Traditional and novel halogenated flame retardants in urban ambient air: Gas-particle partitioning, size distribution and health implications
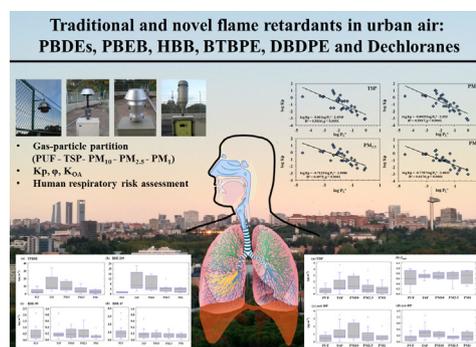
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HIGHLIGHTS

- PBDE affinity for particulate matter increases with congener bromination degree.
- DP levels obtained in TSP were higher than those in the gas phase (PUF).
- Active and passive samplers derived similar PBDE and DP concentrations.
- Hazard quotients for PBDEs and DP reflect low cancer risk through inhalation.
- PBDEs were the FR with the highest levels followed by DP, mirex, PBEB, and BB-153.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Urban ambient air samples, including gas-phase (PUF), total suspended particulates (TSP), PM_{10}, $PM_{2.5}$ and PM_1 airborne particle fractions were collected to evaluate gas-particle partitioning and size particle distribution of traditional and novel halogenated flame retardants. Simultaneously, passive air samplers (PAS) were deployed in the same location. Analytes included 33 polybrominated diphenyl ether (PBDE), 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), dechloranes (Dec 602, 603, 604, 605 or Dechorane plus (DP)) and chlordane plus (CP). Clausius-Clapeyron equation, gas-particle partition coefficient (K_p), fraction partitioned onto particles (φ) and human respiratory risk assessment were used to evaluate local or long-distance transport sources, gas-particle partitioning sorption mechanisms, and implications for health, respectively. PBDEs were the FR with the highest levels (13.9 pg m^{-3}, median TSP + PUF), followed by DP (1.56 pg m^{-3}), mirex (0.78 pg m^{-3}), PBEB (0.05 pg m^{-3}), and BB-153 (0.04 pg m^{-3}). PBDE congener pattern in particulate matter was dominated by BDE-209, while the contribution of more volatile congeners, BDE-28, -47, -99, and -100 was higher in gas-phase. Congener contribution increases with particle size and bromination degree, being BDE-47 mostly bounded to particles ≤ PM_1, BDE-99 to > PM_1 and BDE-209 to > $PM_{2.5}$. No significant differences were found for PBDE and DP concentrations obtained with passive and active samplers, demonstrating the ability of the formers to collect particulate material. Deposition efficiencies and fluxes on inhaled PBDEs and DP in human respiratory tract were calculated. Contribution in respiratory track was dominated by head airway (2.16 and 0.26 pg h^{-1}, for PBDE and DP), followed by tracheobronchial (0.12 and 0.02 pg h^{-1}) and alveoli (0.01–0.002 pg h^{-1}) regions. Finally, hazard quotient values on inhalation were proposed (6.3 × 10^{-7} and 1.1 × 10^{-8} for PBDEs and DP), reflecting a low cancer risk through inhalation.

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1. Introduction

Flame retardants (FR) are chemicals added to a wide variety of materials like electric and electronical equipment, textiles, paints and construction products, among others, to increase their fire resistance, retarding their ignition and reducing the human and material damages of fire. For these reasons their use saves lives and avoids large economic costs. However, there are increasing evidences that it also causes harm to the people health and ecosystems. Therefore, it has triggered the implementation of successive regulations regarding their use, commercialization or production (i.e. inclusion of hexabromobiphenyl and polybrominated diphenyl ethers (PBDE) commercial mixtures (c-pentaBDE, c-octaBDE and c-decaBDE) in annex A of Stockholm Convention). As a result of this, chemical industry has been forced to design, produce and use non-regulated compounds capable of satisfying market requirements in terms of fire prevention. This is the case of decabromodiphenyl ethane (DBDPE), a proposed substitute for c-decaBDE mixture in Europe (ECB, 2007), whose use is expected to exponentially grow in the coming years due to restriction from March 2019 of c-decaBDE use (EU, 2017). There are a lot of traditional and novel halogenated flame retardants, including PBDEs, polybrominated biphenyls (PBBs), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) or dechloranes (Dec 602, 603, 604, 605 or Dechorane plus (DP)) and related compounds (chlordane plus (CP)), whose presence in the environment should be monitored to (i) identify substitution patterns, (ii) study their presence and mobilization patterns across environmental compartments, and (iii) evaluate the implication that their presence implies for human health.

Atmosphere has been described as a very important route for human and ecosystem exposure to this pollution. It is also a well-mixed global transport matrix, which presents short response time to pollution phenomena, resulting its monitoring an effective tool for the establishment of consumption patterns and source identification. Considering flame retardant uses, it is not strange that most of air quality studies focused on these chemicals had been performed in urban areas, where anthropogenic activities can be identified as main potential sources. Moreover, in these locations, the availability of electric supply makes possible the use of active samplers, which allow to collect separately gas and particulate phases, very useful data when carrying out risk analysis studies. However, to establish background levels and to identify contamination phenomena and locate their sources, it is essential to obtain at the same time representative samples of remote or background locations. In these sites, there is often no electrical supply, and it is necessary to resort to passive samplers (PAS). Air passive sampling has been carried out for many years, however the use of this sampling method can raise some doubts (i) when establishing the air volumes sampled and (ii) to clearly discern the aerosol phase (gas or particulate) that has been sampled. The first one has been saved from extensive studies carried out by Harner and coworkers, who have developed reliable tools to obtain the volume sampled by PAS (Harner, 2017). There is also a general consensus that PAS sample mainly gas phase, although it has been proven that they also collect a part of particulate matter (PM; Holt et al., 2017), requiring further studies to determine the particle retention degree.

The present study is aimed at evaluating the results derived with both samplers (active and passive air samplers) in urban outdoor air in Madrid (Spain), and to consider the seasonality and the influence of meteorological parameters like temperature, relative humidity, solar radiation among others, in the results obtained and their comparability. To achieve these objectives, an annual experiment was designed to obtain samples of gas phase (PUF). Given the importance of particulate matter size on human health effects, particulate matter with an aerodynamic diameter (d_{ae}) equal or <10 μm (PM$_{10}$), 2.5 μm (PM$_{2.5}$), 1 μm (PM$_1$) and total suspended particulates (TSP) were sampled. Simultaneously, PAS were deployed at the same site. Presence of traditional

and emerging halogenated flame retardants was evaluated in all matrices, in order to later study their gas-particle partitioning, size particle distribution and congener profiles. Besides, data were used to estimate the implications that the presence of these compounds in ambient air could cause to human health.

