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Atmospheric Occurrence and Gas-Particle Partitioning of PBDEs in an Industrialised and Urban Area of Florence, Italy

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ABSTRACT

Air samples were collected both at an urban and an industrial area of Florence (Italy) in order to evaluate the occurrence, profiles, seasonal variation and gas/particle partitioning of polybrominated diphenyl ethers (PBDEs). The mean total (gas + particle phase) PBDE concentrations were 42.8 ± 7.8 and 89.0 ± 21.1 pg/m^3 in the urban and industrial sites, respectively. In all samples, BDE-209 was the most abundant congener, followed by BDE-47 and BDE-153 in the industrial site, and by BDE-99 in the urban site. The Σ_6 PBDE (sum of BDE-28, -47, -99, -100, 153, -154) concentrations in the urban ($12.1\text{--}27.9$ pg/m^3) and industrialised ($21.4\text{--}44.3$ pg/m^3) sites were comparable to, or slightly lower than measured at other sites. The partition coefficient of PBDEs between the gas and particle phases (K_p) was well correlated with the subcooled liquid vapor pressure (P°_L) for all samples. The measured particulate sorption of PBDEs was compared to the predictions from Junge-Pankow (J/P) model and K_{OA} absorption model. While the Junge-Pankow model tends to overestimate the particulate sorption, the K_{OA} based model seemed to fit the PBDE data.

Keywords: PBDEs; Gas phase; Particulate phase; Seasonal variation; Emissions.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a group of additive flame retardants that have been extensively used around the world in numerous common products including building materials, electronics, furnishings, vehicles, textiles, plastics, coatings. The afore-mentioned products constitute the main sources of PBDEs in the atmosphere, together with the other “secondary” sources, as for example are the emissions from vehicular exhausts (e.g., Hsieh *et al.*, 2011), or waste incinerators, or fly ash treatment plants (e.g., Wang *et al.*, 2010b; Liao *et al.*, 2012). Three major industrial formulations have been commonly used: penta-, octa- and deca-bromodiphenyl ethers mixtures. Although the penta- and octa- formulations have been banned in Europe since 2004 and the deca-BDE was prohibited in July 2008 (ECJ, 2008; Mandalakis *et al.*, 2008; Lagalante *et al.*, 2009), these

chemicals are still ubiquitous in the environment. Their occurrence in the indoor and outdoor atmosphere is the result of their emission from products, a process that will continue until all PBDE-containing products are disposed of. Recent concern about their presence in the atmosphere is related to their environmental fate and human exposure, because some of these compounds are persistent, bioaccumulative, toxic and endocrine disrupting chemicals. Several epidemiological studies were reported that humans exposure to PBDEs has caused the health effects for disrupting thyroid and reproductive hormone homeostasis (Chevrier *et al.*, 2010; Shy *et al.*, 2012), adverse birth outcomes (Chao *et al.*, 2007; Harley *et al.*, 2011), and changes in neurodevelopment (Herbstman *et al.*, 2010; Chao *et al.*, 2011; Gascon *et al.*, 2012) and reproduction (Chao *et al.*, 2010; Harley *et al.*, 2010). The atmospheric fate of PBDEs (i.e., deposition, degradation, long range transport) is strongly influenced by their physical chemical properties and meteorological factors (particularly temperature, wind speed and direction) which drive, not only their distribution between the vapour and particulate phases, but also their atmospheric dispersion and transport. Although several studies have reported the occurrence and levels of PBDEs in the atmosphere (Lee *et al.*, 2004; Li *et al.*, 2009; Birgul *et al.*, 2012; Martellini *et al.*, 2012a; Piazza *et al.*, 2013), there is scarce data about the gas/particle PBDE distributions

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and PBDE air concentrations in Italy and only few studies in general reporting on the partitioning of PBDEs in the atmosphere (Shoeib *et al.*, 2004; Chen *et al.*, 2006; Cetin and Odabasi, 2008, Lin *et al.*, 2012). Measuring the ambient concentrations of particle-bound contaminants is important for evaluating the adverse health effects arising from the inhalation of suspended particulate matter in urban areas.

Florence is the most populous city in Tuscany, with approximately 370,000 inhabitants. It is a major production and commercial centre in Italy, with industrial establishments manufacturing a variety of products, spanning from furniture, rubber goods, leatherwork, high fashion clothes, chemicals, food and building materials and is also characterised by important emissions from traffic/vehicles (Martellini *et al.*, 2012b). Notwithstanding the big production of goods that contain flame retardants, this category of pollutants has never been studied in a comprehensive way, in this area. Hence, the main aims of this study were to study the occurrence of PBDEs in an urban and an industrial area of Florence, Italy, in order to assess the seasonal variations and to better understand the interactions of PBDEs between the gas and particle phase, as well as to assess human exposure to PBDEs.

MATERIALS AND METHODS

Sampling

The air sampling campaign was undertaken in June and December 2011. Air samples were simultaneously collected at an urban centre and industrialised area in Florence. The samples were collected at open spaces (at around 4 m from the ground) of various buildings. The industrial site was located close to establishments where electronic/electrical equipment, plastics and other goods suspected to contain flame retardants are produced.

Meteorological parameters such as wind speed, wind direction, rainfall and temperature were monitored during all the sampling campaign. For the calculation of the prevailing wind directions only measurements with wind speed > 0.5 m/s were used.

Air samples were collected using a high volume air sampler (TE-1000BL X PUF, Tisch environmental Inc., USA) as described in Cincinelli *et al.* (2007, 2009, 2012). In summary, the air was drawn at a flow rate of 12 m³/h through a Quartz fiber filter (QFF, size 102 mm, SKC, Eighty Four, PA, USA) to collect particles and then through two polyurethane foam (PUF) plugs (height 75 mm, diameter 65 mm, SKC, Eighty Four, PA, USA) to collect vapour phase compounds. The back half of the second foam plug served as an indicator of breakthrough of vapour phase compounds through the front plug. Sampling events were restricted to 12 h to avoid large changes in air temperature in an attempt to minimize volatilization artefacts from particles on the filter.

