



Wet deposition of brominated flame retardants to the Great Lakes basin – Status and trends



Matthew Robson^a, Lisa Melymuk^b, Lisa Bradley^c, Brenda Treen^c, Sean Backus^{c,*}

^a EmPOPs, 169 Holmwood Avenue, Plymstock, Plymouth PL9 9EY, United Kingdom

^b Masaryk University, RECETOX – Research Centre for Toxic Compounds in the Environment, Faculty of Science, Kamenice 5/753, Pavilion A29, Brno 62500, Czech Republic

^c Environment Canada, 867 Lakeshore Road, Burlington L7R 4A6, Ontario, Canada

ARTICLE INFO

Article history:

Received 18 April 2013

Received in revised form

8 July 2013

Accepted 12 July 2013

Keywords:

Brominated flame retardants

Wet deposition

Great Lakes

Temporal trends

Spatial trends

ABSTRACT

This study examined the temporal and spatial trends in wet deposition of 19 legacy and emerging brominated flame retardants (14 polybrominated diphenyl ethers (PBDEs), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE), hexabromocyclododecane (HBCD) and pentabromoethylbenzene (PBEB)) at 9 sites in the Canadian Great Lakes between 2004 and 2010. Concentrations of BDE-209 in wet deposition declined significantly. This indicates that the voluntary actions taken to phase out the use of BDE 209 in North America are having an immediate effect on its environment concentrations. The analysis also revealed the presence of 22 short-term high concentration events that dominated overall wet deposition loadings of current-use BFRs to the lakes. For instance, one sample in 2007 was responsible for 37% of the total loadings of HBCD to Lake Huron over the entire six-year sampling period. This questions the current paradigm of how we believe such pollutants enter the environment.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The brominated flame retardants (BFRs) are a class of organo-bromine chemicals that have been widely used as flame retardants since the late 1970s (Hites, 2006). BFRs are now ubiquitous global pollutants, and have been identified as persistent, bioaccumulative and toxic (De Wit, 2002). Due to concerns about rapidly increasing environmental concentrations (Hites, 2004), and concerns about both ecosystem (Ross et al., 2009; Tomy et al., 2004; Van den Steen et al., 2009) and human health impacts (Costa and Giordano, 2007; Harley et al., 2010; Roze et al., 2009), many BFRs have been subject to increasing regulations/bans over the past ten years (Environment Canada, 2012a; U.S. Environmental Protection Agency, 2009; Ward et al., 2008).

Historically, the most important BFRs were the polybrominated diphenyl ethers (PBDEs). These were marketed as three products: pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). As of 2009

penta- and octaBDE manufacturing has been phased out in North America, Europe, Australia and Japan (UNEP, 2009). North American manufacturers plan to voluntarily cease production of decaBDE in 2013 (U.S. Environmental Protection Agency, 2009), and it is expected that use will decline as the supply decreases. However, in order to continue to meet flammability standards in consumer products, the PBDEs have been replaced by other flame retardants, most often other halogenated flame retardants, as these are most cost-effective (Shaw et al., 2010).

Many of these “alternative or emerging” BFRs (eBFRs) have been in production for many decades, however their use is increasing rapidly as PBDE use declines. Recent reports have indicated that these eBFRs are now also becoming widespread in the environment (De Wit and Muir, 2010) and potentially pose a risk to human health (Covaci et al., 2011). Consequently there is a growing need for information concerning their entry and distribution into the environment.

The aim of this study is to examine the long term temporal and spatial trends of a range of current and legacy BFRs: the PBDEs and a suite of eBFRs: decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromoethylbenzene (PBEB) and hexabromocyclododecane (HBCD) in wet deposition in the Great Lakes basin with a view to elucidating any changes in the environmental loadings of these chemicals to the Great Lakes.

* Corresponding author.

E-mail addresses: matthewrobson@hotmail.com (M. Robson), melymuk@recetox.muni.cz (L. Melymuk), lisa.bradley@ec.gc.ca (L. Bradley), brenda.treen@ec.gc.ca (B. Treen), sean.backus@ec.gc.ca (S. Backus).

Wet deposition was chosen for this study as it is an important loading pathway for both gas and particle-phase compounds to aquatic ecosystems (Blanchard et al., 2008; Halse et al., 2012; Hornbuckle et al., 2006) such as the Great Lakes, and has been shown to effectively capture large-scale spatial and temporal trends (Brun et al., 2008; Holoubek et al., 2007; Melymuk et al., 2011). It is also likely to be highly important with respect to the environmental behaviour of BFRs due to their high particulate affinities and thus greater tendency to be scavenged by precipitation (Zhang et al., 2009).

Further details on all analytes are given in the [Supplementary Materials \(Table S1\)](#).

2. Materials and methods

2.1. Sampling sites

Samples were collected from nine sites in the Great Lakes basin (Fig. 1). The sites ranged from peri-urban locations at the highly populated western end of Lake Ontario to virtually unpopulated remote sites along the north shore of Lake Superior. Details of all of the sites, their geographical characteristics, and climate are given in [Table S2](#).

2.2. Sample collection

One sample was collected from each site every month (approximately 30 days). Samples were collected using a Meteorological Instruments of Canada (MIC-B) automated wet deposition sampler. This comprised a moisture-activated lid covering a stainless steel funnel (0.212 m² surface area) connected to two 4 L amber glass bottles connected in series, the first containing 200 mL of dichloromethane (DCM) as a stabilizing agent.

