



## Concentrations of legacy and emerging flame retardants in air and soil on a transect in the UK West Midlands



Daniel S. Drage<sup>a, b, \*</sup>, Seth Newton<sup>c</sup>, Cynthia A. de Wit<sup>c</sup>, Stuart Harrad<sup>a</sup>

<sup>a</sup> School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

<sup>b</sup> National Research Centre for Environmental Toxicology, University of Queensland, 39 Kessels Road, Coopers Plains, Queensland, 4108, Australia

<sup>c</sup> Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Stockholm, SE-10691, Sweden

### HIGHLIGHTS

- First ambient air and soil data for emerging flame retardants in the UK.
- An update of PBDE levels provided 10 years after their UK ban.
- Data shows role of urban activity as a source of flame retardants to environment.
- BDE-209 levels higher in Birmingham than similar studies elsewhere.
- HBCDD in ambient air double levels measured 5 years previously.

### ARTICLE INFO

#### Article history:

Received 5 November 2015

Received in revised form

8 January 2016

Accepted 8 January 2016

Available online 22 January 2016

Handling Editor: Myrto Petreas

#### Keywords:

PBDEs

HBCDD

HBCD

EFRs

Air

Soil

### ABSTRACT

Passive air samples were collected monthly for 6 months from 8 sites along a transect of Birmingham, United Kingdom between June 2012 and January 2013. Soil samples were collected once at each site. Average concentrations of BDE-209,  $\Sigma$ PBDEs<sub>17:183</sub> and  $\Sigma$ PBDEs in ambient air were 150, 49, and 180  $\text{pg m}^{-3}$ , respectively. Atmospheric concentrations of PBDEs were negatively correlated with distance from the city centre, exhibiting an “urban pulse”. The average  $\Sigma$ HBCDD air concentration was 100  $\text{pg m}^{-3}$ , however concentrations were not correlated with distance from the city centre. Several emerging flame retardants (EFRs) were identified in air and/or soil samples: 2,3,4,5-tetrabromo-bis(2-ethylhexyl) phthalate (BEH-TEBP), 1,2-dibromo-4-(1,2 dibromoethyl)cyclohexane (TBECH or DBE-DBCH), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), decabromodiphenyl ethane (DBDPE), and dechlorane plus (DP or DDC-CO). Average concentrations of BDE-209,  $\Sigma$ PBDEs<sub>17:183</sub> and  $\Sigma$ PBDEs in soil were 11, 3.6, and 15  $\text{ng g}^{-1}$  soil organic matter. PBDE concentrations in soil were higher at sites closest to the city centre, however correlations with distance from the city centre were not significant. BDEs-47 and -99 contributed more to  $\Sigma$ PBDEs in soil samples than air samples, but in both, the predominant congener was BDE-209. BATE was more abundant in air than soil but ATE was abundant in soil but not air.

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### 1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have been used extensively as flame retardants in textiles, plastics and electronic and electrical equipment. Concerns over their potential toxic nature have led to

bans on Penta- and Octa-BDE technical products within Europe in 2003, and globally under the UNEP Stockholm Convention (SC) in 2009 (Stockholm Convention, 2009). Significant restrictions have been put on the DecaBDE technical product since 2008 (Deffree, 2008) and HBCDD was listed under the SC in 2013 (Health and Environment Alliance, 2013).

Previous studies of PBDEs in outdoor air along rural-urban transects of cities in Canada (Gouin et al., 2005; Harner et al., 2006; Melymuk et al., 2012) the UK (Harrad and Hunter, 2006), Australia (Hearn et al., 2012) and Sweden (Newton et al., 2015) have found an “urban pulse” of higher concentrations within the city,

\* Corresponding author. National Research Centre for Environmental Toxicology, University of Queensland, 39 Kessels Road, Coopers Plains, Queensland, 4108, Australia.

E-mail address: [d.drage@uq.edu.au](mailto:d.drage@uq.edu.au) (D.S. Drage).

decreasing with distance from the city centre. This urban pulse was also seen in soil samples in the UK study (Harrad and Hunter, 2006). Higher PBDE concentrations have been found in indoor air than outdoor air (Harner et al., 2006; Newton et al., 2015) and recent studies have shown that indoor air released via ventilation systems is a major pathway for outdoor air contamination with PBDEs (Björklund et al., 2012; Newton et al., 2015). Thus, the urban pulse for PBDEs seems to be directly linked to the higher density of buildings within a city, which contain flame-retarded goods that emit PBDEs to the indoor environment and subsequently to outdoor air. The possible urban pulse behaviour of HBCDDs has not been studied and measurements in urban outdoor air samples are limited (Remberger et al., 2004; Hoh and Hites, 2005; Abdallah et al., 2008; Yu et al., 2008; Takigami et al., 2009; Hu et al., 2011; Li et al., 2012).

PBDEs and HBCDDs are being replaced by a number of emerging flame retardants (EFRs). Firemaster<sup>®</sup> 550 has been used widely as a replacement for PentaBDE and contains 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), and triphenyl phosphate (TPHP) (Stapleton et al., 2008). Potential replacements/substitutions also include: bis(2,4,6-tribromophenoxy) ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) for OctaBDE and DecaBDE respectively. Other EFRs in use include dechlorane plus (DP or DDC-CO), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH or DBE-DBCH), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), hexabromobenzene (HBB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE) and pentabromotoluene (PBT) (Covaci et al., 2011; Bergman et al., 2012).