Before sampling, the QFFs were baked at 450°C for 12 h and stored in aluminium foil packages in a dessicator until used. The PUF cartridges were cleaned by Soxhlet extraction for 24 h in acetone followed by 24 h in petroleum ether. PUF plugs were dried into a vacuum dessicator, placed in glass jars and stored in plastic bags in a freezer. Cleaned and prepared QFFs and PUF were transported to the field

in their containers without allowing exposure to ambient air. After sampling, PUF and filters were placed into containers brought back to the laboratory and stored in the dark at –20°C until analysed.

Sample Preparation and Analysis

Samples were Soxhlet extracted for 24 h with acetone followed by 24 h in hexane. Both extracts were combined and reduced in volume to 1 mL by rotary evaporation followed by blow down under a high purity nitrogen stream. Extracts were cleaned up by silica column chromatography with the addition of anhydrous sodium sulphate. Total suspended particulate (TSP) concentrations were determined by weighing the filters under controlled temperature and moisture conditions (25°C, 50% RH) before and after sample collection.

Samples analysis were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer operating in negative chemical ionization (NCI) and selective ion monitoring (SIM) mode as described elsewhere (Dickhut *et al.*, 2005). The samples were subsequently analysed for BDE-209 using a DB-5MS capillary column, 15 m, 0.25 mm i.d., 0.25 µm film thickness. Quantification of tri- to hepta-BDE (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183) was carried with the internal calibration procedure, whereas BDE-209 was quantified with the external standard method.

Materials

The PBDE analytical standards were purchased from Wellington laboratories Inc. (Ontario, Canada).

All organic solvents were pesticide grade and obtained from Supelco (Bellefonte, PA, USA).

Other chemicals were of analytical grade.

Quality Control

In order to prevent any possible photolysis of PBDE analytes, special care was taken to avoid exposure of samples to light during their storage and analysis. The sample preparation and treatments were conducted under/reduced light conditions and all glassware was wrapped in aluminium foil. Prior to extraction, each sample was spiked with a known amount of 3,3',4,4'-tetrabromodiphenyl ether (BDE-77) to monitor the analytical recovery efficiency. Average recovery of surrogate standard was 82 ± 13% for PUF and 88 ± 7% for filter samples. The recoveries of target compounds were also tested by spiking experiments (n = 5) and average recovery efficiencies were between 82 ± 7% for BDE-28 and 98 ± 6% for BDE-153. Laboratory blanks showed no detectable PBDE concentrations. A breakthrough test was made by using a second half PUF in series with the first PUF and no breakthrough was observed. The limit of detection (LOD) for individual PBDEs were between 0.05 pg/m³ (BDE-28) to 0.6 pg/m³ (BDE-209).

RESULTS AND DISCUSSION

Atmospheric Concentrations

Gas and particle phase concentrations of individual

PBDEs at both sites are reported in Table 1, whereas the mean concentrations are presented in Fig. 1.

The mean total (gas + particle phase) PBDE concentrations were 42.8 ± 7.8 and 89.0 ± 21.1 pg/m^3 in the urban and industrial sites, respectively. In all samples, BDE-209 was the most abundant, followed by BDE-47 and BDE-153 in the industrial site, and by BDE-99 in the urban site. These congeners are typically reported as the most abundant, something in agreement with the fact that they were the dominant ones in the most broadly used technical formulations that are decabromodiphenylether, pentabromodiphenylether and octabromodiphenylether (La Guardia et al., 2006). This difference in the abundance of BDE-153 between urban

and industrial sites, can be considered as a first indication that the sources that affect these two sites are different.

In the present study, BDE-209 accounted for 58% of the total PBDEs in the industrial site and 53% in the urban. In literature studies BDE-209 normally dominates the PBDE profiles, and can account in some cases for > 80% (Rahman et al., 2001; Law et al., 2006; Stapleton et al., 2006; Su et al., 2007; Cetin and Odabasi, 2008; Venier and Hites, 2008; Wilford et al., 2008; Wang et al., 2010a; Lin et al., 2012; Lin et al., 2012b; Shoeib et al., 2012; Tu et al., 2012), being in good agreement with the share in the global market of the deca-formulation, which at least for the year 2001, accounted for 83.3% of the overall PBDE production

Table 1. Gas and particle-phase concentrations (pg/m^3) in urban and industrial sites in Florence (Italy).

