

## Spatial distribution of tetrabromobisphenol A, bisphenol A and debrominated degradation products in sediments from Lake Erie

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### Introduction

Lake Erie is the southernmost, shallowest, warmest, and most biologically productive of the five Great Lakes. Intense urban and industrial activities on its shores, and upstream in the Lake Huron-Detroit River-Lake Erie corridor, means that Lake Erie is vulnerable to contamination by organohalogen contaminants such as PCBs.<sup>1</sup> Organohalogens of emerging environmental concern to the Great Lakes basin include classes of brominated flame retardants (BFRs), e.g., polybrominated diphenyl ethers (PBDEs). Another BFR is tetrabromobisphenol A (4,4'-isopropylidenebis(2,6-dibromophenol)), which is the primary component in a high volume, commercially-used BFR known as TBBPA.<sup>2</sup> TBBPA is used as a reactive or additive flame retardant in polymers, e.g., ABS, epoxy and polycarbonate resins, high impact polystyrene, phenolic resins and adhesives. Despite the reactive properties of TBBPA, environmental release occurs for TBBPA and degradation products from both additive- and reactive-treated products. TBBPA has been found in samples of air, soil, sediment and sludge, wildlife and human serum.<sup>3,4,5</sup>, but to our knowledge not in the Great Lakes system.

Biodegradation studies show that TBBPA could be partly degraded to lower brominated analogues under both aerobic and anaerobic conditions, in soil, and in river sediment.<sup>6</sup> For example, anaerobic incubation of the sediment with TBBPA and peptane-tryptone-glucose-yeast extract medium resulted in an 80% decrease in the TBBPA concentration and transformation to a non-brominated bisphenol A (BPA) metabolite.<sup>7</sup> BPA is also a major industry product that is widely used in the production of epoxy resins and polycarbonate plastics, and is commonly found in sediment, sludge and environmental water samples. TBBPA are expected to associate with sediments and suspended particulate matter as indicated by its partition coefficient (log K<sub>ow</sub>= 4.5) and low water solubility (0.72 mg/L). BPA has a lower log K<sub>ow</sub> of 3.4, and it has been predicated that about 50% of BPA in the environment is bound to sediments or soils.

The bioaccumulation of polybrominated-BPA and BPA in aquatic ecosystems by avian and piscine predators at the top of the food web is a concern from an endocrine perspective. BPA is also recognized as a relatively potent xenoestrogenic compound in human and wildlife. TBBPA and lesser brominated analogues share structural similarities to thyroxine (T<sub>4</sub>), the major circulating form of thyroid hormone, and have been shown to competitively bind with T<sub>4</sub> to human transthyretin (TTR), the major thyroid hormone transport protein in mammals and avian species.<sup>8</sup> As the numbers of bromine atoms decrease, polybrominated BPAs become poorer TTR binding competitors, but become increasingly potent agonists for estrogen receptor (ER)-mediated gene expression. We presently report on the patterns, concentrations and distribution of TBBPA and its debrominated analogues in sediment samples from sites spanning Lake Erie.

### Materials and Methods

A subset of sediment samples (n=48) was selected from a suite collected at 284 stations throughout Lake Erie during May to June 2004. Sampling was conducted using a 50 ´ 50 cm box corer. A 30 cm long x 5 cm diameter plug was removed with a coring tube, and the top 10 cm of surface sediment was extruded as 'top' sediment. After collection, samples were stored at -20 °C until analysis. The choice of sample sites was based on a stratified-random site selection procedure area and variance-weighted by depth class and substrate characteristics to permit whole-basin and whole-lake estimates of mass balance to be calculated.<sup>9</sup> Disproportionately more samples were analyzed from western basin sites, where organohalogen contaminant inputs are more substantial and complex than elsewhere in the lake.<sup>1</sup> We also recently investigated several sludge samples from waste water treatment plants

(WWTPs) for the City of Windsor, Ontario, and discharging into the upper Detroit River.<sup>10</sup>

