

Global atmospheric concentrations of BFRs and OPFRs from the GAPS Network

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame retardants in plastics, textiles and other materials.¹ Due to increasing concerns over the persistent, bioaccumulative and toxic properties of these chemicals the PentaBDE and OctaBDE formulations are listed under Annex A of the United Nations Environment Programme's Stockholm Convention on Persistent Organic Pollutants (POPs)² with DecaBDE recommended for listing under Annex A.² As a result of the banning or restrictions on use of these chemicals the production and use of alternative flame retardants including the novel Brominated Flame Retardants (novelBFRs) and the organophosphate flame retardants (OPFRs) has risen. Atmospheric concentrations of these alternative flame retardants have been reported however more data is needed on global background concentrations to establish baseline global levels.

The Global Atmospheric Passive Sampling (GAPS) Network was established in 2005 to support domestic and international monitoring programs including the Global Monitoring Plan (GMP) of the Stockholm Convention. In particular, the GAPS Network provides atmospheric data on legacy and newly listed POPs, emerging contaminants and candidate POPs being considered for listing by the POPs Review Committee of the Stockholm Convention. The GAPS Network currently collaborates with over 50 research institutes indicated in Figure 1.

In this study we report global atmospheric concentrations of PBDEs, novelBFRs and OPFRs from passive air samplers deployed during 2014 at 41 sites in the GAPS Network. The sites where samplers were deployed cover a range of location types from polar (n=4) to rural (n=6) and urban (n=4) however the majority sites are classed as background (n=27) providing an indication of regional, continental and global background concentrations of these flame retardants.

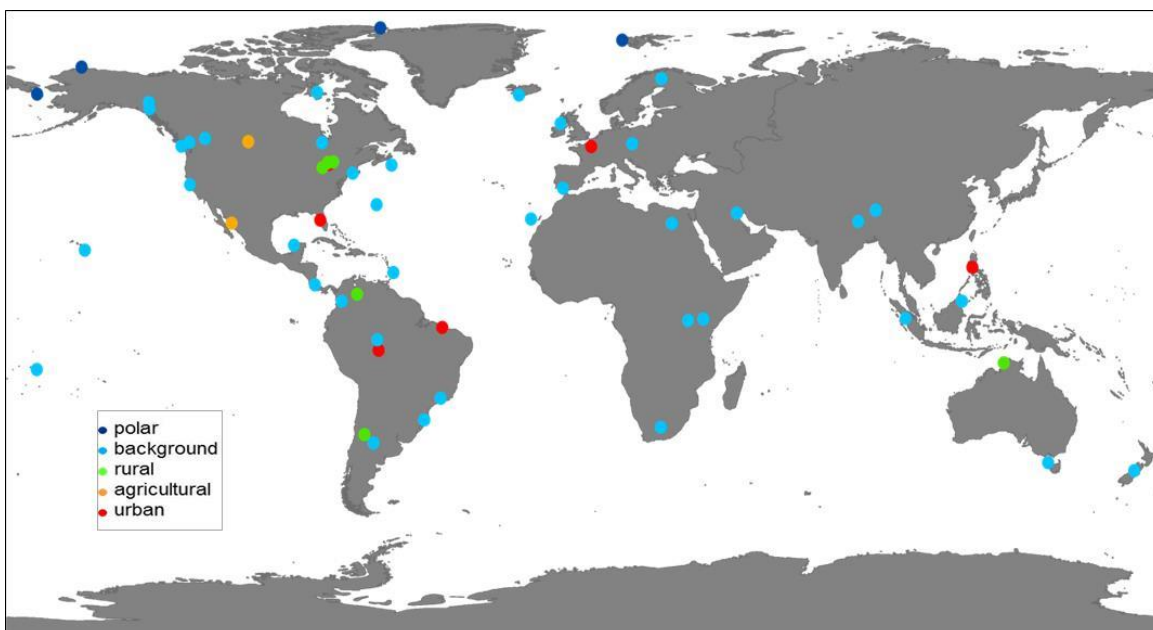
Materials and methods

Polyurethane foam (PUF) disk samplers were deployed quarterly at 41 sites during the 2014 sampling year. Sample preparation, shipping and storage procedures have been previously reported.³ The PUF samples were extracted and processed for the analysis of target analytes using previously reported methods.⁴