| | 8-Jun | 9-Jun | 10-Jun | 11-Jun | 15-Jun | 16-Jun | 2-Dec | 6-Dec | 14-Dec | 15-Dec | 16-Dec | 17-Dec |
|------------------------|-------|-------|--------|--------|--------|--------|-------|-------|--------|--------|--------|--------|
| URBAN SITE | | | | | | | | | | | | |
| Gas phase | | | | | | | | | | | | |
| BDE-28 | 3.30 | 2.32 | 1.98 | 2.76 | 1.22 | 1.25 | 1.15 | 0.98 | 1.08 | 1.08 | 1.02 | 1.44 |
| BDE-47 | 7.98 | 5.01 | 5.48 | 5.91 | 6.13 | 5.01 | 3.20 | 3.89 | 3.65 | 3.45 | 3.64 | 2.89 |
| BDE-99 | 3.95 | 3.02 | 2.67 | 2.98 | 2.89 | 2.34 | 2.68 | 2.90 | 1.99 | 1.68 | 1.96 | 1.09 |
| BDE-100 | 0.84 | 0.67 | 0.64 | 0.76 | 0.71 | 0.68 | 0.84 | 0.68 | 0.89 | 0.62 | 0.60 | 0.69 |
| BDE-153 | 0.45 | 0.43 | 0.55 | 0.41 | 0.44 | 0.47 | 0.64 | 0.48 | 0.48 | 0.51 | 0.54 | 0.56 |
| BDE-154 | 0.44 | 0.53 | 0.57 | 0.32 | 0.41 | 0.46 | 0.42 | 0.34 | 0.54 | 0.46 | 0.43 | 0.49 |
| BDE-183 | 0.52 | 0.42 | 0.56 | 0.38 | 0.45 | 0.35 | 0.45 | 0.56 | 0.47 | 0.54 | 0.39 | 0.27 |
| BDE-209 | 1.30 | 1.45 | 1.38 | 1.09 | 1.17 | 1.40 | 1.34 | 1.37 | 1.76 | 1.05 | 1.54 | 0.67 |
| Σ PBDEs | 18.8 | 13.9 | 13.8 | 14.6 | 13.4 | 12.0 | 10.7 | 11.2 | 10.9 | 9.4 | 10.1 | 8.1 |
| Particle phase | | | | | | | | | | | | |
| BDE-28 | 0.89 | 0.74 | 0.56 | 0.65 | 0.56 | 0.36 | 0.24 | 0.21 | 0.34 | 0.43 | 0.23 | 0.34 |
| BDE-47 | 4.76 | 2.98 | 3.06 | 3.45 | 3.48 | 3.15 | 0.75 | 1.99 | 1.03 | 0.89 | 1.01 | 1.34 |
| BDE-99 | 3.02 | 2.12 | 2.03 | 2.87 | 2.86 | 2.78 | 0.79 | 0.73 | 0.88 | 0.93 | 0.73 | 0.64 |
| BDE-100 | 0.64 | 0.42 | 0.94 | 1.05 | 0.99 | 1.03 | 0.99 | 0.78 | 1.04 | 0.83 | 0.86 | 0.98 |
| BDE-153 | 0.99 | 0.88 | 1.23 | 0.97 | 0.84 | 1.07 | 0.88 | 0.66 | 0.67 | 0.87 | 0.77 | 0.76 |
| BDE-154 | 0.68 | 0.76 | 0.64 | 0.88 | 0.67 | 0.77 | 0.96 | 0.89 | 0.87 | 0.98 | 0.65 | 0.88 |
| BDE-183 | 2.89 | 2.56 | 2.29 | 3.04 | 3.14 | 2.45 | 1.23 | 1.67 | 1.58 | 1.23 | 1.85 | 1.56 |
| BDE-209 | 25.54 | 24.76 | 17.42 | 23.67 | 24.56 | 21.46 | 20.54 | 23.65 | 18.64 | 17.09 | 16.56 | 22.53 |
| Σ PBDEs | 39.4 | 35.2 | 28.2 | 36.6 | 37.1 | 33.1 | 26.4 | 30.6 | 25.0 | 23.2 | 22.7 | 29.0 |
| INDUSTRIAL SITE | | | | | | | | | | | | |
| Gas phase | | | | | | | | | | | | |
| BDE-28 | 6.32 | 4.56 | 7.23 | 4.45 | 5.66 | 7.45 | 2.34 | 3.45 | 2.07 | 3.65 | 2.02 | 3.44 |
| BDE-47 | 9.47 | 7.61 | 9.58 | 8.72 | 7.23 | 9.02 | 5.23 | 5.89 | 4.65 | 5.39 | 3.39 | 6.89 |
| BDE-99 | 4.34 | 3.93 | 3.20 | 3.60 | 3.22 | 3.34 | 2.31 | 2.05 | 2.30 | 1.98 | 1.58 | 2.34 |
| BDE-100 | 2.02 | 1.79 | 1.10 | 0.99 | 1.28 | 1.29 | 1.24 | 1.04 | 0.73 | 0.83 | 0.99 | 0.88 |
| BDE-153 | 3.84 | 2.59 | 1.82 | 2.37 | 2.45 | 2.10 | 1.69 | 2.76 | 2.60 | 2.40 | 1.13 | 0.46 |
| BDE-154 | 3.29 | 2.97 | 1.59 | 2.03 | 1.87 | 1.67 | 1.77 | 2.89 | 2.21 | 3.78 | 1.05 | 0.40 |
| BDE-183 | 2.80 | 1.40 | 1.20 | 1.60 | 1.43 | 1.32 | 1.89 | 1.77 | 1.60 | 2.50 | 0.70 | 0.30 |
| BDE-209 | 1.11 | 1.24 | 0.87 | 1.30 | 1.65 | 1.10 | 1.78 | 5.87 | 1.54 | 1.76 | 1.54 | 1.90 |
| Σ PBDEs | 33.2 | 26.1 | 26.6 | 25.1 | 24.8 | 27.3 | 18.3 | 25.7 | 17.7 | 22.3 | 12.4 | 16.6 |
| Particle phase | | | | | | | | | | | | |
| BDE-28 | 0.87 | 0.65 | 0.83 | 1.00 | 1.12 | 0.90 | 0.98 | 0.84 | 1.00 | 0.77 | 0.99 | 0.87 |
| BDE-47 | 4.12 | 3.43 | 3.57 | 3.70 | 3.86 | 3.87 | 2.60 | 1.88 | 1.54 | 1.46 | 1.84 | 1.76 |
| BDE-99 | 2.10 | 2.30 | 1.91 | 1.28 | 1.88 | 1.89 | 0.84 | 0.89 | 1.02 | 1.05 | 1.08 | 0.98 |
| BDE-100 | 1.03 | 1.53 | 1.19 | 0.77 | 0.93 | 0.05 | 0.89 | 1.24 | 0.78 | 1.21 | 0.99 | 0.81 |
| BDE-153 | 4.12 | 5.12 | 4.19 | 4.05 | 4.07 | 5.34 | 3.55 | 2.55 | 3.56 | 4.13 | 3.54 | 3.87 |
| BDE-154 | 2.78 | 2.17 | 2.57 | 2.38 | 2.56 | 2.07 | 1.88 | 2.54 | 1.29 | 2.26 | 2.98 | 2.31 |
| BDE-183 | 3.20 | 3.32 | 2.31 | 4.09 | 3.60 | 3.30 | 2.80 | 3.66 | 2.69 | 3.40 | 4.72 | 4.02 |
| BDE-209 | 78.05 | 52.78 | 67.42 | 69.54 | 54.21 | 57.54 | 30.62 | 23.76 | 47.67 | 38.08 | 39.24 | 42.52 |
| Σ PBDEs | 96.3 | 71.3 | 84.0 | 86.8 | 72.2 | 75.0 | 44.2 | 37.4 | 59.5 | 52.4 | 55.4 | 57.1 |