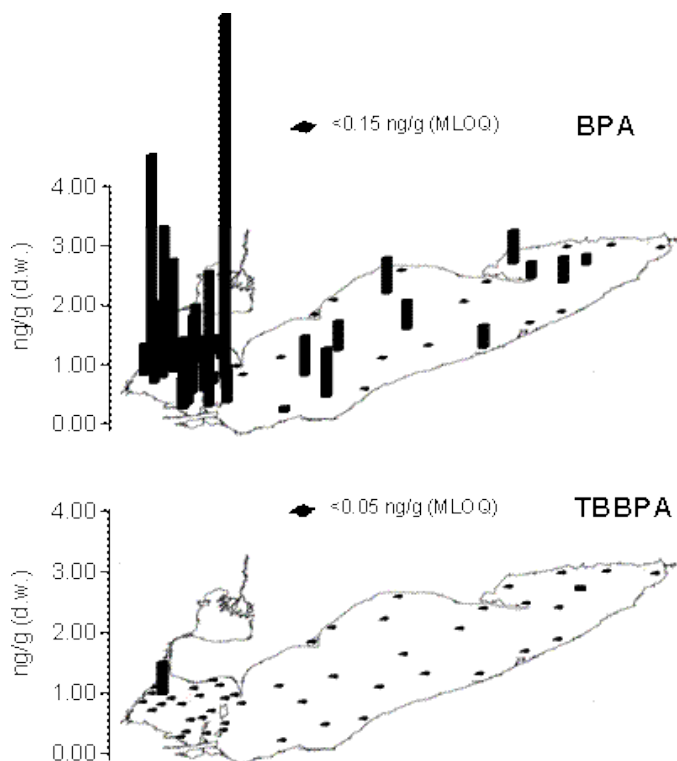
TBBPA and BPA standards were obtained from Aldrich Chemical Co (WI, USA) and were of minimum 97% purity. <sup>13</sup>C<sub>12</sub>-labeled TBBPA was obtained from Cambridge Isotope Laboratories, Inc (MA, USA; >99% purity). Monobromo-BPA and tribromo-BPA were a kind gift from Drs. Göran Marsh and Åke Bergman (Department of Environmental Chemistry, Stockholm University, Sweden). Dibromo-BPA was synthesized in our lab according to Eriksson et al.<sup>11</sup> The details on analytical methodology for polybrominated-BPAs and BPA are described elsewhere.<sup>10</sup> Briefly, 10 g sediment samples were Soxhlet extracted with *tert*-butyl methyl ether (MTBE) for 12 h. Polybrominated-BPAs and BPA in the extract were separated by partitioning between hexane and sodium hydroxide (1 M). After acidification of the aqueous phase, the target analytes were enriched and desalted by SPE using an LC-C18 cartridge (500 mg × 3 mL), then target analytes were eluted by 10 mL acetone. The eluant from the cartridge was concentrated and cleaned up by LC-Si SPE cartridges (500 mg × 3 mL; Supelco, USA). This eluant was concentrated, and reconstituted in methanol (100 µL) for high performance liquid chromatography-electrospray(-)-tandem quadrupole mass spectrometry (HPLC-ESI(-)-MS-MS) analysis. Target analytes were monitored in the multiple reaction monitoring (MRM) mode (Table 1). Quantification used an internal standard method with a six multi-level calibration curve. The recoveries and method limits of quantification (MLOQs) are listed in Table 1.

**Table 1.** Multiple reaction monitoring (MRM) channels, spiked recovery efficiencies (n=6) and the method limits of quantification (MLOQs) for HPLC-ESI(-)-MS-MS determination of BPA and polybrominated-BPA analogues in Lake Erie sediment samples.<sup>10</sup>

Compound	MRM Channels	Recovery (RSD)	MLOQ (ng/g, d.w.)
BPA	227 > 212	71 (10)	0.15
monobromo-BPA	307 > 81	72 (10)	0.02
dibromo-BPA	385 > 81	70 (5)	0.02
tribromo-BPA	465 > 81	97 (10)	0.04
TBBPA	543 > 81	102 (5)	0.05
<sup>13</sup> C <sub>12</sub> -TBBPA	555 > 81		

## Results and Discussion

In the eastern and central basins, BPA was detectable in 33% of the samples at concentrations up to 1.48 ng/g (d.w.) (Figure 1). In the western basin, BPA was detectable in all samples, reaching a maximum concentration of 6.10 ng/g (d.w.), but averaging 1.42 ng/g (d.w.). High concentrations of BPA were found near the mouth of the Detroit River would suggest that the Detroit River and surrounding urban complex is an important source of BPA to Lake Erie. The Detroit River accounts for the bulk water in-flow to Lake Erie. However, the greatest concentration of BPA was found directly at a location south of Pelee Island and adjacent to South Bass Island, remote from the main flow path of the Detroit River (Figure 1). The distributional pattern of elevated concentrations in this region suggests that local activity or in-flows from the Maumee River are also important sources of BPA. BPA concentrations decreased at sites further removed from the western basin.



**Figure 1.** TBBPA and BPA concentrations in surface sediment samples from 48 sites from across Lake Erie.

In contrast to BPA, TBBPA was only quantifiable at two sites, one at the mouth of the Detroit River (0.51 ng/g d.w.), and at near detection levels (Table 1) in the mid-eastern basin (Figure 1). Morris et al.<sup>12</sup> reported TBBPA in freshwater sediments from North Sea Estuaries, where the highest concentration (9800 ng/g d.w.) was from the River Skerne in northeast England. TBBPA concentrations in western Scheldt in Belgium range from <math><0.1</math> to 67 ng/g (d.w.). Tribromo-BPA was also quantifiable in Lake Erie sediments at the same site as for TBBPA at the mouth of the Detroit River at 0.34 ng/g (d.w.). Dibromo- or monobromo-BPA were not detectable (Table 1) in sediments from any of the Lake Erie sites. Sludge samples from waste water treatment plants (WWTPs) for the City of Windsor, Ontario, and discharging into the upper Detroit River<sup>10</sup> contained TBBPA and BPA at levels of 2.09-28.3 ng/g (d.w.) and 3.78-74.38 ng/g (d.w.), respectively, considerably higher than the levels observed in Lake Erie sediments (Figure 1). Furthermore, tribromo-BPA, dibromo-BPA and monobromo-BPA were also quantifiable in the sludge samples analyzed.

If City of Windsor WWTPs are representative of the ~75 WWTPs discharging into the Lake Huron-Detroit River-Lake Erie corridor, the potential loading of polybrominated-BPAs and BPA into Lake Erie is substantial. Our findings of mainly undetectable concentrations of polybrominated-BPAs and relatively higher BPA levels in Lake Erie sediment would suggest relatively short half-lives, effective debromination, and/or low levels of deposition of polybrominated-BPAs in Lake Erie.

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## EMG - General - Emerging Contaminants, Phenolic Compounds, Current Use Pesticides

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