



Methodology and determination of tetradecabromo-1,4-diphenoxybenzene flame retardant and breakdown by-products in sediments from the Laurentian Great Lakes



Lennart Trouborst^{a,b}, Shaogang Chu^a, Da Chen^c, Robert J. Letcher^{a,b,*}

^a Ecotoxicology and Wildlife Health Division, Wildlife and Landscape Science Directorate, Science and Technology Branch, National Wildlife Research Centre, Environment Canada, Carleton University, Ottawa, ON K1A 0H3, Canada

^b Department of Chemistry, Carleton University, Ottawa, ON K1S 5B6, Canada

^c Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University Carbondale, Carbondale, IL, USA

HIGHLIGHTS

- A unique method for sediment was developed for Br₁₄- to Br₁₀-DiPhOBz flame retardants.
- Br₁₄- to Br₁₀-PB-DiPhOBz recovery efficiency ranged from 33% to 104%.
- Br₁₀- to Br₁₄-PB-DiPhOBz quantification limits ranged from 0.17 to 0.49 ng g⁻¹ dw.
- Polybrominated DiPhOBzs were not detectable in Great Lakes sediment samples.

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ABSTRACT

Tetradecabromo-1,4-diphenoxybenzene (TeDB-DiPhOBz) is a brominated polyphenyl ether flame retardant (FR) that is known to photolytically degrade to produce lower brominated polybrominated-diphenoxybenzenes (PB-DiPhOBzs), which may be precursors to MeO-PB-DiPhOBzs recently reported in the Great Lakes herring gulls eggs. To our knowledge, there are no reports on TeDB-DiPhOBz or other PB-DiPhOBz by-products in any environmental sample. The present study analyzed for the presence of PB-DiPhOBzs (including TeDB-DiPhOBz) and MeO-PB-DiPhOBzs in surficial sediment from sites in Saginaw Bay in western Lake Huron ($n = 7$), and in comparison to southern Lake Huron (open water) ($n = 5$) and Lake Erie ($n = 3$) sediment collected in the summers of 2012 or 2013. To analyze for possible PB-DiPhOBzs (Br₁₄-Br₀), the first known analytical method was developed for extraction and cleanup of sediment samples, and analysis by HPLC-atmospheric pressure photoionization (–)–quadrupole time-of-flight-mass spectrometry. The overall recovery efficiency was optimized to on average 33–104% progressing from Br₁₄- to Br₁₀-PB-DiPhOBzs. Br₁₀- to Br₁₄-PB-DiPhOBz detection and quantification limits ranged from 0.05 to 0.15 ng g⁻¹ dw and 0.17 to 0.49 ng g⁻¹ dw, respectively. Although this is the first report, PB-DiPhOBzs (Br₁₄-Br₁₀) and MeO-PB-DiPhOBzs were not detectable in any sediment sample. This included a site near the mouth of the highly FR-contaminated Saginaw River, near the confined disposal facility (CDF) located in Saginaw Bay at Channel-Shelter Island, which receives dredged sediment from the Saginaw River. Our findings suggest sediments from the presently studied sites in the Great Lakes ecosystem are not a sink for TeDB-DiPhOBz and PB-DiPhOBz by-product contaminants.

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1. Introduction

Research on brominated flame retardants (BFRs) has revealed the hazards, both environmental and otherwise, of established

* Corresponding author at: Ecotoxicology and Wildlife Health Division, Wildlife and Landscape Science Directorate, Science and Technology Branch, National Wildlife Research Centre, Environment Canada, Carleton University, Ottawa, ON K1A 0H3, Canada. Tel.: +1 613 998 6696; fax: +1 613 998 0458.

E-mail address: robert.letcher@ec.gc.ca (R.J. Letcher).

substances (e.g. polybrominated diphenyl ethers (PBDEs)). As a consequence, a broader class of non-PBDE BFRs have been developed to replace PBDEs, following the restrictions on PBDE use as a result of their persistence in the environment, bioaccumulation, and biomagnification in biota and their food webs (Rahman et al., 2001; de Wit, 2002; Law et al., 2014).

