from Norway (Cequier et al., 2014), UK (Tao et al., 2016), Slovakia (Demirtepe et al., 2019), USA (Venier et al., 2016), China (Ren et al., 2018) or Nepal (Yadav et al., 2017), but lower than data described for the Czech Republic and Canada (Melymuk et al., 2016; Venier et al., 2016) (Table S11). To date, only two DP producers have been identified. Commercially available mixtures present anti-DP fractions (f_{anti}), calculated as the concentration of the anti-DP divided by the sum of syn-DP and anti-DP, of around 0.75 (OxyChem; Sverko et al., 2011) and 0.60 (Anpon, China; Wang et al., 2010), but once in the environment it has been described that anti-DP presents higher degradation rates and can be subjected to isomerization processes towards the syn-DP (Sverko et al., 2011). Therefore, as the distance to the emission source increases, it could be expected a f_{anti} decrease. f_{anti} values determined in the present study for the four countries (0.63 median; Table S3) closely resembles technical products and underlined an indoor origin. DP has been used as a flame retardant since the 1960s in wide range applications like electronic wiring and cables, plastic roofing materials, and hard plastic connectors in televisions and computer monitors, and furniture (UNEP, 2019). Nevertheless, the Spearman test showed the inexistence of correlations for DP and home characteristics that could support this origin (Table S6). Furthermore, no significant associations were found among DP and other targeted analytes, including DecaBDE congeners (BDE-209, 206 and 207) which results of special interest since DP is currently marketed as a replacement for DecaBDE (UNEP, 2019). Only 7 samples aroused values for BDE-209 and DP above MDL but in these homes levels of DP were significantly lower than BDE-209 (Fig. S8), indicating a lower use of the former compared to the latter in the four countries. As happened for BDE-209, DP is mainly associated with particles in the atmosphere (de la Torre et al., 2018) so its presence in the PUF samples corroborates again the PAS feasibility to collect particles and allow direct evaluation of their air concentrations.

3.6. Implications for human exposure

The results of inhalation risk assessment are included in Table 1. As a consequence of the high levels of HCHs and PCBs in indoor air, the estimated inhalation intakes of these pollutants are also comparatively high. Ranking of inhalation risks showed that Σ HCHs and Σ PCBs gave high-end scenario (P95) intakes of 887–360 and 659–267 pg/kg bw/day (toddler–adults) which are consistently greater than the estimate Σ DDXs, HCB, Σ PBDEs and DP inhalation intakes, 416–169, 241–97.7, 39.0–15.8 and 0.31–0.13 pg/kg bw/day, respectively. Unfortunately, only a few studies of inhalation toxicity have been published and there is a profound lack of data on Reference Concentration for Chronic Inhalation Exposure (RfCs) for substances evaluated here. Therefore, oral Reference Dose (RfD, chronic or subchronic; US EPA, 2020) and

Table 1

Estimated Daily Intakes via inhalation (EDI inhalation pg/kg bw/day) calculated for toddlers and adults at central (P50) and upper (P95) scenarios. Daily reference dose (RfD) and Minimal Risk Levels (MRL) in pg/kg bw/day.