2. Materials and methods

2.1. Sample collection

Sixty-eight ambient air samples (n = 68) were collected in the city of Madrid during fifteen sampling campaigns, from January to December 2013 (winter, n = 3; spring, n = 3; summer, n = 5; autumn, n = 4; Table S1). Samplings were carried out at the Center for Energy, Environmental and Technological Research (CIEMAT, 40° 27′27″ N, 3° 43′ 23″ W), one of the twenty-three sampling stations belonging to the National Environmental Monitoring Network of POPs, within the Spanish Plan of Implementation of the Stockholm Convention and the Global Monitoring Plan of POPs (UNEP, 2015). The site can be classified as an urban background station (EEA, 1999), as (i) it is located >50 m from the traffic emission sources, with not >2500 vehicles per day within a radius of 50 m, (ii) there are no industrial point sources in the area, and (iii) sources of small scale domestic heating with coal, fuel, oil or wood, or small boiler houses are >50 m away from the measurement point. The weather station of CIEMAT monitors at this site meteorological parameters such as air temperature, atmospheric pressure, relative humidity, wet precipitation, solar irradiance and wind speed and direction. All samples were taken on days with a stable weather forecast, without precipitation. Gas and particle phases were collected simultaneously using four high-volume active samplers (HVS, CAV A/m model; MCV Spain) working at 30 m³ h⁻¹ flow rate (1020 m³ per sample). Polyurethane foam cylinders (PUF, 10 cm diameter, 10 cm height, and 0.03 g cm⁻³ density; TechnoSpec, Spain) and circular glass fiber filters (GFF, 15 cm diameter; 0.26 mm thickness; GF/A grade; Whatman, UK) were used for gas phase and particle sampling, respectively. Prior to use, GFFs were wrapped in aluminum foil and heated at 450 °C for 24 h to remove any organic contaminant. They were weighed and stored in a controlled temperature (20 ± 1 °C; mean ± SD) and humidity (50 ± 5%) weighing chamber until sampling, following the reference standards for the gravimetric determination of particulate matter in ambient air (EN 12341:1999; EN 14907:2006). One of the HVSs was equipped with a circular filter holder to collect TSP, followed by a PUF holder (CBE-CAV model; MCV, Spain) in order to sample the gas phase. The remaining HVSs were equipped with PM$_{10}$ and PM$_{2.5}$ (PM1025-CAV model; MCV Spain), and a PM$_1$ (DIGITEL DPM01/30/ 00) cutoff inlet. A silicone spray (Dow Corning, USA) was applied to the impaction plate placed after the cutoff nozzles, to prevent the bouncing of coarse particles, which may cause their re-introduction into the air flow and collection in the GFF. Passive air samplers with PUF disks as the sorbent media were used for passive sampling as described elsewhere (Shoeib et al., 2004). 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 aluminum foil and stored in polyethylene bags at −20 °C until deployment. PAS were deployed for 1 and 2 months (Table S1). Active (n = 12) and passive (n = 8) field blanks were also collected. Specific sample air volumes were calculated according to the Tom Harner Template (Harner, 2017, see Supplementary material Eq. (S1)).

2.2. Chemical analysis

Complete details about chemical analysis have been previously reported (de la Torre et al., 2016). Briefly, samples were spiked with ¹³C-labelled surrogate standards (Table S2) including PBDEs, DBDPE, BTBPE, BB-153, HBB, and DP congeners, and Soxhlet extracted with

toluene for 24 h. Extract obtained was solvent exchanged into hexane prior to cleanup. The cleanup was performed in two steps. First a manual purification was conducted, by solid-liquid adsorption chromatography on an open column (20 g acid silica modified with 44% H_2SO_4), eluted with 150 mL of hexane. The extract was concentrated in a rotary evaporator and purified in an automated Power Prep™ System (FMS, Inc., USA) including silica, alumina and carbon columns. Prior to HRGC-HRMS, samples were concentrated to dryness under a flow of nitrogen and redissolved in nonane spiked with internal standards (Table S2). Brominated flame retardant (PBDEs, DBDPE, PBEB, HBB, BB-153 and BTBPE) instrumental analysis was performed by high resolution mass spectrometry (Micromass Ultima NT HRMS) operated in electron ionization mode EI, 10,000 resolving power (10% valley). Dechloranes (*syn*-DP, *anti*-DP, Dec 602, -603, 604, CP and Mirex) instrumental analysis was carried out by low resolution mass spectrometry (Agilent 5973 MSD) operated in electron capture negative ionization (ECNI). Both mass spectrometers were coupled with high resolution gas chromatographs (Agilent 6890N) fitted with 15 m DB-5-MS capillary columns (0.25 mm id, 0.10 μm film thickness; J&W Scientific). Complete details for both methods are shown in Table S3.

2.3. Quality assurance/quality control

In order to ensure a correct identification and quantification of analytes, three criteria were used: i) ± 2 s retention time between the analyte and the standard, ii) the ratio of quantifier and qualifier ions within ±15% of the theoretical values and iii) a signal to noise ratio >3:1. Quantification was carried out using isotopic dilution method. The average recovery of surrogates (Table S4) ranged from 69 to 97% for PBDEs, 62–107% BTBPE, 87–114% BB-153, 45–81% HBB and 77–83% TDP. The limits of detection (LODs, Table S5) of the method were calculated as the concentration corresponding to a signal-noise ratio ≥ 3 and ranged between 0.01 and 100 fg m^{-3} for BDE-77 and *anti*-DP. Injections of nonane, as instrumental blanks, were used to assess instrumental contamination. Field and procedural blanks were treated as samples through the entire process. Concentrations of all analytes in both procedural and field blanks were below LODs. Effect of the silicone spray applied on the inlets was evaluated. No significant differences were found between blanks with or without silicone spray.

2.4. Data analysis

Statistical analyses were performed with Statgraphics Centurion™ XVII software. In order to find statistically significant differences, the following tests were applied: ANOVA, Kruskal-Wallis, Mood median, Pearson correlations (Tables S6-S12) and Fisher's Least Significant Difference test (LSD). Clausius-Clapeyron equation, gas-particle partition coefficient (K_p), fraction partitioned onto particles (φ), octanol-air partition coefficient (K_{OA}) and human respiratory risk assessment (see Supplementary material for details) were used to evaluate local or long-distance transport sources, gas-particle partitioning sorption mechanisms, and implications for health, respectively.

3. Results and discussion

To establish a first flame retardant pattern, total concentrations (sum of gas phase and total suspended particles; PUF + TSP) obtained with active samplers were used. Main descriptive statistics of these concentrations are shown in Table 1 and Fig. S1, where only analytes with quantification frequency (Qf; number of samples above LOD/number of samples analyzed) > 50% are displayed. PBDEs were the main pollutants (13.9 pg m^{-3}, 14/14; median, Qf), followed by TDP (1.56 pg m^{-3}, 14/14), mirex (0.78 pg m^{-3}, 9/14), PBEB (0.05 pg m^{-3}, 10/14), and BB-153 (0.04 pg m^{-3} 11/14).

3.1. Brominated flame retardants

3.1.1. Polybrominated diphenyl ethers (PBDEs)

As mentioned before, sampling location is classified as an urban background site, therefore it is not strange that total PBDE concentrations (sum of 33 congeners, TPBDE; PUF + TSP) obtained in this study (5.35–35.1 pg m^{-3}; min-max) are in the low range of those described for European urban locations: UK (10–33 pg m^{-3}, Harrad et al., 2004), Greece (4–44 pg m^{-3}, Mandalakis et al., 2009), Italy (107 pg m^{-3}; Mariani et al., 2008) and France (158–230 pg m^{-3}, Castro-Jiménez et al., 2011). Although higher PBDE levels could be expected in warm months (Cetin and Odabasi, 2008), total concentrations (PUF + TSP) obtained in this study did not show this trend, nor did they correlate with any meteorological variable (Table S6). However, significant differences were found when evaluating TPBDE content associated with each matrix (PUF, TSP, PM_{10}, $PM_{2.5}$ and PM_1; Fig. 1a) separately. Total PBDE air content was mainly associated to particulate matter (77 ± 17% of PBDEs in TSP filters) with TSP concentration (8.01 pg m^{-3}; median) being significantly higher than those obtained in gas-phase (PUF, 2.51 pg m^{-3}) (Kruskal-Wallis and Mood, $p < 0.01$). As shown in Fig. 1b, this result is mainly due to BDE-209, with statistically higher levels in PM compared to PUF (Kruskal-Wallis, $p < 0.01$). When the congener bromination degree decreases, the content is shifted towards the PUF, with no differences between PUF and TSP for BDE-99 (Fig. 1c), and significant higher levels in the gas phase compared to TSP for BDE-47 (Fig. 1d) case. It is also interesting to observe that BDE-47 levels are similar in all particle sizes (Kruskal-Wallis, $p > 0.05$), indicating that concentration in PM is mostly attributable to the smaller particles (PM_1). At the opposite end, BDE-209 showed no significant differences between $PM_{2.5}$ and PM_1, but concentration in these size fractions were statistically lower (Kruskal-Wallis, $p < 0.01$) compared to PM_{10} and TSP. This result indicates that the decabrominated congener would tend to be associated with coarse particles, larger than $PM_{2.5}$. BDE-99 is placed in an intermediate position, being associated mainly to particles > PM_1.