Tetradecabromo-1,4-diphenoxybenzene (TeDB-DiPhOBz) (CAS# 58965-66-5), also abbreviated as 4'-PeBPO-BDE208 according to Bergman et al. (2012), is a halogenated polyphenyl ether, a

non-PBDE BFR chemical, and is the main constituent of several commercial technical formulations (Energy Chemical, 2014; MHP Chemical, 2014; TCI Chemicals, 2014). A 1973 US Patent to Dow Chemical (3760003) detailed the production of halogenated polyphenyl ethers that included TeDB-DiPhOBz. A major manufacturing location for the halogenated polyphenyl ethers under this patent was in Midland, Michigan, U.S.A. and on the Saginaw River flowing into Lake Huron, one of the Laurentian Great Lakes of North America.

TeDB-DiPhOBz is of a similar chemical structure to 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209), but with an additional pentabromophenoxy ring, and suspected to be a replacement for BDE-209. TeDB-DiPhOBz has a molecular weight of 1366.9 Da and a $\log K_{OW}$ of 12.67 (i.e. highly or "super" hydrophobic) (Howard and Muir, 2010). TeDB-DiPhOBz is estimated to have a very low bioconcentration factor (BCF) of 3.0 and therefore would not be predicted to be a chemical of environmental concern. According to a recent European Food Safety Authority (EFSA, 2012) report, it was also speculated that TeDB-DiPhOBz is poorly bioavailable, and therefore not potentially bioaccumulative. However, it was recently reported that when dissolved in organic solvents (e.g. tetrahydrofuran (THF)) TeDB-DiPhOBz rapidly photolytically degraded under UV-A, -B, -C, and/or sunlight irradiation (Chen et al., 2013; Su et al., 2014). They observed the production of sequentially debrominated TeDB-DiPhOBz by-products or polybrominated diphenoxybenzenes (PB-DiPhOBzs). Such photolytic debromination was also found for TeDB-DiPhOBz powder but occurred much more slowly (Chen et al., 2013). Regardless, the lower brominated PB-DiPhOBzs are predicted to be more bioavailable and to be less hydrophobic than TeDB-DiPhOBz. Also known is the photolytic and/or metabolic degradation of low bioavailability BDE-209 and the analogous BFR decabromodiphenyl ethane (DBDPE) to less brominated congeners (Söderström et al., 2004; Stapleton et al., 2006; Van den Steen et al., 2007; Wang et al., 2012; Chen et al., 2013; Letcher et al., 2014; Su et al., 2014).

Chen et al. (2011) discovered novel brominated contaminants in the eggs of herring gulls (*Larus argentatus*) from colony sites in the Laurentian Great Lakes of North America. These contaminants were methoxylated-polybrominated-diphenoxybenzenes (MeO-PB-DiPhOBzs), containing between 4 and 6 bromine atoms; and were found at concentrations as high as 30 ng g⁻¹ egg wet weight (420 ng g⁻¹ lipid weight). It was hypothesized that MeO-PB-DiPhOBzs are metabolic products and sourced from more brominated diphenoxybenzene BFRs, specifically PB-DiPhOBzs and TeDB-DiPhOBz. Chen et al. (2012) also retrospectively quantified the concentrations of MeO-PB-DiPhOBzs in Great Lakes herring gull eggs sampled from 1982 to 2010. They observed concentrations of Σ MeO-PB-DiPhOBzs consistently between 30 and 100 ng g⁻¹ ww across all sites and all years, and concentrations were highest in eggs from colony sites in western Lake Erie and Saginaw Bay (Lake Huron). The highest concentrations of MeO-PB-DiPhOBzs were found on Channel-Shelter Island, which is a confined disposal facility (CDF) located in Saginaw Bay. This CDF is used to contain dredged sediment from the highly FR-contaminated Saginaw River (Velleux et al., 1993).