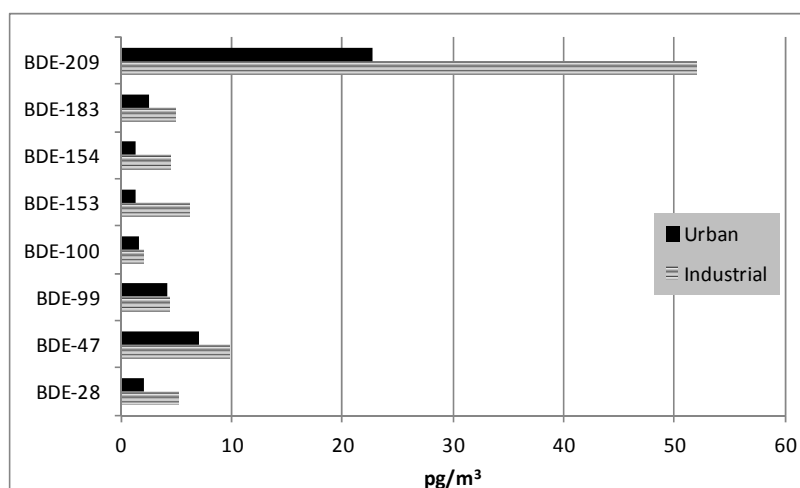


Fig. 1. Mean concentrations of BDEs in the urban and industrial sites in Florence, Italy.

(La Guardia *et al.*, 2006). In the present study, the relatively low percent of BDE-209 is likely attributed to debromination, or simply to a different BDE mixtures consumption behavior in the Tuscany region (or in Italy in general). However, if BDE-209 was debrominated, this would probably lead to formation of lighter PBDEs, and we would probably observe considerably higher concentrations of the penta-BDEs (#99 and #100). To explore this further, we plotted the concentrations of BDE-47 (tetra-BDE) vs BDE-99 both in gas and in particle phases (Fig. 2). From the subfigures presented, we note that the levels of BDE-47 are in all samples higher (or in few cases equal) than BDE-99. Similar concentrations of BDE-47 and BDE-99 is expected, because these two congeners were at the same levels in the technical formulations. Thus, their similar levels also in real samples can be perceived also as an evidence that no (or limited) debromination of heavier PBDEs takes place, because if that was happening, the ratio of BDE-47 to BDE-99 would be “disturbed”.

At the present study, the seasonal variation was also studied and is presented in Fig. 3. It can be seen that the lighter and more volatile BDEs (BDE-28, BDE-47 and BDE-99) exhibited much higher concentrations in the summer period in both the industrial and the urban sites. BDE-100, BDE-153 and BDE-154 were almost at the same levels in both seasons at the urban sites, and were slightly higher in the summer at the industrial sites. Opposite trends finally are observed for BDE-183 and BDE-209. The higher summer concentrations for semivolatile organic compounds that are contained in household products (e.g., PCBs, PBDEs) have been observed in various cases, and is likely to be attributed to emission rates enhanced due to the higher temperatures, contrarily to what is observed for POPs that are characterised by higher emissions in the winter due to space heating activities etc. (Katsoyiannis *et al.*, 2010; Katsoyiannis *et al.*, 2011).

In order to compare PBDE levels observed in the present study with data reported in the literature, the sum of the six most frequently monitored congeners (Σ_6 PBDE, sum of BDE-28, -47, -99, -100, -153, -154) was used (excluded

BDE-209). Σ_6 PBDE concentrations levels in the urban (12.1–27.9 pg/m^3) and industrialized (21.6–44.3 pg/m^3) sites in Florence are moderate and they are fully comparable to values found for other urban and industrialized air samples collected in Athens and Heraklion, Greece (3–41 pg/m^3) (Mandalakis *et al.*, 2009), Birmingham, UK (10–33 pg/m^3) (Harrad *et al.*, 2004), Kyoto, Japan (1.5–52 pg/m^3) (Hayakawa *et al.*, 2004); Izmir, Turkey (4.5–64 pg/m^3) (Cetin and Odabasi, 2008), Chicago, USA (34–77 pg/m^3) (Strandberg *et al.*, 2001). Instead, there exist in literature studies where much higher concentrations were reported for other urban sites such as Lake Maggiore, Italy (101 pg/m^3) (Mariani *et al.*, 2008) and Guangzhou, China (76–3600 pg/m^3) (Chen *et al.*, 2006). The study of Birgul *et al.* (2012) reported levels of Σ_6 PBDEs at the order of $< 5 \text{ pg/m}^3$ for the year 2010, in four sites in the UK, however they reported that at the same places, the levels of PBDEs have decreased substantially over the last 10 years.

If we instead compare the concentrations of BDE-209 with other sites, the Florence concentrations can be considered among the highest ones in Europe, however, they are orders of magnitude lower from what has been measured in China (concentrations up to 6900 pg/m^3 , Li *et al.*, 2009).