At the beginning of each sampling period the sampler was cleaned using methanol and deionised water, and new tubing and sampling bottles were fitted. The entire sampler was heated to approximately 10 °C during cold periods to prevent the sample freezing and to allow the collection of snow. After each sampling period the funnel was rinsed with DCM into the sample bottle to collect any remaining material, the sample removed, transported back to the laboratory and stored at 4 °C until analysis. Samples were collected from Burnt Island and Point

Petre from April 2004 to February 2010, from Burlington, St. Clair, and Sibley from April 2004 to February 2005 and April 2006 to February 2010, and from Point Pelee, Rock Point, Grand Bend and Turkey Lakes from April 2004 to February 2005 and April 2006 to February 2008. This is summarised in [Fig. S1 in the Supplementary Materials](#).

2.3. Sample analysis

All samples were analysed at the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario, Canada and followed established Integrated Atmospheric Deposition Network (IADN) standard operating and quality assurance/quality control (QA/QC) procedures (Wu et al., 2009).

The combined water and DCM was placed into a separatory funnel and allowed to separate. The DCM was removed and the volume of precipitation was measured. The aqueous phase was then extracted twice with fresh DCM. Large volume samples (>10 L) were similarly extracted using a Goulden Large Volume Extractor. The DCM extracts were then combined, reduced in volume by rotary evaporation and solvent exchanged to isooctane. The extract was then transferred to a 3% (w/w) water-deactivated silica gel column and fractionated to remove non-targeted analytes. Hexane was used to elute the first fraction containing the bulk of the PBDEs and nBFRs. The remaining PBDEs and nBFRs were then eluted with 1:1 (v/v) hexane:DCM. The extracts were concentrated by nitrogen evaporation to 1.0 mL.

Each fraction was analysed for 15 PBDE congeners (17, 28/33, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190 and 209), DBDPE, BTBPE, PBEB and HBCD. They were quantified on an Agilent 6890 GC with a 5973 MSD in NICI mode using a 30 m HP5-MS column (0.25 mm ID, 0.1 µm film thickness). Data was acquired by selected ion monitoring of ions 79 and 81 (BDE-209; 486, 484). Most PBDEs and BFRs split between fractions and were quantified by summing the amount found in each fraction. The same analytical method was used throughout the 6-year sampling campaign in order to ensure intra-comparability of the data throughout the wider IADN program.

2.4. QA/QC

Sample recoveries were monitored using three recovery standards added to the samples at extraction. These were BDE-71, ¹³C₁₂-BDE 209 and d₁₆-HBCD. Mean recoveries were 84 ± 15%, 85 ± 23%, and 94 ± 25% respectively. Additionally, recoveries were also monitored by the performance of regular spike tests (n = 60) for all analytes. Mean recoveries of individual PBDEs were 100 ± 19%, HBCD was 88 ± 31%, BTBPE 117 ± 36%, PBEB 94 ± 8% and DBDPE 182 ± 62%. Due to the high variability of the DBDPE recovery data, these results should be taken as indicative only. Samples were not corrected for recoveries.

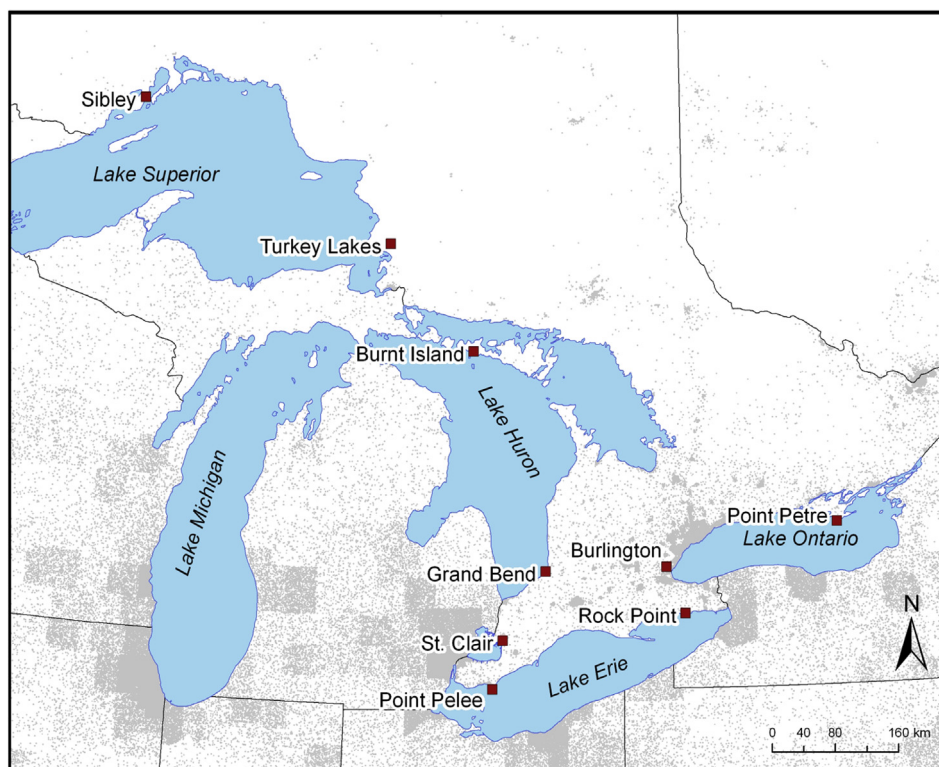


Fig. 1. Wet deposition sampling sites in the Great Lakes Basin. Grey shading reflects population density across the study region.

Download English Version:

<https://daneshyari.com/en/article/6317089>

Download Persian Version:

<https://daneshyari.com/article/6317089>

[Daneshyari.com](https://daneshyari.com)