A number of EFRs have been found in outdoor air (Hermanson et al., 2010; Möller et al., 2010, 2011a, 2011b; Salamova and Hites, 2013; Salamova et al., 2014) and deposition samples (Meyer et al., 2012; Newton et al., 2014) from remote sites in the Arctic. HBCDDs have also been found in several air and deposition samples from the Arctic (Remberger et al., 2004; de Wit et al., 2010) (Hermanson et al., 2010; Meyer et al., 2012). This indicates that these FRs are released to the atmosphere from source regions and undergo long range atmospheric transport to the Arctic. Thus it may be that EFRs and HBCDDs in indoor air behave similarly to PBDEs and are emitted from flame-retarded products to indoor air and released from buildings to the outdoor environment. If this is the case, they should also show an urban pulse similar to that found for PBDEs. In support of this, Newton et al. (2015) recently found an urban pulse in outdoor air for several EFRs (DBDPE, EH-TBB, PBT,  $\alpha$ - and  $\beta$ -DBE-DBCH) in Stockholm, Sweden. However, concentrations of many EFRs were below the detection limits and their atmospheric behaviour could therefore not be determined. Higher PBDE and HBCDD concentrations have been observed in UK compared to Swedish indoor environments (Harrad et al., 2010), and we hypothesise this will also be the case for EFRs. Thus, if HBCDD and EFRs are escaping from indoor environments to outdoor air from buildings, their atmospheric concentrations may be higher in Birmingham than Stockholm. The aim of this study was therefore to investigate the role of a city centre (Birmingham, UK) on concentrations of HBCDDs and EFRs in outdoor air and soil along a transect in the West Midlands conurbation of the UK, of which Birmingham is the major city. PBDEs were included for comparison with a previous such study carried out in 2003/2004 (Harrad and Hunter, 2006) in order to evaluate their response to the bans in 2003 (Penta- and OctaBDE) within the EU. BDE-209 is also included to evaluate its behaviour in outdoor air for this congener related to the use of the DecaBDE formulation. To our knowledge this study presents the first ambient air and soil data on EFRs for the UK.

## 2. Materials and methods

### 2.1. Sampling & site selection

Eight sampling sites were located on a 60 km transect along the prevailing wind direction from the south-west, through the city of Birmingham, to the north-east of the West Midlands conurbation (Fig. 1, Table S1, Supporting Information (SI)) and reflected varying degrees of urbanisation (i.e. building density). Outdoor passive air samples (PAS) were collected monthly from each location between June 2012 and January 2013 (Table S2, SI) using the same configuration previously developed (Abdallah and Harrad, 2010).

Each PAS consisted of a polyurethane foam (PUF) disc (140 mm diameter, 12 mm thickness, 360.6 cm<sup>2</sup> surface area, 0.07 g cm<sup>-3</sup> density, PACS, Leicester, UK) and a glass fibre filter (GFF) 125 mm diameter, 1  $\mu$ m pore size, Whatman, UK) as the sampling media. This configuration (Figure S1, SI) samples both the gaseous and particulate phases, thereby facilitating detection of higher molecular weight compounds such as BDE-209, and other compounds including HBCDDs, which are present in both phases (Harrad and Abdallah, 2008; Abdallah and Harrad, 2010). This is important as if only the vapour phase was sampled concentrations of such compounds would be underestimated. The PUF disk and filter are sheltered between two stainless steel housings (top housing – 23 cm diameter, 2 L volume; and bottom housing – 18 cm diameter, 1 L volume). The GFF is suspended in the middle of the sampler, supported by a wire mesh. The sampler was designed so that air would flow over the GFF and the particulate phase would be sampled by the upper face of the GFF by a combination of gravitational settling and turbulent deposition. The GFF was lost from site 5 (Edgbaston) during sampling period 3 and so no BDE-209 data were available for that particular sample.

Soil sampling was performed at each site in January 2013 using the method of Evans (2007). Briefly, three sub-samples were taken at each location, at least 1 m apart within a 1 m<sup>2</sup> area from the top 5 cm of surface soil and were transferred using a stainless steel trowel into (dichloromethane (DCM) and *n*-hexane pre-rinsed) amber jars on site. The sub-samples were combined, sieved (<2 mm), homogenised, and stored at <4 °C prior to extraction.

### 2.2. Extraction and clean-up

Target compounds were extracted from PAS (PUF and GFF from each sample combined) at the University of Birmingham (UB) using pressurised liquid extraction (PLE). Samples were concentrated to near dryness and reconstituted in 100  $\mu$ L methanol. Full extraction parameters are provided as supplementary material. The final extract was sonicated for 30 s and transferred to an inserted autosampler vial. After analysis via LC-MS/MS for HBCDDs and BDE-209, sample extracts were reconstituted in *n*-nonane for PBDE analysis via GC-EI/MS.

The extracts underwent further clean-up and fractionation for EFRs at Stockholm University (SU) as previously described (Sahlstrom et al., 2012; Newton et al., 2015). Further detail is provided as supplementary material.

PBDEs were extracted from soil samples via complete in-cell extraction and clean-up at UB as previously described (Abdallah et al., 2013). More details are provided as supplementary material. The final volume was adjusted to 100  $\mu$ L in methanol. The sample was sonicated for 30 s and transferred into an inserted vial and analysed for BDE-209 via LC-APPI-MS/MS. The sample was then solvent exchanged into 50  $\mu$ L in *n*-nonane before analysis of tri-hepta PBDEs via GC-EI/MS. Organic matter (OM) content in soil samples was determined (gravimetrically) as the loss on ignition after heating the dried samples at 500 °C for 4 h.

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