Although 33 PBDE congeners were evaluated, only 15 of them accounted for >99% of the TPBDE. BDE-209 was the major congener (59%, annual average, PUF + TSP; Fig. S2a), followed by BDE-47 (15%) and BDE-99 (6%). This pattern is similar to that obtained in other studies in Europe (Besis and Samara, 2012; Cetin and Odabasi, 2008) and Asia (Chen et al., 2006; Hayakawa et al., 2004; Möller et al., 2011a; Yang et al., 2013). Relatively high contributions were obtained for BDE-207 and BDE-206 (≈4%), correlating positively with BDE-209 ($r > 0.740$, $p < 0.01$, Table S6). This congener pattern reflects the use of c-decaBDE (94% BDE-209, 4% BDE-207 and 2% BDE-206, average contributions for Saytex 102E and Bromkal 82-0DE commercial mixtures, La Guardia et al., 2006) in Spain. Considering the differences in physical chemical properties (Table S13) between PBDEs it is not surprising that BDE-209 annual contribution in air is lower than that described in commercial blends. The models of Mackay and Junge-Pankow, as well as the work of other researchers such as Harner and Shoeib (Shoeib et al., 2004; Shoeib and Harner, 2002), clearly predict that 99% of the BDE-209 content will be associated with the particulate material, and when subjected to deposition phenomena will result in a clear decrease in content of the decabrominated congener to the total concentration of PBDEs. Although no significant seasonal differences were found in the PBDE pattern, being BDE-209 always the major congener, it is interesting to observe that when its concentration levels were studied throughout the year they showed significant differences (ANOVA and Kruskal-Wallis, $p < 0.05$). Samples obtained during winter and summer (14 ± 9 y 16 ± 6 pg m^{-3}, respectively) presented higher values than those reported for spring and autumn (4.1 ± 0.2 and 4.5 ± 2.1 pg m^{-3}). If BDE-209 air levels depended on temperature ($p > 0.05$; Tables S6-S11), they would increase in spring and summer, however the presence of non-seasonal bias could reflect the existence of local sources and/or a low influence of long distance transport phenomena.

Table 1
Concentrations (pg m^{-3}) obtained with active (PUF + TSP)[a] and passive (PAS) samplers.

	Season	TPBDE[b]	BTBPE	BB-153	HBB	PBEB	DBDPE	TDP[c]	f_{anti}	Mirex	Dec 602	Dec 603	Dec 604	CP
PUF + TSP														
A1	Winter	25.6	ND	0.04	ND	0.05	0.01	1.95	0.61	0.01	ND	ND	ND	ND
A2		8.87	ND	0.02	ND	0.02	0.01	0.93	0.60	0.02	ND	ND	ND	ND
A3		35.1	ND	0.05	ND	0.06	ND	0.93	0.43	0.10	ND	ND	ND	ND
A4	Spring	9.18	ND	0.06	ND	0.12	ND	6.53	0.73	0.78	0.01	ND	ND	ND
A5		7.16	ND	0.01	0.02	0.05	ND	2.62	0.63	ND	ND	ND	ND	ND
A6		6.28	ND	0.03	0.04	0.04	ND	1.23	0.77	ND	ND	ND	ND	ND
A7	Summer	22.7	ND	0.25	ND	ND	ND	0.91	0.72	0.65	0.01	ND	ND	ND
A8		16.1	ND	ND	ND	ND	ND	0.14	0.54	ND	ND	ND	ND	ND
A9		30.4	ND	ND	ND	ND	ND	2.53	0.62	ND	0.02	ND	ND	ND
A10		22.4	ND	0.001	5.25	20.8	ND	1.33	0.48	1.90	ND	ND	ND	ND
A11		28.0	ND	0.17	11.6	23.1	ND	4.61	0.73	2.57	0.01	0.01	0.25	ND
A12	Autumn	11.6	1.19	0.04	7.82	18.0	ND	1.59	0.88	2.30	ND	ND	0.10	ND
A13		5.35	2.56	0.16	9.05	6.25	ND	1.71	0.96	2.04	ND	ND	0.14	ND
A14		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
A15		10.8	ND	ND	ND	ND	ND	1.54	0.90	ND	ND	ND	ND	0.03
	Average ± SD	17.1 ± 10.0	–	0.06 ± 0.08	–	4.89 ± 8.75	–	2.04 ± 1.68	0.68 ± 0.16	1.15 ± 1.05	–	–	–	–
	Median	13.9	–	0.04	–	0.05	–	1.56	0.68	0.78	–	–	–	–
	Min-max	5.35–35.1	ND–2.56	ND–0.25	ND–11.6	ND–23.1	–	0.14–6.53	0.43–0.96	0.01–2.57	ND - 0.02	ND - 0.01	ND - 0.25	ND - 0.03
	Qf[d]	14/14	2/14	11/14	6/14	10/14	2/14	14/14	14/14	9/14	4/14	1/14	3/14	1/14
PAS														
P1[e]	Winter	20.8	ND	0.05	ND	ND	ND	2.10	0.73	ND	ND	ND	ND	ND
P2[f]		14.4	ND	ND	ND	0.06	ND	0.85	0.63	ND	ND	ND	ND	ND
P3[e]	Spring	10.8	ND	0.05	ND	ND	ND	1.19	–	ND	ND	ND	ND	ND
P4[f]		10.2	ND	ND	0.79	27.2	ND	3.30	0.98	ND	0.01	ND	ND	ND
P5[e]	Summer	8.63	ND	ND	ND	81.6	ND	2.08	0.32	ND	0.01	ND	ND	ND
P6[f]		10.1	ND	ND	ND	80.0	ND	0.16	–	ND	0.01	ND	ND	ND
P7[e]	Autumn	5.34	ND	0.04	12.1	ND	ND	0.01	–	ND	ND	ND	ND	ND
P8[f]		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Average ± SD	11.5 ± 4.92	–	–	–	31.5 ± 39.6	–	1.38 ± 1.18	0.66 ± 0.27	–	–	–	–	–
	Median	10.2	–	–	–	13.6	–	1.19	0.68		–	–	–	–
	Min-max	5.34–20.8	–	ND–0.05	ND–12.1	3E−4–81.6	–	0.01–3.30	0.32–0.98		ND–0.01	–	–	–
	Qf[d]	7/7	0/7	3/7	2/7	5/7	0/7	7/7	–	0/7	3/7	0/7	0/7	0/7

ND = not detected (<LOD), NA = not analyzed. Statistical descriptives were only calculated for analytes with Qf >50%.

[a] Only samples with concentrations above LOD in both PUF and TSP were considered.

[b] Sum of BDE-30, −28, −17, −47, −66, −77, −100, −119, −99, −85, −126, −154, −153, −139, −140, −138, −156, −169, −184, −183, −191, −180, −171, −201, −204, −197, −196, −203, −205, −208, −207, −206, and −209.

[c] Sum of *syn*- and *anti*-DP.

[d] Qf = Quantification frequency.

[e] One month passive deployment time.

[f] Two month passive deployment time.