Gas-Particle Partitioning

Concentrations in the gas phase were always lower than the respective in the particulate phase. Total PBDE concentrations in the gas phase ranged from 8.10 to 18.8 pg/m^3 and from 12.4 to 33.2 pg/m^3 for urban and industrial sites, respectively, and in the particulate phase from 22.7 to 39.4 pg/m^3 and from 37.4 to 96.3 pg/m^3 for urban and industrial, respectively.

BDE-28 and BDE-47 were present predominantly in the gas phase (urban, 13 and 37.8%, respectively; industrial 18.6 and 30.1%, respectively), BDE-99, -100, -153, -154, -183 were present in both phases at similar concentrations, whereas deca-BDE (BDE-209) was found predominantly in the particulate phase and was the most abundant congener for the total PBDEs at all sampling sites, contributing 70.5 and 74.9%, respectively.

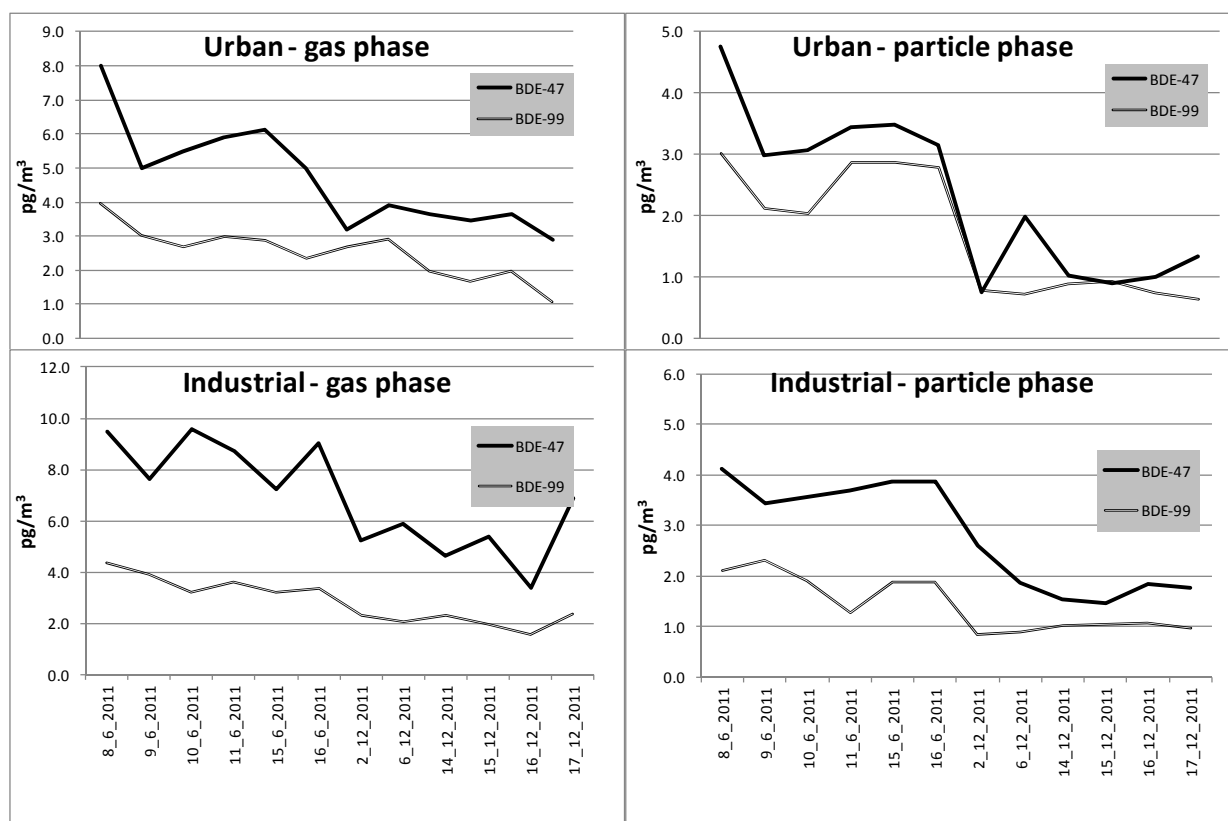


Fig. 2. BDE-47/BDE-99 ratio in the gas- and particle- phases in urban and industrial sites in Florence, Italy.

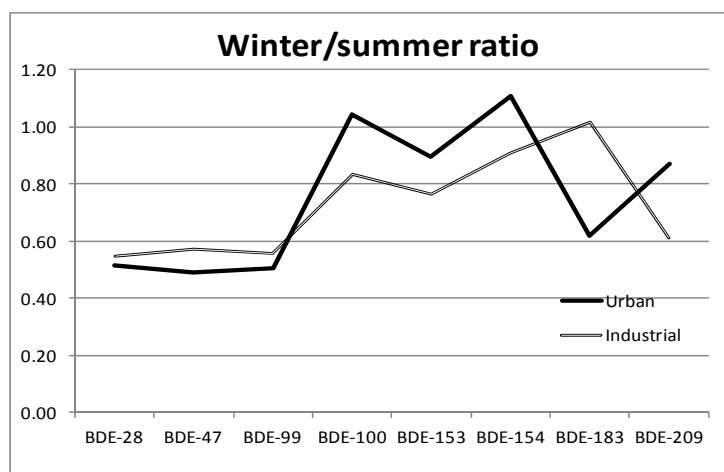


Fig. 3. Seasonal variation in PBDE concentrations (winter/summer air concentrations).

The distribution of semivolatile organic compounds (SVOCs) between the gas and particulate phases in air is commonly defined using the particle/gas partition coefficient K_p (Pankow, 1994) defined as $K_p = (F/TSP)/A$ where F and A are the concentrations of SVOCs associated with particles and gas phase (pg/m^3) respectively, and TSP is the concentration of total suspended particulate matter in air ($\mu\text{g}/\text{m}^3$). In the present study, average TSP concentrations were in the range $47.5\text{--}86.2 \mu\text{g}/\text{m}^3$ and $58.2\text{--}98.5 \mu\text{g}/\text{m}^3$ in the urban and industrialised sites, respectively. Two different mechanisms have been proposed to describe the association

of SVOCs with particles, that is, adsorption into the aerosol surface and absorption into the organic matter.