Sample extracts were analysed for OPFRs using previously reported methods.⁴ The BFRs that were analysed included 14 PBDE congeners (BDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 209) and 15 novel BFRs (Allyl-2,4,6-tribromophenyl ether (ATE), Beta tetrabromoethylcyclohexane (β -BDE-DBCH), 2-Bromoallyl-2,4,6-tribromophenyl ether (BATE), Beta 1,2,5,6 tetrabromocyclooctane (β -TBCO), 2,3-Dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), Hexabromobenzene (HBB), Dechlorane-602 (Dec 602), Dechlorane-604 (Dec 604), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-Bis(2,4,6-tribromophenoxy) ethane (BTBPE), Bis(2-ethyl-1-hexyl) tetrabromophthalate (BEH-TEBP), Octabromotrimethylphenylindane (OBIND), Syn- and Anti-Dechlorane (syn-DP, anti-DP) and Decabromodiphenyl ethane (DBDPE)). The BFRs were separated with a Restek Rtx-1614 column (15m, 0.25mm i.d., 0.1 μ m film) and detected using an Agilent 7890B Gas Chromatograph coupled with an Agilent 7010 tandem quadrupole Mass Spectrometer (GC-MS/MS, Agilent, Santa Clara, CA) using an electron ionization (EI) source.

Field blanks (n=44) were collected at sampling sites for assessment of sampling/laboratory contamination and samples were blank subtracted using the mean analyte concentration detected. Air concentrations (pg/m^3) of PBDEs were derived from the mass of the chemical (pg) collected on the PUF sampler divided by an effective air sample volume (m^3) determined using the GAPS Template.⁵ The novel BFRs were assumed to stay in the linear sampling phase during deployment, as described in Lee et al. (2015)⁶, and the effective air volume was calculated as the number of days the PUF was deployed (~90) multiplied by a sampling rate of 4 m^3/day . Similarly, the OPFRs have been shown to stay in the linear sampling phase during a 3 month deployment period⁷ and the effective air volume for the OPFRs was calculated as the number of days deployed multiplied by a sampling rate of 4 m^3/day . We note the uncertainty associated with the estimated effective sample air volumes of about 360 m^3 , especially for extreme sites that are subject to high wind speeds.

Figure 1: Map of the global sites participating in the GAPS Network, with location type indicated by the colour of the site.