Evaporation of PBDEs from surface to air depends on vapor pressure of the different congeners, which is defined by Clausius-Clapeyron equation. Temperature dependence of atmospheric concentrations can be expressed as linear regressions of the logarithm of the partial pressure (P_a, atm) in air versus reciprocal absolute temperature: $\ln P_a = \frac{m}{T} + b$, where m reflects thermodynamics of air-surface partitioning, extent
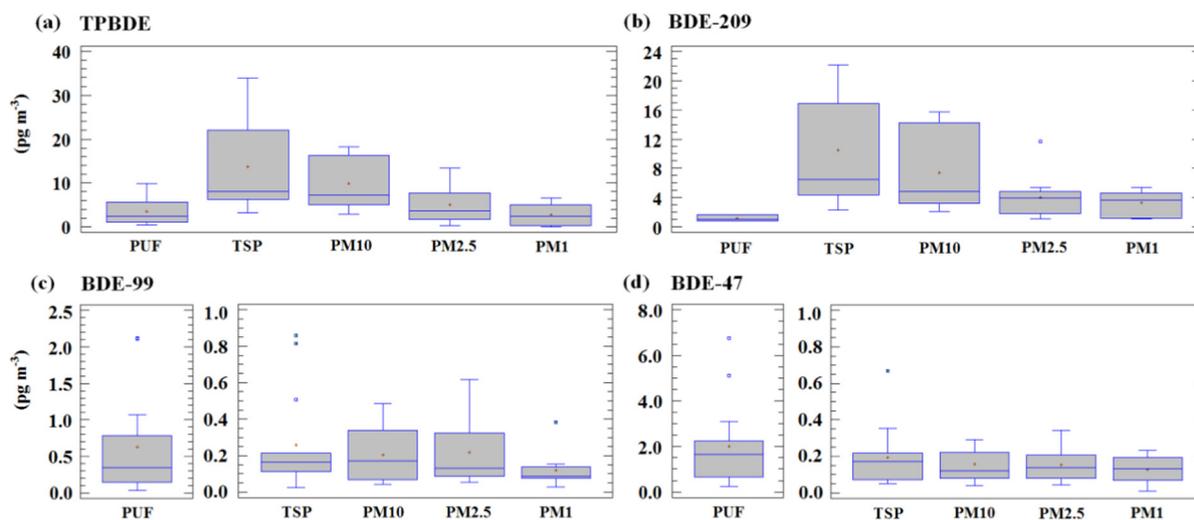
Fig. 1. Box and whiskers plots for (a) TPBDE, (b) BDE-209, (c) BDE-99 and (d) BDE-47 concentrations (pg m^{-3}) in PUF, TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$.

to which air concentrations are controlled by evaporation from surface close to sampling location or by advection of air masses with background concentrations (Wania et al., 1998). To evaluate this influence in our data, partial pressures were calculated from air concentrations through the ideal gas law. Then, logarithms of P_a of the gas were regressed with reciprocal absolute temperature (Fig. 2). Steeper slopes (m) obtained for BDE-47, -99, -100 and -28 ($R^2 > 0.64$; $p < 0.01$) together with a high temperature dependence indicates that a strong local source in the vicinity of sampling location controls the atmospheric levels and a weak influence of long range transport (Yang et al., 2013).

Presence of the BDE-47 and -99 in air could be associated to thermal stress, during infusion of technical mixture, photolytic and/or anaerobic debromination processes that can undergo BDE-209 (UNEP, 2010). Nevertheless, no significant correlations were found between BDE-209 and BDE-47 nor -99 ($p > 0.05$; Tables S6–S11) in any of the matrices evaluated that could support these physico-chemical mechanisms. BDE-47 and -99 concentrations in air are positive correlated ($r = 0.927$ and 0.871 in PUF and TSP; $p < 0.01$; Tables S7 and S8) reflecting a common origin that could be related to the historical use of c-pentaBDE mixtures (Bromkal 70-5DE and DE-71; La Guardia et al., 2006). Data show a high BDE-47 and -99 temperature dependence. It can be observed that when temperature increased, BDE-47 and -99 contents decreased in the particulate phase ($r < -0.624$, $p < 0.05$, Table S8)

and increased in the gas phase ($r > 0.707$, $p < 0.01$, Table S7). This result points at the bromination degree as a key feature in the adsorption-desorption processes of PBDEs and how it should be taken into account especially for low-brominated congeners (tetra- and penta-BDE). Solar irradiance seems to play an important role in BDE-47 air levels. It has been previously mentioned that the contribution of the particulate material, mainly PM_1, to the total BDE-47 content in the air is low. However, results in this matrix revealed a decrease in BDE-47 concentration with solar irradiance ($r = -0.726$, $p < 0.05$, Table S11) that did not correspond to an increase in the gas phase (PUF; Table S7), and could reflect the existence of photodegradation processes of BDE-47 in PM_1. The PBDE pattern changed significantly between the PUF and TSP. Heavier congeners (BDE-209, -207, -206) dominate PBDE pattern in TSP filters ($> 95\%$ of octa-, nona- and decabrominated congeners were associated with TSP), while those with lower bromination degree presented higher contribution to the PUF (Fig. 1). This result evidenced that the gas-particle partitioning of the semi-volatile compounds is controlled by their vapor pressure, which is inversely proportional to the halogenation degree (Hayakawa et al., 2004).

The gas-particle partition coefficient, (K_p; m^{-3} μg^{-1}) defined in Eq. (1), where $_i$ is the particle size fraction, PM is the particulate matter concentration ($\mu g\ m^{-3}$), F and A are the concentrations (pg m^{-3}) in the particle and gas phase (Lee et al., 2008), is used to define the gas-particle
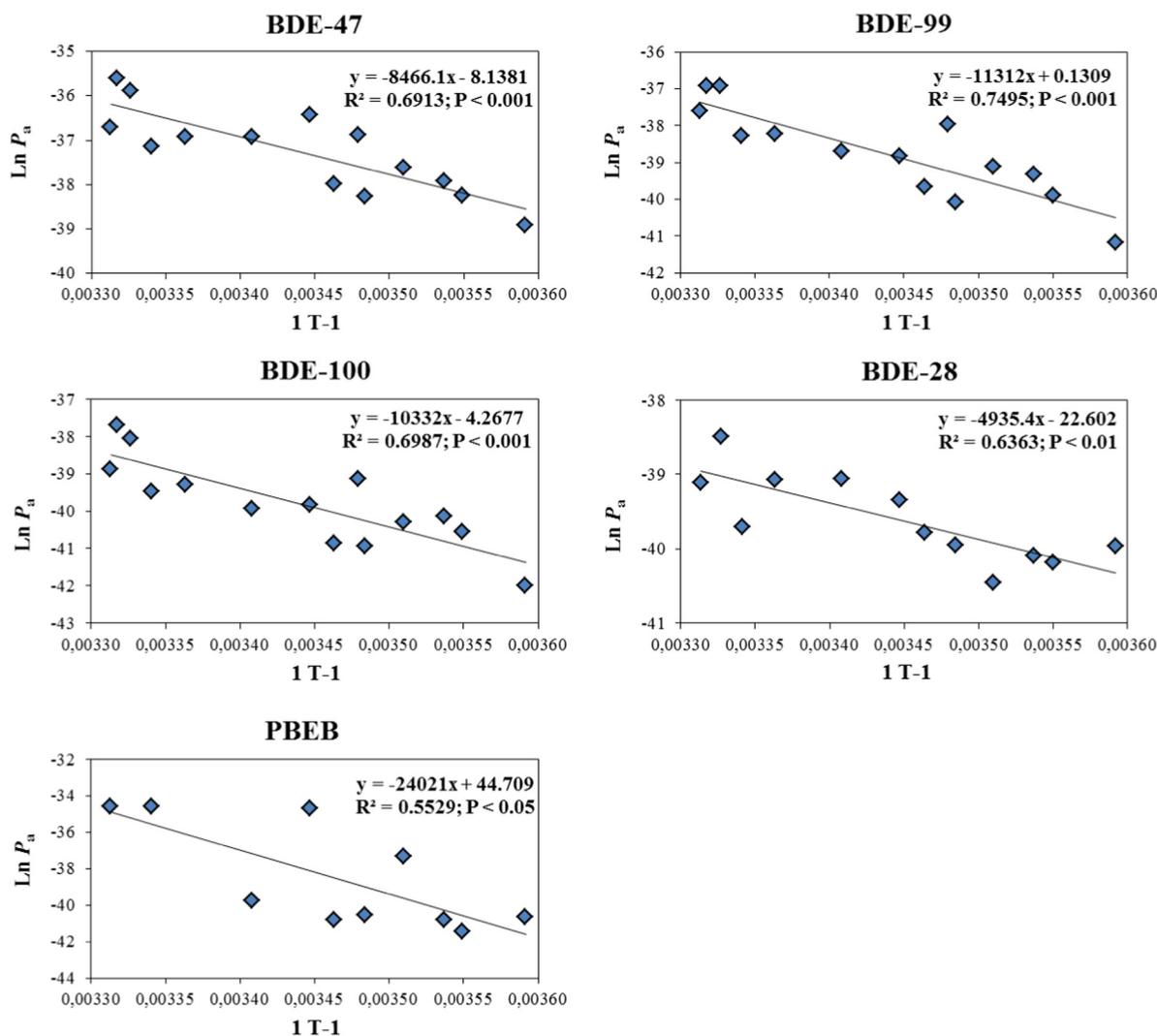