The adsorption model, also known as the Junge-Pankow (J-P) model, relates the particulate fraction (ϕ) of SVOC adsorbed on the particulate matter to the subcooled liquid vapour pressure (P_L° , Pa) of the pure compound, the particulate surface area per unit volume of air (θ , cm^2 aerosol cm^{-3} air) and a constant (c , Pa cm), as shown in the following equation $\phi = c\theta/(P_L^\circ + c\theta)$. Parameter c depends on the heat of desorption from the particulate surface, the heat of vaporization of the compound and the moles of adsorption

sites on the aerosol. Values of $c = 0.172 \text{ Pa cm}$ and $\theta = 1.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ for urban air were used (Bidleman, 1988) in this study. In Fig. 4 the particulate fractions (ϕ) of PBDEs predicted by the J-P model with the measured ϕ data calculated as the amount of the chemical in the particulate phase divided by the total amount of the chemical ($\phi = F/(A + F)$) are compared.

As also observed in other studies (Chen *et al.*, 2008) and for other classes of SVOCs (Cotham and Bidleman, 1995; Harner and Bidleman, 1998; Lee and Jones, 1999; Helm and Bidleman, 2005), the J-P model tends to overestimate the particulate sorption. In particular, the disagreement between the experimental and theoretical data for the industrial site may be attributed to the choice of the θ and c values which were more specific for urban sites and as suggested by Junge (1977) and Pankow (1987) may vary with the class of SVOCs.

The octanol-air partitioning coefficient (K_{OA}) model is also suggested as an alternative to P°_L for describing absorption of SVOC to particles (Harner and Mackay, 1995; Finizio *et al.*, 1997). SVOCs would dissolve in the organic matter in the atmosphere, which exists both as primary and as secondary organic aerosols (Lohmann and Lammel, 2004). The K_{OA} can be used to predict K_p with the assumption that the predominant distribution process is absorption (Harner and Bidleman, 1998). K_{OA} -based absorption model relates K_p to K_{OA} and the organic matter fraction (f_{om}) in aerosols according to the following equation $\log K_p = \log K_{OA} + \log f_{om} - 11.9$ (Harner and Bidleman, 1998). Temperature dependent K_{OA} values of the PBDE congeners were calculated using the regression parameters (A and B) given by Harner and Shoeib (2002) ($\log K_{OA} =$

$A + B/T$). The fraction of SVOCs on particles (ϕ) is then calculated as $\phi = K_p \text{TSP}/(1 + K_p \text{TSP})$. Sample specific organic matter contents and TSP concentrations were used in calculations for both sites. The K_{OA} based model seemed to fit the PBDE data better than the J-P model (see Fig. 5). The best agreement between measured particulate fractions and those calculated by the equilibrium partitioning model was found for BDE-28 and BDE-47. All the other PBDE congeners were slightly overestimated by the model, although the summer data were closer to values predicted by the absorption model than the winter data.

Both mechanisms, adsorption onto the aerosol surface and absorption into the aerosol organic matter, drive gas-particle partitioning of SVOCs and lead to a linear relationship between $\log K_p$ and $\log P^{\circ}_L$ (Pankow and Bidleman, 1992) expressed as:

$$\log K_p = m_r \log P^{\circ}_L + b_r \quad (1)$$

where the slope m_r and t-intercept of the trend line b_r are constants (Pankow, 1994). The values of $\log P^{\circ}_L$ for PBDE congeners were calculated from the Clausius-Clapeyron equation ($\log P^{\circ}_L = A/T - B$). The regression parameters A and B were obtained by Tittlemier *et al.* (2002) using the average ambient temperature during each sampling time. The regression parameters were not available for BDE-209. When plotting $\log K_p$ values against $\log P^{\circ}_L$ a slope m_r of -1 is expected for either adsorption and absorption model. However a variety of m_r values unequal to 1 have been reported for various SVOCs which is attributed to sampling artefacts or non equilibrium conditions and/or difference in sorbent effects (Bidleman and Harner, 2000). The slope m_r

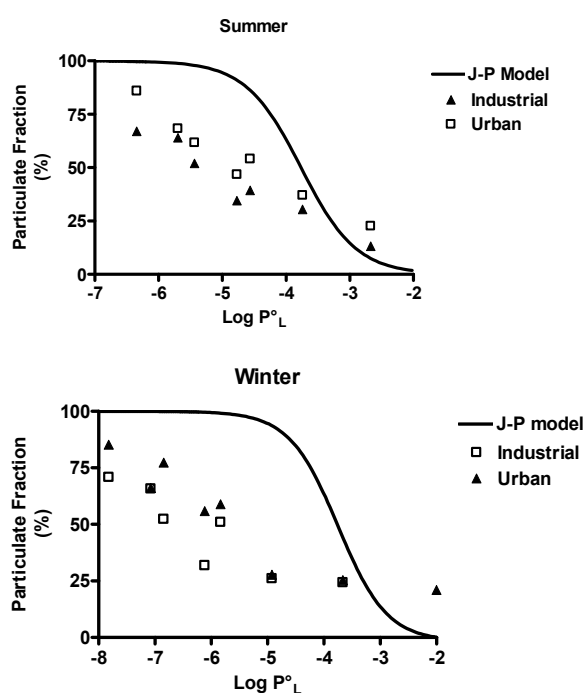


Fig. 4. Comparison of the measured particulate fractions ($\phi \times 100\%$) of PBDEs with theoretical predictions of the Junge-Pankow model for industrial and urban sites.