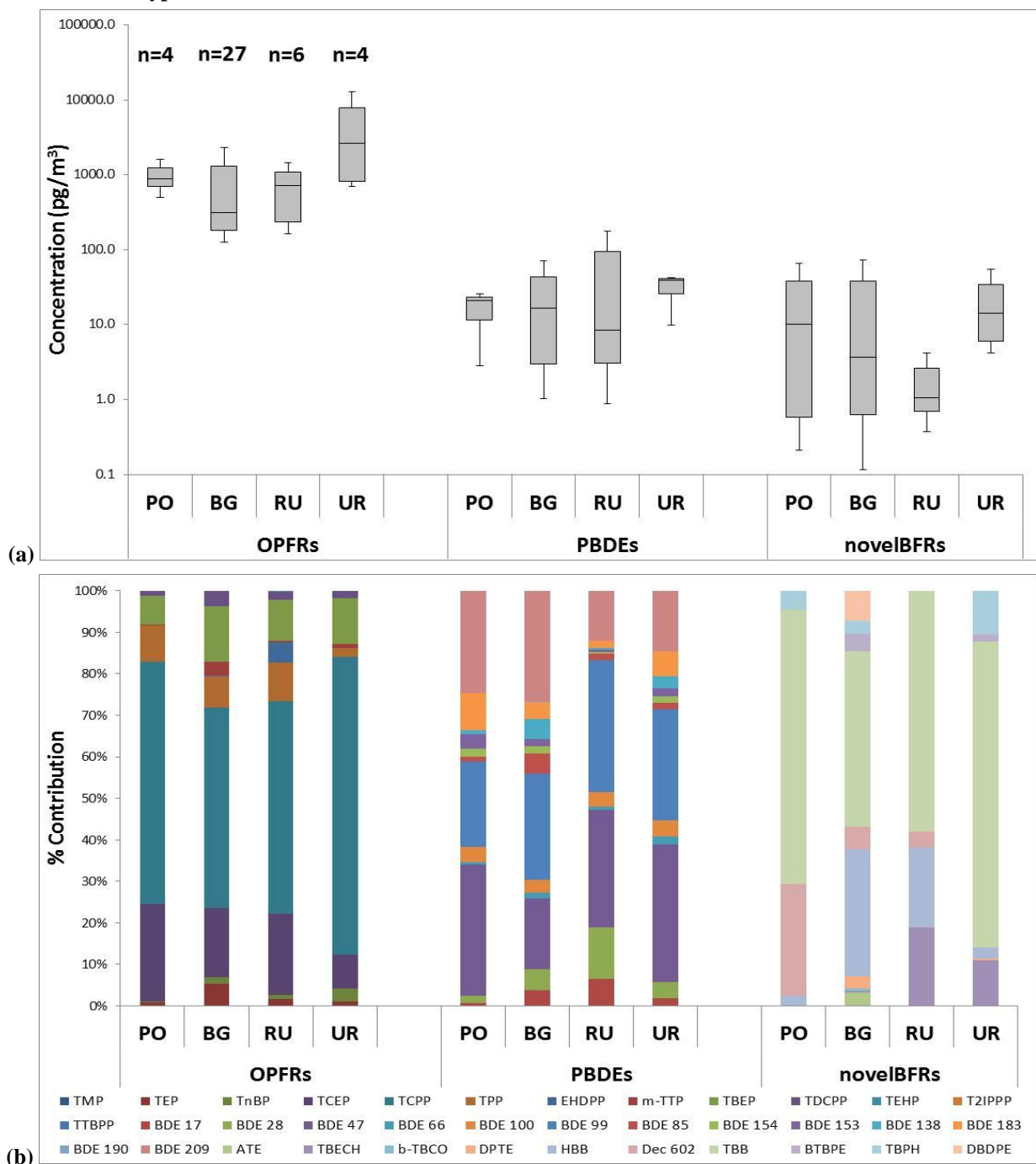
Results and discussion

OPFRs were detected in all samples and concentrations were at least an order of magnitude higher than the PBDEs at most sites. Paris, France displayed the highest concentrations with a mean Σ_{18} OPFR concentration during the sampling year of 7800 pg/m^3 . The other 40 sites ranged in concentration from 40 to 1300 pg/m^3 and at all sites the dominant OPFRs were the tris (chloroisopropyl) phosphate (TCPP), tris (2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPP) and tris (2-butoxyethyl) phosphate (TBEP) at concentrations of <MDL to 6500, 350, 950 and 600 pg/m^3 respectively. Tri-ethyl phosphate (TEP), tri-n-butyl phosphate (TnBP), tris (1,3-dichloro-2-propyl) phosphate (TDCPP) were detected frequently at lower concentrations of <MDL to 120, 80 and 80 pg/m^3 . 2-ethylhexyl diphenyl phosphate (EHDPP), tri-m-tolyl phosphate (m-TTP), tris (2-ethyl hexyl) phosphate (TEHP), tris (2-isopropylphenyl) phosphate (T2IPPP) and tris (tribromo neopentyl) phosphate (TTBPP) were detected less frequently and at lower concentration of <MDL to 70, 30, 6.3, 6.4 and 0.2 pg/m^3 . The OPFR levels determined at different location types (polar, background, rural or urban) were similar and within an order of magnitude and no concentration trends were determined between location types. The mean OPFR profile at each location type was also similar with the TCPP and TCEP dominating. Figure 2a displays box and whisker plots of Σ_{18} OPFRs at each location type and 2b presents the mean % contribution profile at each location type. Concentrations of TCEP, TCPP, TPP and TBEP were within the same range to that previously reported from countries in the Group of Latin American and Caribbean region during a special campaign in the GAPS Network in 2014 (<MDL to 1200, 320, 130 and 1280 pg/m^3 respectively).⁸ This suggests the potential for long range atmospheric transport of these chemicals and that background global concentrations of the OPFRs are consistent.