Fig. 2. Plot of the logarithm of the calculated partial pressure (P_a) of BDE-47, -99, -100, -28 and PBEB concentrations in air versus reciprocal absolute temperature.

partitioning of semivolatile organic compounds.

$$K_p = \left(\frac{F_i}{PM_i}\right)/A \qquad (1)$$

K_p can be expressed as the linear relationship with: (i) subcooled liquid vapor pressure (P_L, Eq. (2); Yang et al., 2013), when the adsorption on the particle surface is the main sorption process, and (ii) octanol-air partition coefficient (K_{OA}, Eq. (3); Harner and Shoeib, 2002) with the assumption that the dominant distribution process is absorption into the aerosol organic matter. In these equations the slopes (m_r and m_O) and intercepts (b_r and b_O) are fitting constants, and absolute slopes are equal to 1 when chemicals in gaseous and particulate phases are in equilibrium. The smaller the absolute values are, the farther away that the states deviates from equilibrium (Yang et al., 2013).

$$\log K_p = m_r \, \log P_L + b_r \qquad (2)$$

$$\log K_P = m_O \, \log K_{OA} + b_O \qquad (3)$$

Both models were applied to data in this study. Regressions between $\log K_p$ and $\log P_L$ showed strong significant linear correlations ($r^2 > 0.50$, $p < 0.0001$; Fig. 3a) with m_r values closer to −1 (−0.86, −0.89, −0.71, and −0.78 for TSP, PM_{10}, $PM_{2.5}$ and PM_1, respectively). These results could indicate a mixed (adsorption or absorption) sorption model for the PBDE (Zhang et al., 2016). Nevertheless, the slopes obtained with $\log K_p$ and $\log K_{OA}$ regression ($m_O = 0.63$, 0.63, 0.50, and 0.57 for TSP, PM_{10}, $PM_{2.5}$ and PM_1; $r^2 > 0.62$, $p < 0.001$; Fig. 3b) were farther away from 1 than in the previous model, revealing that the adsorption onto the particle surface could play a more important role than absorption in the gas-particle partitioning of PBDEs in the studied area. The fraction partitioned onto particles (φ) was calculated from Eq. (1), and the particulate matter concentration ($\mu g \, m^{-3}$) for every particle size (i) fraction, $\varphi = (K_p \times PM_i)/(1 + K_p \, PM_i)$. Then, the logarithm of the octanol-air coefficient was plotted against the fraction partitioned onto particles (Fig. S3), confirming that heavier PBDE congeners with higher $\log K_{OA}$ present a higher fraction bounded to particles.

To compare concentrations derived with active and passive samplers and evaluate the presence of particulate matter in the latter ones, median concentrations of PUF + TSP, PUF + PM_{10}, PUF + $PM_{2.5}$ and PUF + PM_1 were calculated and compared to those obtained in the PAS (Fig. S4). PBDE concentrations obtained with passive samplers ($11.5 \pm 4.92 \, pg \, m^{-3}$; media ± SD) are similar to those described in other Spanish urban locations ($16 \pm 27 \, pg \, m^{-3}$; de la Torre et al., 2016) with the same devices. Wilford et al., 2004 reported similar levels for the sum of BDE-17, -28, -47, -99 and -100 in Ottawa, Canada, (<0.1–4.4 pg m⁻³, range) compared to Madrid (0.46–3.41 pg m⁻³). Annual median concentration for TPBDE (10.2 pg m⁻³) and BDE-209 (5.97 pg m⁻³) obtained with PAS presented no statistically significant differences (U Mann-Whitney; $p > 0.05$) to the ones obtained in PUF + TSP (13.9 and 5.93 pg m⁻³ for TPBDE and BDE-209) and PUF + PM_{10} (10.5 and 4.49 pg m⁻³). Size particle analysis described before concludes that BDE-209 was mainly associated with particles $d_{ae} > 2.5$ μm, therefore this result evidences the presence of particles > $PM_{2.5}$ in the PAS. In contrast BDE-47 and -99 levels, whose gas-particle partitioning is displaced towards the PUF and smaller particles, revealed similar concentrations between PAS (0.97 and 0.38 pg m⁻³; BDE-47 and -99 annual medians) and the PUF (1.66 and 0.35 pg m⁻³). PBDE annual profiles obtained with both types of samplers are also comparable (59–61% BDE-209 > 15–14% BDE-47, 6–6% BDE-207, 4–5% BDE-206, 6–4% BDE-99; PUF + TSP and PAS, Fig. S2) nevertheless seasonal patterns could vary between the two samplers depending on the PBDE congeners considered. Data derived with active devices evidence a seasonal trend for BDE-47 in the gas phase, with higher values in summer and autumn. This tendency was also observed with passive sampling (Fig. S2b), however when the congener partitioning moves to

particulate matter, as happened for BDE-209, the establishment of seasonal patterns with PAS is hampered by the presence of particles in the samples.

3.1.2. Pentabromoethylbenzene (PBEB)

Pentabromoethylbenzene was positive quantified in ten active samples (ranging from not detected (N.D.) to 23.1 pg m⁻³ in PUF + TSP, N.D. to 19.2 pg m⁻³ in PUF, and N.D. to 34.9 pg m⁻³ in TSP). This great dispersion was also found in passive data (from 0.05 to 81.6 pg m⁻³; PAS) and also in the literature, reporting total concentrations from 0.01 pg m⁻³ in Canada (Gouteux et al., 2008) to 8.9 and 90 pg m⁻³ in UK (Lee et al., 2002). A high variability in the concentration of a chemical quantified frequently (10/14) over one year period time could indicate the existence of local sources with a rapid influence on ambient air levels. PBEB is an additive flame retardant mainly produced by Albemarle Chemical Corporation and classified as a low production volume (LPV) chemical in the EU (ESIS, 2010). PBEB is mostly in thermoset polyester resins: circuit boards, textiles, adhesives, wire and cable coatings and polyurethane foam (Covaci et al., 2011). PBEB levels (PUF + TSP) showed a positive correlation with temperature ($r = 0.776$, $p < 0.01$, Table S6), mainly due to an increase in their gas phase concentration ($r = 0.766$ and 0.957, $p < 0.01$–0.05, Tables S7 and S12) which reached maximum levels in active and passive samples deployed during summer. Nevertheless, the low quantification frequency in particle phase (5/14, 3/14, 7/14 and 3/14 for TSP, PM_{10}, $PM_{2.5}$ and PM_1) does not allow to identify desorption processes from particulate matter. A positive relationship between PBEB and mirex concentrations was obtained for total concentration ($r = 0.880$; $p < 0.01$ for PUF + TSP; Table S6) and gas-phase ($r = 0.787$; $p < 0.05$ PUF Table S7) obtained with active samplers. As far as authors know this result has not been previously described in ambient air and could reflect a common origin for both compounds.