	Toddlers		Adults		MRL ^a	RfD ^d
	P50	P95	P50	P95		
PCB-28	31.2	215	12.7	87.2	2.0E+04 ^b	
PCB-52	35.5	147	14.4	59.4	2.0E+04 ^b	
PCB-101	18.5	189	7.51	76.7	2.0E+04 ^b	
PCB-118	4.78	62.5	1.94	25.3	2.0E+04 ^b	
PCB-138	3.58	71.8	1.45	29.1	2.0E+04 ^b	
PCB-153	6.17	130	2.50	52.5	2.0E+04 ^b	
PCB-180	0.87	47.6	0.35	19.3	2.0E+04 ^b	
∑PCBs	108	659	43.8	267		
α-HCH	6.07	51.0	2.46	20.7	8.0E+06	8.E+06
β-HCH	3.08	12.8	1.25	5.18	6.0E+05	
γ-HCH	121	866	49.0	352	1.0E+04	3.0E+5
∑HCHs	129	887	52.3	360		
o,p'-DDE	2.43	25.9	0.98	10.5		
p,p'-DDE	20.6	193	8.38	78.1		
o,p'-DDD	2.83	43.7	1.15	17.7		
p,p'-DDD	3.14	41.7	1.27	16.9		
o,p'-DDT	1.83	30.8	0.74	12.5		
p,p'-DDT	0.67	29.3	0.27	11.9	1.0E+05	3.0E+04
∑DDXs	33.3	416	13.5	169		
HCB	45.7	241	18.5	97.7	7.0E+04	8.0E+05
BDE-17	0.01	0.45	0.00	0.18		
BDE-28	0.14	2.44	0.06	0.99		
BDE-47	0.64	16.6	0.26	6.73	3.0E+03 ^c	1.0E+05
BDE-66	0.01	0.23	0.004	0.10		
BDE-99	0.09	3.49	0.04	1.42		1.0E+05
BDE-100	0.02	0.76	0.01	0.31		
BDE-153	0.01	0.99	0.005	0.40		2.0E+05
BDE-154	0.01	0.42	0.01	0.17		
BDE-183	0.03	0.27	0.01	0.11		
BDE-206	0.04	0.77	0.02	0.31		
BDE-207	0.05	0.79	0.02	0.32		
BDE-209	0.19	28.4	0.08	11.4	2.0E+05	7.0E+06
∑PBDEs	2.14	39.0	0.87	15.8		
syn DP	0.03	0.14	0.01	0.06		
anti DP	0.07	0.18	0.03	0.07		
DP	0.11	0.31	0.04	0.13		

^a ATSDR, 2020.

^b Aroclor 1954.

^c Lower brominated.

^d US EPA, 2020.

Minimal Risk Levels (MRLs, chronic or intermediate; ATSDR, 2020) were used to evaluate the toxicity of quantified indoor levels. Calculated EDI_{inhalation} even at worst case scenario were 2 to 5 orders of magnitude lower than RfDs, which at first suggested a negligible exposure risk via inhalation. However, calculated upper EDIs via inhalation for PCB-28 and γ-HCH were only 90 and 12 times lower than MRLs in toddlers case. Route to-route extrapolation of inhalation benchmarks from oral reference values may underestimate risks especially for volatile pollutants like PCBs of which inhalation exposure could account for up to 61% of total exposure for children (Lehmann et al., 2015). Therefore, estimated exposures provided in the present study are of high relevance and could help to support exposure and exposure-response assessment for inhaled pollutants.

4. Conclusions

In summary, this study reports the occurrence of PBDEs, PCBs, and OCPs (HCB, HCHs, DDTs, DDEs, DDDs) in domestic indoor air from four European countries. To the best of our knowledge, this is the first time that some of these pollutants are described in households from Belgium, Italy, Portugal and Spain. Interestingly, levels found in samples from Portugal exhibited lower values for PCBs and DDXs than those obtained in the other countries. Italian samples presented also lower

ΣHCH concentrations. On the other hand, concentrations of BDE-209 and HCB in samples from Spain reached higher levels. Influence of building characteristics and inhabitant habits only seems to affect BDE-209 (bedrooms > other rooms), γ-HCH (houses > flats) and HCB (EED use) levels. Besides, historical chlorine related industry for HCB and industrial areas for PCBs were identified as outdoor sources. Inhalation risk assessments were conducted for non-occupationally exposed population. Calculated EDIs via inhalation for more volatile compounds were only 1 order of magnitude lower than MRLs in toddlers case, arousing high concern over their potential health impacts and highlight the importance to develop RfCs for these pollutants.

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CRediT authorship contribution statement

Adrián de la Torre: Data curation, Formal analysis, Investigation, Validation, Visualization, Writing - original draft. **Paloma Sanz:** Data curation, Investigation, Methodology, Writing - review & editing. **Irene Navarro:** Investigation, Methodology, Writing - review & editing. **María de los Ángeles Martínez:** Conceptualization, Funding acquisition, Investigation, Project administration, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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