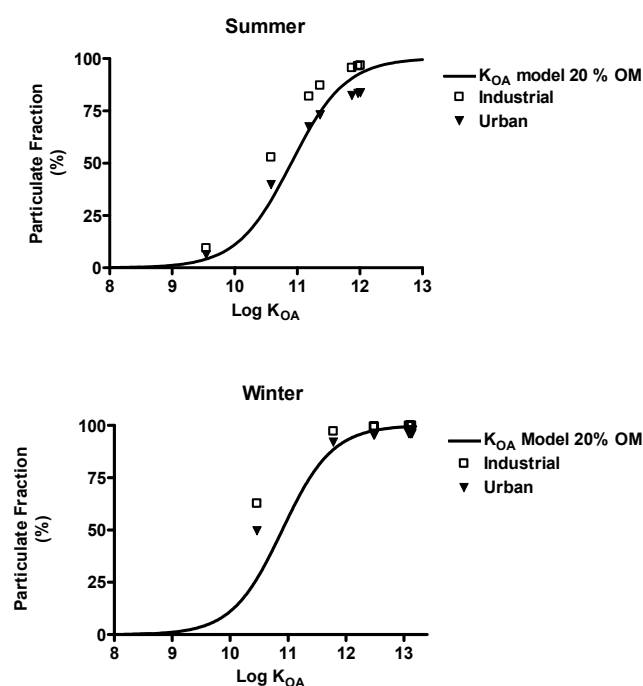


Fig. 5. Comparison of the measured particulate fractions ($\phi \times 100\%$) of PBDEs with theoretical predictions of the K_{OA} absorption model for industrial and urban sites.

also contains information about the type and factors that determine the sorption process. The y-intercept of the trend line (b_r) depends mainly on the properties associated with SVOCs.

Fig. 6 shows the regression data of $\log K_p$ versus $\log P^{\circ}_L$ for PBDE measured in the industrial and urban sites. In Table S11 (Supplementary Information) the m_r , b_r and r^2 values are reported for each sampling date. Significant linear correlations between $\log K_p$ and $\log P^{\circ}_L$ were obtained with r^2 in the range 0.49–0.954 ($p < 0.05$) and 0.668–0.949 ($p < 0.05$) for industrial and urban site, respectively, with the regression parameter m_r ranging between -0.469 and -0.162 (industrial) and between -0.388 and -0.228 (urban) and parameter b_r in the range -4.757 and -2.921 for industrial and -3.861 and -3.026 for the urban site. The correlation coefficients were similar for both sites suggesting that an equilibrium state could not be established probably due to the fresh PBDEs continuously emitted from local sources as observed also by Chen *et al.* (2008) for gas-particle samples collected in Guangzhou (China). Good correlations were also obtained plotting $\log K_p$ against $\log K_{OA}$, with r^2 ranging between 0.35 and 0.94 (industrial) and 0.64–0.86 (urban). However the m_r values were ranging from 0.165 to 0.615 and from 0.31 and 0.51 for industrial and urban sites, respectively) (see Table S11, Supplementary Information), as observed in other studies (Chen *et al.*, 2008).

According to Goss and Schwarzenbach (1998), $m_r < -1$ suggests surface adsorption, whereas -0.6 absorption by the

organic matter and between -1 and -0.6 coexistence of both mechanisms, m_r values suggested that absorption process should be the dominant sorption process in this study.

CONCLUSIONS

The present study gave an overview of the status of air pollution by PBDEs in the city of Florence, Italy. BDE-209 was the most compound and was routinely analyzed in all samples collected. Based on the concentrations found for all studied PBDEs in the two sites, it can be extracted that industrial and urban sources are slightly different to each other, however in good agreement with the known global pattern describing the consumption rates of the technical mixtures that is decabromodiphenyl ether, pentabromodiphenyl ether and otobromodiphenyl ether.

The industrial site exhibited higher concentrations than the urban site, and presented also some differences in the overall PBDE profile, suggesting that the primary sources that mainly affect these two sites are probably different.

The measured particulate sorption of PBDEs was compared to the predictions from Junge-Pankow (J/P) model and K_{OA} absorption model. While the Junge-Pankow model tends to overestimate the particulate sorption, the K_{OA} based model seemed to fit the PBDE data.

Given the big production of goods where flame retardants are massively added, the emissions from vehicles and industrial applications, and the fact that PBDEs in the