3.1.3. Hexabromobenzene (HBB)

Even though quantification frequency decreases for HBB both in active (6/14, 6/15, 4/13, 7/13 and 2/10 in PUF, TSP, PM_{10}, $PM_{2.5}$ and PM_1, respectively) and passive samples (2/7) compared to PBEB, as it happened for the latter, HBB concentrations peaked in late summer and early fall. Considering structural similarity of HBB and PBEB, it is not strange to find a comparable atmospheric behavior. However, the non-existence of correlations between both compounds in any of the matrices evaluated (Tables S6–S12) would reflect a different origin for both chemicals. HBB is not reported by the EU industry as a currently produced chemical, but is widely used in China and Japan as an additive in paper, woods, textiles, electronic and plastic woods (Covaci et al., 2011). HBB concentrations obtained in this study (from N.D. to 11.6 pg m⁻³, PUF + TSP) are in the same order of magnitude as those described in Great Lakes (4.6 ± 1.0 pg m⁻³; average ± SD, Venier et al., 2012), Chinese rural locations (4.49 pg m⁻³; average, Tian et al., 2011), and higher than those obtained in Canadian rural/suburban ambient air (0.02–0.09 pg m⁻³, range; Gouteux et al., 2008). Lee et al., 2016 reported concentrations of HBB from <0.02 to 5.5 pg m⁻³ in passive samples from 40 global sites over the period 2005–2006, which are in agreement with the ones obtained in the PUF in the present study (from N.D. to 4.95 pg m⁻³; Qf = 6/14), and in the same order of magnitude than the two concentrations above LOD quantified with PAS (0.79 and 12.1 pg m⁻³; Qf =2/7).

3.1.4. 2,2′, 4,4′, 5,5′-Hexabromobiphenyl (BB-153)

BB-153 levels obtained in this study (0.04 pg m⁻³; median PUF + TSP) are similar to those reported in remote areas from Norway (0.04 pg m⁻³, Manø et al., 2008a, 2008b) and lower than those reported in electronic waste recycling areas from China (49.7 pg m⁻³; Tian et al., 2011). There were statistically significant differences between the concentrations obtained in the PUF (0.0002 pg m⁻³, median) and the TSP (0.02 pg m⁻³, median) samples, (U Mann-Whitney, $p < 0.05$); being
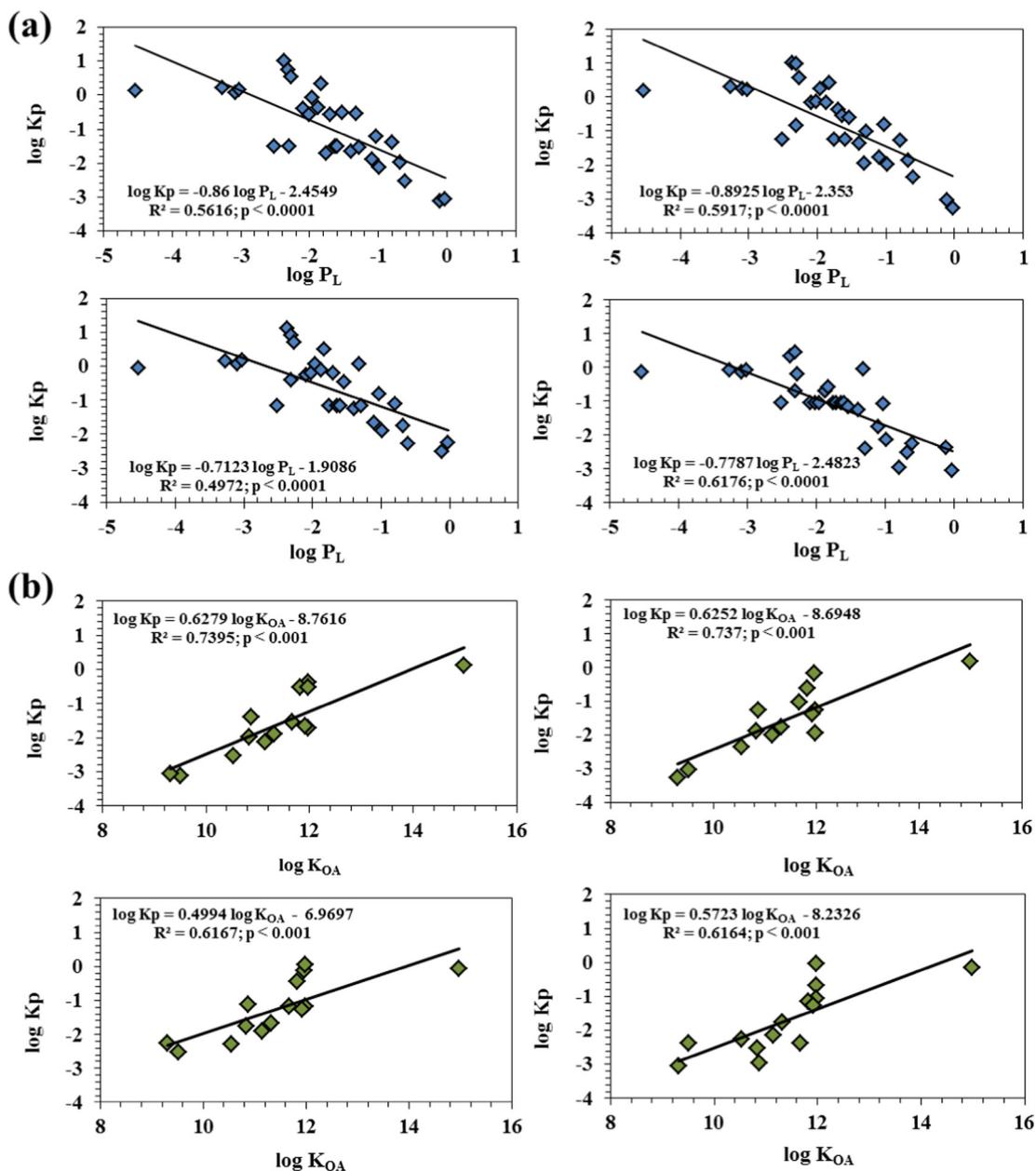
Fig. 3. Plot of the logarithm of (a) the subcooled liquid vapor pressure (P_L) and the (b) octanol-air partition coefficient (K_{OA}) of PBDE in TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$ versus the logarithm of the gas-particle partition coefficient (K_p).

gas-particle partitioning clearly influenced by meteorological factors (Table S8). Data showed that increasing the temperature and decreasing the relative humidity the BB-153 content increases in the PUF and decreases in the TSP (Fig. S5). This result could indicate the existence of particle-PUF desorption processes. The change in this trend observed in autumn, with greater presence of BB-153 in the gas phase, could be attributed to the existence of phenomena of increased pollution. Cetin and Odabasi explained that, when certain congeners with high octanol-air coefficients (K_{OA}) are emitted into the air in gaseous form, they can remain in this phase for several months, before reaching equilibrium with the atmospheric particles (Cetin and Odabasi, 2008).

3.1.5. 1,2-bis (2,4,6-tribromophenoxyethane) (BTBPE)

In BTBPE case only five samples obtained with active samplers in autumn reported concentration above LOD. There are very few studies that report BTBPE levels in ambient air, although the concentrations

obtained in the present study, (2.56, 1.19, 0.35, 0.24 and 0.13 pg m^{-3} for PUF, TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$) are similar to those described in urban air for Chicago (0.8 ± 0.2 and 1 ± 0.2 pg m^3; average ± SD for gas and particle phases) and Cleveland (0.5 ± 0.1 and 0.9 ± 0.1; Salamova and Hites, 2011), higher than those reported in background locations (ND - 0.06 and ND-0.02 pg m^{-3}; range for gas and particle phase in East Greenland Sea; Möller et al., 2011b) and lower than those described in China (30.7, 3.8–67.4 pg m^{-3}; average and range for gas + particle phases; Shi et al., 2009). BTBPE is an additive flame retardant marketed for use in acrylonitrile butadiene styrene (ABS), high-impact polystyrene (HIPS), thermoplastics, thermoset resins, polycarbonate and coatings, but listed as a LPV chemical in EU (Covaci et al., 2011). However, BTBPE indoor air levels reported by Sjödin et al., 2001 in working environments (a plant engaged in recycling electronic goods (20 ng m^{-3}, average), a factory assembling printed circuit boards (41 pg m^{-3}), or offices equipped with computers (5.8 pg m^{-3}) from Sweden, evidenced it usage in EU consumer products.

