"New" Flame Retardants in the Global Atmosphere under the GAPS Network

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame retardants and detected in the environment globally. However, commercial PBDE mixtures, specifically penta-, octa- and/or decaBDE technical formulations, have been banned in Europe and North America (Ward *et al.* 2008; BSEF 2010). Recently, in an agreement negotiated between three companies (Albemarle and Chemtura, manufacturers of decaBDE in the U.S., and Israel's ICL Industrial Products, the largest U.S. importer of decaBDE) and the USEPA, production, importation and sale of decaBDE for most uses will be phased out by December 31, 2012 and all other uses by the end of 2013 (Hess 2009). Consequently, alternative non-BDE flame retardants are being used increasingly in commercial applications. For instance, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) is a replacement for the octaBDE mixture (Renner 2004). Firemaster 550 (FM550) is a pentaBDE replacement that contains 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethyl-1-hexyl)tetrabromophthalate (TBPH) (USEPA, 2005). Decabromodiphenylethane (DBDPE) has been marketed as an alternative to decaBDE (Kiekegaard *et al.* 2004). However, alternative non-BDE flame retardants have been detected also in environmental matrices such as biota and sediment and in humans (Gauthier *et al.* 2009; Kolic *et al.* 2009; Karlsoon *et al.* 2007; Eljarrat *et al.* 2009). Data relating to concentrations of non-BDE flame retardants in ambient air is limited to a few studies (Hoh and Hites, 2005; Hoh *et al.* 2005; Gouteux *et al.* 2008; Venier and Hites 2008).

Under the Global Atmospheric Passive Sampling (GAPS) Network, globally-resolved concentrations of persistent organic pollutants (POPs) in air have been reported (Pozo *et al*. 2009). Internationally, the GAPS program helps to assess effectiveness of control measures that have been implemented for POPs under treaties such as the Stockholm Convention on POPs under the United Nations Environment Programme (UNEP). Domestically, the GAPS Network contributes to the monitoring and surveillance efforts for priority chemicals identified under Canada's Chemicals Management Plan (CMP). For example, globally-resolved data are being generated for PBDEs to assess long-range atmospheric transport and inputs to the Canadian environment. To obtain information on the presence of non-BDE flame retardants in the global atmosphere, air samples collected from the GAPS Network in 2005 have been screened for these priority chemicals.

Materials and Methods

Polyurethane foam (PUF)-disk passive air samplers (PAS) were deployed at more than 40 sites worldwide in 2005 (Pozo *et al.* 2009) (see Figure 1). They were installed mainly in background sites away from local emission sources. Air samples were collected every three months. Details for the extraction of the PUF-disk samples and field blanks are given in Pozo *et al.* (2009). All samples and field blanks were screened for target analytes shown in Table 1. The analysis was performed by gas

chromatography negative-ion mass spectrometry using an Agilent 6890N GC-5973 mass selector detector in selected ion monitoring mode on a DB-5MS capillary column (30 m × 0.25 mm ID × 0.10 micron film thickness) with helium as the carrier gas and methane as the reagent gas. The temperature program was 80 °C initially, 5 °C/min to 250 °C, 15 °C/min to 300 °C and held for 5 min. The transfer line, source and quadrupole temperatures were 290, 230 and 150 °C, respectively. The injection was performed at 250 °C under pulsed splitless mode. The injection volume was 1 µL.