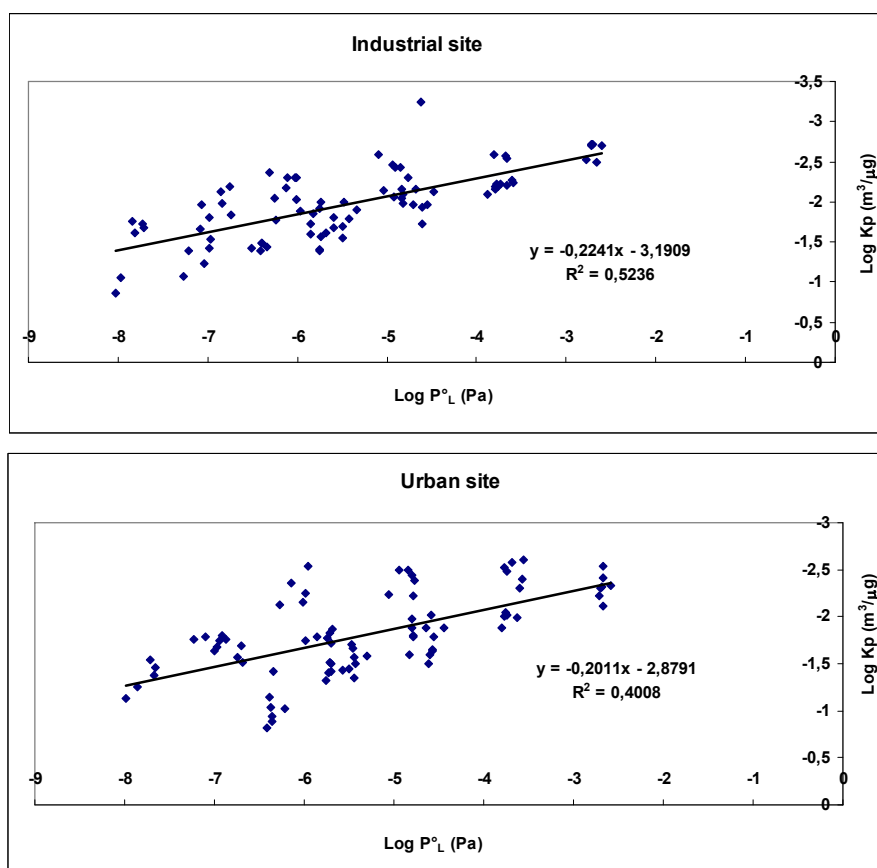


Fig. 6. Plots of $\log K_p$ versus $\log P^{\circ}_L$ for industrial and urban sites.

Florence atmosphere are at the highest-end of air concentrations around Europe, it is rather reasonable that monitoring continues to take place, in order for the Authorities to have all necessary information and decide the necessary measures and also in order for some temporal trends to be registered.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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Supplementary Materials

Table S11. Regression data of Log K_p versus Log P°_L and Log K_{OA} versus Log P°_L for industrial and urban sites.

| Log K_p vs Log P°_L | | | | | | | | |
|--------------------------------|-----------------|---------|--------|------------------|------------|---------|--------|------------------|
| Sampling date mm/dd/yy | Industrial site | | | | Urban site | | | |
| | m | b | r^2 | Significance (p) | m | b | r^2 | Significance (p) |
| 06/08/2009 | -0.2466 | -3.2436 | 0.9284 | <0.005 | -0.3348 | -3.2831 | 0.9231 | <0.005 |
| 06/09/2009 | -0.3107 | -3.4942 | 0.8946 | <0.01 | -0.3168 | -3.3036 | 0.8544 | <0.025 |
| 06/10/2009 | -0.355 | -3.5688 | 0.9065 | <0.01 | -0.2901 | -3.1074 | 0.878 | <0.01 |
| 06/11/2009 | -0.2851 | -3.3259 | 0.848 | <0.025 | -0.3883 | -3.4937 | 0.9488 | <0.005 |
| 06/15/2009 | -0.2861 | -3.3048 | 0.954 | <0.005 | -0.2869 | -3.0261 | 0.8463 | <0.025 |
| 06/16/2009 | -0.3885 | -3.9581 | 0.4939 | <0.005 | -0.2278 | -3.3113 | 0.7067 | <0.05 |
| 12/02/2009 | -0.1615 | -2.9214 | 0.6019 | <0.005 | -0.3395 | -3.1511 | 0.9321 | <0.005 |
| 12/06/2009 | -0.2075 | -3.3498 | 0.7586 | <0.05 | -0.2972 | -3.7268 | 0.7394 | <0.05 |
| 12/14/2009 | -0.209 | -3.3427 | 0.759 | <0.05 | -0.2715 | -3.6055 | 0.6681 | <0.05 |
| 12/15/2009 | -0.2102 | -3.3398 | 0.6566 | <0.05 | -0.2565 | -3.4878 | 0.7739 | <0.025 |
| 12/16/2009 | -0.2818 | -3.4711 | 0.8156 | <0.025 | -0.3005 | -3.8613 | 0.7731 | <0.025 |
| 12/17/2009 | -0.4689 | -4.7572 | 0.7999 | <0.025 | -0.2918 | -3.701 | 0.839 | <0.025 |

| Log K_p vs Log K_{OA} | | | | | | | | |
|---------------------------|-----------------|---------|--------|------------------|------------|---------|--------|------------------|
| Sampling date mm/dd/yy | Industrial site | | | | Urban site | | | |
| | m | b | r^2 | Significance (p) | m | b | r^2 | Significance (p) |
| 06/08/2009 | 0.3416 | -5.8912 | 0.9354 | <0.005 | 0.4246 | -6.4401 | 0.781 | <0.025 |
| 06/09/2009 | 0.4106 | -6.617 | 0.811 | <0.025 | 0.3920 | -6.1859 | 0.6802 | <0.05 |
| 06/10/2009 | 0.5008 | -7.4928 | 0.9359 | <0.001 | 0.3724 | -5.8987 | 0.7515 | <0.05 |
| 06/11/2009 | 0.3687 | -6.0975 | 0.7391 | <0.05 | 0.5115 | -7.3755 | 0.8572 | <0.025 |
| 06/15/2009 | 0.3854 | -6.2622 | 0.8915 | <0.001 | 0.3550 | -5.6388 | 0.672 | <0.05 |
| 06/16/2009 | 0.5006 | -7.7193 | 0.4252 | <0.005 | 0.4375 | -6.4338 | 0.8061 | <0.025 |
| 12/02/2009 | 0.2147 | -4.5936 | 0.511 | <0.05 | 0.4112 | -6.9992 | 0.6821 | <0.05 |
| 12/06/2009 | 0.2811 | -5.5668 | 0.6654 | <0.05 | 0.3825 | -6.6791 | 0.6378 | <0.05 |
| 12/14/2009 | 0.1651 | -4.117 | 0.3478 | <0.05 | 0.3365 | -6.0879 | 0.6397 | <0.05 |
| 12/15/2009 | 0.3002 | -5.777 | 0.6395 | <0.05 | 0.3131 | -5.8022 | 0.6366 | <0.05 |
| 12/16/2009 | 0.3586 | -6.2019 | 0.627 | <0.05 | 0.3979 | -6.9671 | 0.642 | <0.05 |
| 12/17/2009 | 0.6149 | -9.5128 | 0.6511 | <0.05 | 0.3900 | -6.7655 | 0.7088 | <0.05 |