3.1.6. Decabromodiphenyl ethane (DBDPE)

Decabromodiphenyl ethane (DBDPE) was proposed in 2007 as a substitute for c-decaBDE mixtures in Europe (ECB, 2007). DBDPE and BDE-209 share structural similarities that a priori attribute them similar physical chemical properties. However concentrations of DBDPE above the LOD were only obtained in winter (0.01 pg m^{-3} PUF; 0.002 and 0.01 pg m^{-3} TSP; 0.01 pg m^{-3} PM$_{10}$; 0.01 pg m^{-3} PM$_{2.5}$), and they were several orders of magnitude lower than those quantified for BDE-209 in this study (2.25–22.2 pg m^{-3} range, PUF + TSP). Europe does not produce DBDPE, but imports in 2001 were estimated to be between 1000 and 5000 t, primarily to Germany (Covaci et al., 2011). DBDPE is available on the market since the mid-1980s, under trade name SAYTEX 8010 (Albemarle Corp., USA) and Firemaster 2100 (Great Lakes Chemical Corp., USA) and has the same applications as c-decaBDE as an additive to different polymeric materials (HIPS, ABS or polypropylene), and in textiles, such as cotton and polyester. The differences in the concentrations of BDE-209 and DBDPE detected in this study seems to indicate a low degree of substitution of c-decaBDE mixtures by DBDPE in Spain and/or significant differences in terms of leaching from the materials containing them and mobilization towards the ambient air. Obtained DBDPE concentrations are much lower than those described in urban areas in Cleveland (22 ± 13 pg m^{-3}, average ± SD; Venier and Hites, 2008), or China (up to 1919 pg m^{-3} in Guangzhou, a highly industrialized area; Shi et al., 2009; Tian et al., 2011). However, recent inclusion of c-decaBDE mixture in the Stockholm Convention, that undergone EU Regulation 2017/227 according to which c-decaBDE mixture will not be manufactured or commercialized after March 2019 in Europe, will surely influence this result in the future.

3.2. Dechloranes and related compounds

Dechlorane plus (DP) was quantified in all samples. Total DP (TDP, sum of anti- and syn-DP isomers) levels obtained in the present study (2.04 ± 1.68 pg m^{-3}; average ± SD, PUF + TSP) are similar to those detected in other urban areas in the USA (2.4 ± 0.3 pg m^{-3} and 7.2 ± 1.2 pg m^{-3}, averages in Chicago and Cleveland, Venier and Hites, 2008) pointing out urban agglomerations as potential DP source in ambient air. No significant correlations were detected between DP concentration and the meteorological variables (Tables S6–S11), nor seasonal variations (Fig. S1). However TDP concentrations quantified in particulate matter (0.98 pg m^{-3}, median in TSP) were higher than those measured in gas phase (0.43 pg m^{-3} for PUF) (Kruskal-Wallis, $p < 0.05$;

Fig. 4a). This result was maintained for syn-DP isomer, but loosed statistical significance for anti-DP. No statistically significant differences were found between particle sizes, thus associating DP (syn- and anti-DP) to PM$_1$ particles.

Very few studies have been carried out to evaluate physico-chemical properties of DP isomers that can explain their gas-particle partitioning. However, significant differences have been reported in terms of solubility, biological degradation and bioaccumulation (Sverko et al., 2011), which could predict different gas-particle partitioning coefficients, as reflected in the results obtained in the present study. The use of the fraction of the anti-DP isomer (ratio of the anti-DP concentration to TDP; f_{anti}) allows to evaluate the differences in terms of stability, isomerization and transport that the two isomers can present. It has been described in the literature that the commercial mixture produced by OxyChem presents a f_{anti} of 0.75 (average obtained with several commercial batches, Sverko et al., 2011) higher than that marketed by Ampon (0.60, Wang et al., 2010). In addition, it has been described that as the distance to the emission source increases, anti-DP air concentrations decreases due to isomerization processes towards the syn-DP and/or higher degradation rates for anti-DP isomer (Chen et al., 2006; Sverko et al., 2011). Considering this, f_{anti} values (0.68 ± 0.16; average ± SD in PUF + TSP) obtained in the present study could be attributable to the use of American mixtures, leached from the materials containing them and subject to processes of degradation and/or isomerization in the medium. This hypothesis could be also related to the differences obtained in particle and gas phase. No statistically significant differences were found between the f_{anti} values in the different matrices analyzed (Fig. 4b). However the data obtained in the particulate material (0.70 ± 0.11, 0.71 ± 0.12, 0.67 ± 0.22 and 0.65 ± 0.28; annual average ± SD for TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$, respectively) closely resembles OxyChem mixture, whereas values obtained in the PUF (0.56 ± 0.34) are lower. This result, even assuming that it has no statistically significant support, could indicate that the leaching of DP from the materials containing it could be carried out in the first place associated with the particulate phase, where degradation/isomerization processes are catalyzed by the material, for later mobilization towards the gas phase. DP concentrations derived with passive samplers (1.38 ± 1.18 pg m^{-3}; average ± SD; PAS) are similar to those quantified with active ones (PUF + TSP; Fig. S4e.). Even f_{anti} values obtained with both type of samplers exhibit similar results (0.66–0.68, average for PAS and PUF + TSP), evidencing again the capacity of passive samplers to collect particulates and their feasibility to monitor these pollutants in a reliable way.
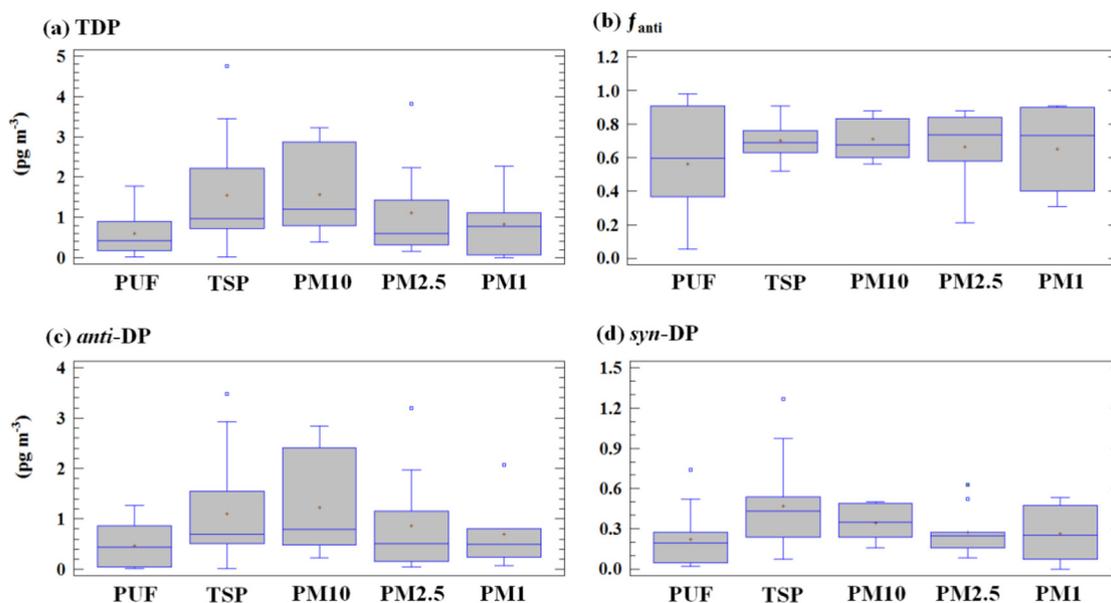

Fig. 4. Box and whiskers plots for (a) TDP, (b) f_{anti}, (c) anti-DP and (d) syn-DP in PUF, TSP, PM$_{10}$, PM$_{2.5}$ and PM$_1$.

