



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

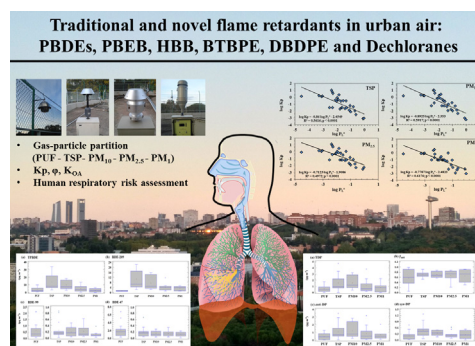
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HIGHLIGHTS

- 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



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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 Dechlorane 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 $\leq PM_1$, 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 electronic 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 Dechlorane plus (DP)) and related compounds (chlordan 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 $<10\ \mu\text{m}$ (PM_{10}), $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$), $1\ \mu\text{m}$ (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, $40^\circ 27'27''\text{N}$, $3^\circ 43'23''\text{W}$), 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 $>50\ \text{m}$ from the traffic emission sources, with not >2500 vehicles per day within a radius of $50\ \text{m}$, (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 $>50\ \text{m}$ 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 $30\ \text{m}^3\ \text{h}^{-1}$ flow rate ($1020\ \text{m}^3$ per sample). Polyurethane foam cylinders (PUF, $10\ \text{cm}$ diameter, $10\ \text{cm}$ height, and $0.03\ \text{g}\ \text{cm}^{-3}$ density; TechnoSpec, Spain) and circular glass fiber filters (GFF, $15\ \text{cm}$ diameter; $0.26\ \text{mm}$ 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 $450\ ^\circ\text{C}$ for $24\ \text{h}$ to remove any organic contaminant. They were weighed and stored in a controlled temperature ($20 \pm 1\ ^\circ\text{C}$; mean \pm SD) and humidity ($50 \pm 5\%$) 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 $\text{PM}_{2.5}$ (PM_{1025} -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 ($14\ \text{cm}$ diameter; $1.2\ \text{cm}$ thickness, and $0.03\ \text{g}\ \text{cm}^{-3}$ density; TechnoSpec, Spain) were precleaned by Soxhlet extraction with acetone and diethyl ether for $24\ \text{h}$, wrapped in aluminum foil and stored in polyethylene bags at $-20\ ^\circ\text{C}$ 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 ^{13}C -labelled surrogate standards (Table S2) including PBDEs, DBDPE, BTBPE, BB-153, HBB, and DP congeners, and Soxhlet extracted with

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