PBDEs were also detected in all samples with PBDE congeners in the PentaBDE formulation (28, 47, 99, 100) present in the highest concentrations at <MDL to 0.9, 30, 35 and 5.7 pg/m^3 respectively. BDE-153 and 154, which are present in both the Penta and OctaBDE formulations, were detected at concentrations of <MDL to 2.2 and 1.5 pg/m^3 while BDE-183 (the major constituent of the OctaBDE formulation) was present at concentrations of <MDL to 0.9 pg/m^3 . BDE-209 (the major constituent of the DecaBDE formulation) was detected with lower frequency but with higher concentrations of <MDL to 32 pg/m^3 . Concentrations of the novelBFRs were lower than the PBDEs and of the 15 novelBFRs investigated 3 were detected frequently: EH-TBB, HBB, and Dec 602, at concentrations of <MDL to 31, 1.7 and 0.15 pg/m^3 respectively. ATE, β -BDE-DBCH, TBP-DPTE, BEH-TEBP and BTBPE were detected less frequently at concentrations of <MDL to 15 pg/m^3 . DBDPE (a suggested replacement for BDE-209) was detected in only 2 background sites at concentrations of 8 and 40 pg/m^3 . The PBDEs and novelBFRs had similar concentrations between location types and the mean % contribution profiles were similar for the PBDEs, with the novelBFRs showing more variation, Figure 2. The GAPS Network has reported global concentrations of novelBFRs previously from a 2005 sampling campaign⁶ and the concentrations in this study are in line with that previously reported for, TBP-DPTE, HBB, BEH-TEBP, ATE, BTBPE and EH-TBB (<MDL to 2.3, 5.5, 6.6, 8.3, 19 and 28 pg/m^3 respectively). This may be an indication that global background atmospheric concentrations of the novelBFRs have remained consistent from 2005 to 2014.

This study reports for the first time global background levels of OPFRs from a single atmospheric passive sampling network. Atmospheric concentrations were consistent, regardless of location type showing the persistency and potential for long range atmospheric transport of the OPFRs. The detection of PBDEs at all sampling sites is also a further indicator of their persistence and long range atmospheric transport potential. The detection of BDE-209 at 40% of the sites sampled and at all location types (including the polar regions) provides a baseline global background atmospheric concentration of this chemical. With the recent decision at the 8th Conference of the Parties (April/May 2017, Geneva) to list DecaBDE to the Stockholm Convention these baseline levels are important for future atmospheric monitoring studies.

Figure 2(a) Box and Whisker plots showing concentrations in air (pg/m^3) of $\Sigma_{12}\text{OPFRs}$, $\Sigma_{14}\text{PBDEs}$ and $\Sigma_{10}\text{nBFRs}$ at 4 locations types: PO = polar (n=4), BG = background (n=27), RU = rural (n=6) and UR = urban (n=4). The boxes show median concentrations and the 25th and 75th percentiles, and 10th and 90th percentiles as indicated by the whiskers. **(b)** Mean % contribution profiles for OPFRs, PBDEs and nBFRs at the 4 location types.



Acknowledgements

These data have been generated in the frame of the Global Monitoring Plan for POPs under the Stockholm Convention, with support from the Secretariat of the Stockholm Convention and UN Environment. The implementation of the project as part of the Global Monitoring Plan for POPs has been made possible thanks to the generous contribution to the Stockholm Convention Voluntary Trust Fund by the European Commission through its Global Public Goods and Challenges (GPGC) programme.

We would like to thank our collaborators at all of the GAPS sampling sites including:

John Barnes, Pernilla Bohlin Nizzetto, Ernst Brunke, Juniper Buller, Marc Chevreuil, Sam Cleland, Brian Congdon, Gary Fellers, Gerry Forbes, Ted Gresiuk, Kimberly Hageman, Martin Haran, Liisa Jantunen, Foday M. Jaward, Begoña Jiménez, Shichang Kang, Jana Klanova, Edison Kurniawan, Dionisia Lambrinidis, Nerina Belén Lana, Matthew Martinsen, Rodrigo O. Meire, Pamela Miller, Jesse P. Milton, Andrew Peters, Andrew Platt, Renata Raina-Fulton, Allison Reeves, Pat Roach, Sergio Rodriguez, Evangelina C. Santiago, Gerður Stefánsdóttir, Richard Tanabe, Mika Vestenius, Doug Worthly and Toh Ying Ying

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