Hydrophobic species like PBDEs, and potentially the structurally analogous PB-DiPhOBzs, are minimally soluble in water and thus partition into sediment and other solid matter in aquatic environments (Hale et al., 2003). Thus, if present PB-DiPhOBzs are probably sediment associated in receiving water bodies. If sediment-associated contaminants are then transferred to benthic species, they may be transferred within food webs and to higher trophic level species (Ciparis and Hale, 2005; Law et al., 2006). However, to our knowledge, no quantitative analytical methods exist for the deter-

mination of TeDB-DiPhOBz, PB-DiPhOBzs or MeO-PB-DiPhOBzs in sediment. The objective of the present study is to develop such a quantitative analytical method for freshwater sediment samples. Employing this developed method, the hypothesis was subsequently tested that TeDB-DiPhOBz, PB-DiPhOBzs and/or MeO-PB-DiPhOBzs are present in e.g. Saginaw Bay (Lake Huron) and Lake Erie surficial sediment samples where high levels of MeO-PB-DiPhOBzs have been reported in eggs of herring gulls that nest in these areas. To our knowledge, there are no reports on the presence of TeDB-DiPhOBz and other PB-DiPhOBz by-products in any environmental sample.

2. Materials and methods

2.1. Standards and chemicals

A technical product of TeDB-DiPhOBz, supplied by Wellington Laboratories (Guelph, ON, Canada), was used in the experiment as a standard. The standard solution (250 μ g mL⁻¹) was prepared by dissolving solid TeDB-DiPhOBz standard into THF, and then stored in the dark at 4 °C. At the beginning of storage, the solution contained TeDB-DiPhOBz with a slight (~5%) impurity of Br₁₃-DiPhOBz. All solvents were HPLC grade and purchased from Caledon (Georgetown, ON), except THF which was purchased from Sigma-Aldrich (Oakville, ON, Canada). Disposable Bakerbond SPE silica gel cartridges (6 mL, 500 mg, 47–60 μ m) were purchased from J.T. Baker (Center Valley, PA, USA). Bio-Beads S-X3 (200–400 mesh) for GPC separation were purchased from Bio-Rad Labs (Hercules, CA, USA). Activated copper powder was prepared by treatment of copper powder (99.5%, Sigma-Aldrich) with 2 M HCl and then washed with water, acetone, and hexane. Diatomaceous earth (DE) (Varian Inc. Mississauga, ON, Canada) and anhydrous Na₂SO₄ were treated at 600 °C for 8 h before using to destroy any possible organic contamination.

2.2. Sampling locations

As reported by Chen et al. (2011, 2012), the highest MeO-PB-DiPhOBz levels in herring gull eggs were determined from colony sites at Channel-Shelter Island (Saginaw Bay, Lake Huron) and western Lake Erie (Fighting Island, Detroit River). Thus, surficial sediment sampling sites for the current study were (opportunistically) obtained in close proximity and/or in the surrounding areas from these two colony sites. Surficial sediment samples were collected by colleagues from Environment Canada and the United States Environmental Protection Agency (Great Lakes Environmental Center (GLEC)). Sampling was conducted using a 15 × 15 cm Petite Ponar Grab (stainless steel box) sampler (EcoEnvironmental, Perth, WA, USA), where a top 6 cm sample of surficial bottom sediment was collected. Grab samples were collected from across Lake Erie ($n=3$; western, central and eastern basins) in May 2012 ($n=1$) and in August 2013 ($n=2$) (Fig. 1, Table 1). The GLEC collected sediment samples in August 2013 from Lake Huron open water sites ($n=5$) and in September 2013 from Saginaw Bay sites ($n=7$) (Fig. 1, Table 1). All sediment samples were collected and stored in amber jars and frozen for transport. The surficial sediment sample size that was available for this study, as well as other emerging contaminant studies, was in the order of 100 g wet weight each. Sediments were shipped and stored until sample preparation at Letcher Group/Organic Contaminants Research Lab (National Wildlife Research Centre, Environment Canada, Carleton University). Blank sediment samples were retrieved from the shore of the Rideau River along Carleton University campus in Ottawa, ON (collected in summer-fall 2013) and immediately prepared for analysis.

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