The total concentration of mirex in the present study was 1.15 ± 1.05 pg m^{-3}, annual average $\pm$ SD, Table 1), with no differences between gas phase (0.77 ± 0.72 pg m^{-3} PUF) and particulate phase (0.82 ± 0.12, 0.59 ± 0.18, 0.53 ± 0.24 pg m^{-3}; TSP, PM$_{10}$ and PM$_{2.5}$). There is no evidence of the use of mirex in Spain, therefore the concentrations quantified in this study must be attributable to long-range atmospheric transport. There are studies that have described levels of mirex in remote areas, far from their known sources, that can support this result (Muir and de Wit, 2010). Mirex concentrations in gas phase were positive correlated with TDP ($r = 0.890$ $p < 0.01$; Table S7) and PBEB ($r = 0.787$ $p < 0.05$), maintaining this relationship for total concentrations (PUF + TSP) in the latter ($r = 0.880$ $p < 0.01$; Table S6). Dechlorane plus was introduced in the market as a mirex substitute, therefore similar sources/applications might be expected.

Quantification frequency is greatly reduced for the other dechloranes (Table 1) making impossible to establish seasonal trends and to study meteorological variables influence. Dec 604, Dec 602, Dec 603 and CP were only quantified in ten (from 0.05 to 0.35 pg m^{-3}; PUF, TSP, PM$_{10}$ or PM$_{2.5}$), four (from 0.01 to 0.02 pg m^{-3}; all summer PUF), two (0.01 pg m^{-3}; PM$_{10}$ and PM$_{2.5}$) and one (0.03 pg m^{-3}; TSP) samples, respectively. However only Dec 602 was quantified (0.01 pg m^{-3}) in passive samplers during spring and summer. This result correlates well with the fact that Dec 602 presented the highest vapor pressure of the four dechloranes (Table S13). There are very few studies reporting levels of dechloranes in air. However they have been quantified in marine environments (Möller et al., 2011a), from 0.01 to 0.2 pg m^{-3} (range for Dec 602), 0.4 pg m^{-3} (Dec 603) and 0.03–0.05 pg m^{-3} (Dec 604), which are higher than those obtained in the present work. Dec 602 has also been quantified at higher concentrations (4.10 and 5.14 pg m^{-3}) in particulate matter collected near DP production facility in China (Wang et al., 2010).

3.3. Inhalation risk assessment

Health risk assessment through inhalation study was conducted adopting the International Commission on Radiological Protection model (ICRP, 1995) to evaluate the deposition efficiencies and fluxes on inhaled PBDE and DP in the human respiratory tract, as described by (Lyu et al., 2016). Complete details of the applied methodology are described in the Supplementary material. Briefly, particle deposition efficiencies (DE) were calculated in three regions of human respiratory tract: head airway (DE$_{HA}$; Eq. (S2)), tracheobronchial (DE$_{TB}$; Eq. (S3)) and alveoli (DE$_{AR}$; Eq. (S4)) regions. Then, deposition flux (DF pg h^{-1}; Eq. (S6)) was obtained to finally calculate hazard quotient (HQ) and assess the non-cancer risk of size-resolved PBDEs and DP through inhalation (Eq. (S7)). The low frequency of quantification of the rest of flame retardants studied did not allow establishing their implications for health. As mentioned in the Materials and methods section, particle sampling were performed with cutoff inlets to obtain samples of particulate matter with an aerodynamic diameter (d_{ae}) equal or <10 μm (PM$_{10}$), 2.5 μm (PM$_{2.5}$) and 1 μm (PM$_1$). For this reason, risk assessment was carried out for two ranges of particles: (i) between PM$_{2.5}$ and PM$_{10}$ (average d_{ae} of 6.5 μm; namely coarse fraction in this study) and (ii) from PM$_1$ to PM$_{2.5}$ (d_{ae} of 1.75 μm, fine fraction here). Total deposition flux (TDF) for PBDE was 2.29 pg h^{-1} (Tables S14 and S15) one order of magnitude lower than the one described by Lyu et al., 2016 at the urban site of Shanghai, China (26.8 pg h^{-1}). This result is clearly influenced by the higher PBDE concentrations described in the Chinese city (86.6, 30.6–141 pg m^{-3}; average, min – max for $\sum_{13}$ PBDE) in particulates compared to the present study (13.7 $\pm$ 9.30, 3.24–33.9 pg m^{-3}; $\sum_{33}$ PBDE in TSP). However, as reported by Lyu et al., 2016, TPBDE contribution in the respiratory tract was dominated by head airway (2.16 pg h^{-1}, 94% of TDF), followed by tracheobronchial (0.12 pg h^{-1}, 5% of TDF) and alveoli (0.01 pg h^{-1}, 1%) regions. Coarse particles contributed most to PBDEs in the head region (1.61/0.55 pg h^{-1}; DF$_{HA}$ for coarse/fine) while fine particles contributed more to PBDEs in the

alveoli region (0.004/0.01 pg h^{-1}; DF$_{AR}$ for coarse/fine). Dechlorane plus showed a TDF of 0.29 pg h^{-1} (0.19 pg h^{-1} coarse particles and 0.10 pg h^{-1} fine particles), of which head airway constituted 94%, tracheobronchial region 5.5% and alveoli region 0.5%. Considering that fine particles can penetrate deeper into the respiratory system compared to coarse particles, fine-particle-bound PBDEs and DP are expected to accumulate in the lower parts of the lungs and pose a greater risk to human health. Total hazard quotients for TPBDE and TDP were 6.3×10^{-7} and 1.1×10^{-8}, much lower than 1 (risk guideline value recommended by the US Environmental Protection Agency), thus reflecting a low cancer risk.

4. Conclusions

PBDEs were the flame retardants with the highest ambient air levels in the urban background site, followed by TDP, mirex, PBEB and BB-153, in decreasing order. PBDEs were mostly associated with the particulate phase, where the pattern of congeners was dominated by BDE-209. The contribution of the congeners with the lowest degree of bromination increased as the particle size decreased. PBDE patterns revealed that, congener contribution increases with particle size and bromination degree, being BDE-209 mostly bounded to particles > PM$_{2.5}$, BDE-99 to > PM$_1$ and BDE-47 to ≤PM$_1$. Although source identification was not included within the main objectives of this study, results clearly reflect the use of c-decaBDE and c-pentaBDE mixtures in consumer products (electrical and electronic equipment, furniture or building materials among others) and their subsequent mobilization towards the medium as a potential source of presence of these pollutants in ambient air. DP levels obtained in the particulate phase were higher than those in the gas phase, with no significant differences between the different particle sizes. The f_{anti} study attributed the concentrations of DP in ambient air to the use of the American mixtures, leached from the materials that contain them and subject to degradation and/or isomerization processes in the environment. No significant differences were found between the concentration levels of TPBDE and TDP obtained with passive and active samplers. The results obtained demonstrate the ability of the passive samplers to collect particulate material, and their suitability to study chemicals associated with PM (and not only gas-phase compounds). At lower concentration and frequency of quantification than PBDE and DP, levels of Mirex, PBEB, BB-153, HBB, BTBPE, DBDPE, Dec 602, 603, 604 and chlordane plus were quantified, demonstrating their use and subsequent dispersion in the environment. Finally, the human respiratory risk assessment evidenced that fine-particle-bound PBDE and DP penetrate deeper into de respiratory system compared to coarse particles. However, results concluded that particulate concentrations of these flame retardants in urban background air from Madrid posed low cancer risk through inhalation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.02.199.

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