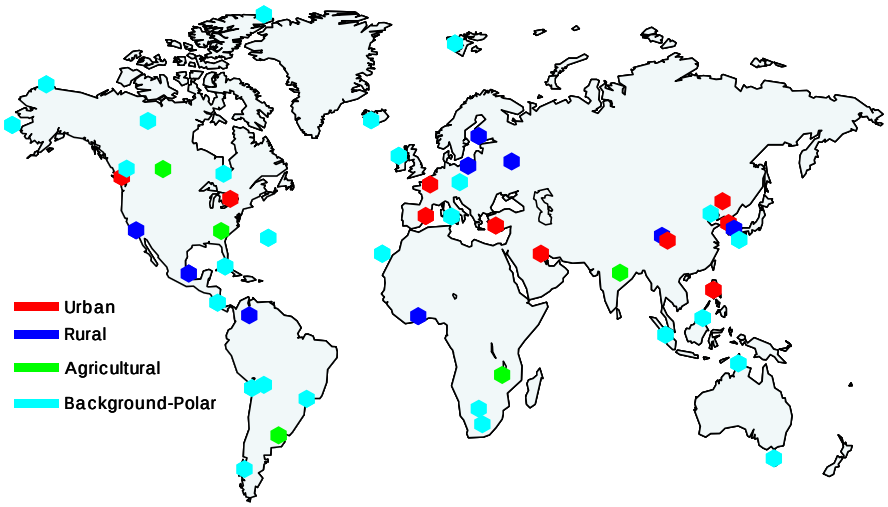

Figure 1. Sampling sites in the GAPS Network for 2005

Table 1. Target compounds – "New" non-BDE flame retardants

Compound	Acronym	CAS Number
1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE	37853-59-1
allyl 2,4,6-tribromophenyl ether	ATE (or TBPAE)	3278-89-5
2-bromoallyl 2,4,6-tribromophenyl ether	BATE	
2,3,5,6-tetrabromo-*p*-xylene	pTBX	23488-38-2
pentabromobenzene	PBBe	608-90-2
hexabromobenzene	HBB	87-82-1
tetrabromo-o-chlorotoluene	TBCT	39569-21-6
pentabromotoluene	PBTo	87-83-2
pentabromobenzylacrylate	PBBA	59447-55-1
2,3-dibromopropyl-2,4,6-tribromophenyl ether	DPTE	35109-60-5
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	TBB (or EHTeBB)	183658-27-7
bis(2-ethyl-1-hexyl)tetrabromophthalate	TBPH or (BEHTBP)	26040-51-7
2,2',4,5,5'-pentabromobiphenyl	BB101	67888-96-4
hexabromocyclododecane	HBCD*	3194-55-6
pentabromoethylbenzene	PBEB	85-22-3
octabromotrimethylphenylindane	OBIND	155613-93-7
decabromodiphenylethane	DBDPE (or DeBDethane)	61262-53-1

* HBCD refers to total HBCD.

Results and Discussion

Results are for air samples collected in the fourth quarter of 2005 (September 30-December 31). Table 2 shows the detection frequencies for specific target analytes grouped within five regions: i) North America; ii) Central and South America; iii) Europe; iv) Africa; and v) Asia and Australia. A measurement was considered to be quantifiable if it was above the instrumental detection limit and the mean field blank value. Of the analytes screened, BTBPE had the highest detection frequencies of 100% in all five regions; next are HBCD and HBB with 100% detection in four and three of the regions, respectively. BTBPE, HBCD and HBB have been detected in a variety of biotic and abiotic media on a global basis (Hoh and Hites, 2005; Hoh *et al.* 2005; Karlsoon *et al.* 2007; Gouteux *et al.* 2008; Venier and Hites 2008; Gauthier *et al.* 2009; Kolic *et al.* 2009). TBB and TBPH, the brominated components in FM550, as well as PBBe and TBCT had high detection frequencies in most samples for the majority of the regions. DBDPE and OBIND exhibited the lowest frequencies of detection.

Table 2. Percent detection frequencies of target analytes by region in fourth quarter GAPS Network air samples from 2005.

Compound	North America (n=9)	Central and South America (n=6)	Europe (n=9)	Africa (n=3)	Asia and Australia (n=10)
BTBPE	100%	100%	100%	100%	100%
HBCD	89%	100%	100%	100%	100%
HBB	89%	100%	100%	100%	90%
TBB	89%	100%	78%	67%	100%
TBPH	100%	100%	90%	67%	70%
PBBe	89%	50%	100%	100%	70%
TBCT	89%	100%	100%	33%	90%
ATE	67%	67%	78%	67%	60%
PBEB	67%	67%	89%	33%	80%
PBTo	67%	67%	78%	33%	90%
DPTE	11%	17%	67%	0%	60%
pTBX	56%	0%	78%	33%	20%
PBBA	11%	33%	22%	33%	70%
BB101	33%	17%	33%	0%	80%
BATE	33%	17%	44%	0%	30%
DBDPE	11%	0%	0%	0%	0%
OBIND	0%	0%	0%	0%	0%

Legend

n = number of sites

Detection frequency: <10% | 10-49% | 50-90% | >90%

Further work will consider other sampling periods to assess seasonal differences in air concentrations for target analytes. Results will also be assessed to see if significant differences exist based on location

of sites in background (the majority of sites), agricultural, urban, and polar regions. Method development work and calibration of the PUF disk samplers for these target analytes are required to allow for greater confidence in quantitative reporting of air concentrations.

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