

DETERMINATION OF TETRABROMOBISPHENOL A IN DETROIT RIVER SEDIMENT AND SEWAGE SLUDGE

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Introduction

Flame-retardants (FRs) are used to slow ignition or spread of fire and can be classified as either additive or reactiveⁱ. Additive FRs are physically mixed with polymers, whereas reactive FRs are incorporated into polymeric materials. Halogenated compounds are particularly useful as they scavenge radicals produced during combustion and are compatible with many polymers. Tetrabromobisphenol A (TBBPA) accounts for over one-half of the major BFRs produced (TBBPA, deca-BDE, HBCDD, penta-BDE, octa-BDE). TBBPA is used primarily as a reactive flame retardant in printed circuit boards. Leaching is less likely to occur from reactive applications; however, TBBPA has been detected in various environmental matrices. In 1979, TBBPA was reported in Arkansas sediment and soilⁱⁱ and in river sediments near the centre of Osaka in 1983ⁱⁱⁱ. Since then, TBBPA has been reported in sewage sludge in Sweden^{iv}, particulate from air in an electronics recycling plant^v and in plasma of occupationally exposed workers^{vi}. TBBPA is structurally similar to the thyroid hormone, thyroxine. In *in vitro* competitive binding assays TBBPA was found to bind with 10 times the potency of the natural hormone to the plasma transport protein, transthyretin^{vii}.

TBBPA is a phenolic in its native state and is not detected by routine analytical procedures in the determination of neutral organic contaminants. Hence there are few reports on its occurrence in the environment. TBBPA has a moderate log K_{OW} (4.5 to 5.3 depending on pH) and low water solubility (0.72 mg/l at 15°C) and is likely to adsorb to sediment^{viii}. A method for the determination of TBBPA in sediment was developed and applied to suspended sediments collected from eight stations in the Detroit River and Trenton Channel during July 2000. In addition, sewage sludge was obtained from treatment plants in the Great Lakes area and various locations in the United States that will allow comparison of population size, level of treatment and degree of industrial input.

Materials and Methods

Freeze-dried samples were ground with a mortar and pestle. Sediment (10 g) was extracted using a Dionex ASE 200 extractor. Cells were heated to 100°C for 5 minutes and extracted with dichloromethane (DCM) at 1800 psi (12.7 MPa) with a 75% flush volume over 3 static cycles.

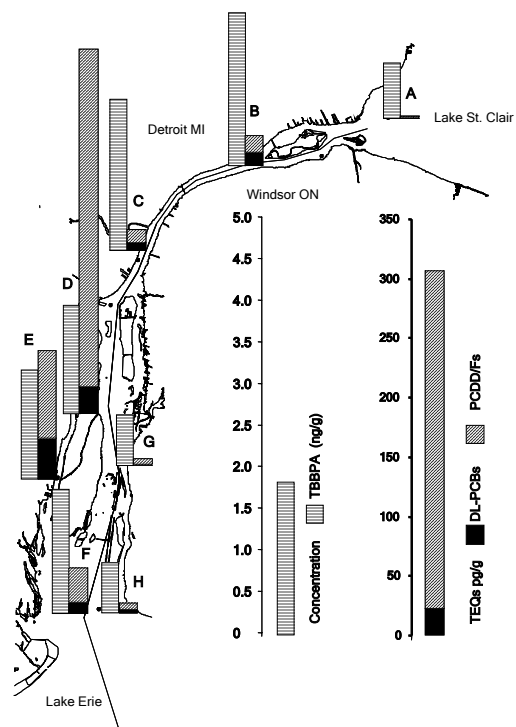
Extracts were roto-evaporated to approximately 1 ml and derivatized overnight with diazomethane. Samples were then applied to the first of two micro-columns, a bi-layer column made with 2 cm silica/deionized water (3%) capped with 1.5 cm silica/sulfuric acid (10%) to remove organics. Columns were eluted with 10 ml hexane, followed by 10 ml 1:1 DCM:hexane. Derivatized TBBPA (MeTBBPA) eluted in the second fraction, which was then evaporated under a flow of nitrogen to approximately 1 ml and applied to a column comprised of 2 cm silica/silver nitrate (~20%) to remove sulfur. Samples were eluted with 10 ml 1:1 DCM:hexane that was reduced to a final volume of 100 μ l in toluene. Octachloronaphthalene (10 μ l at 24 pg/ μ l) was added as a performance standard. Conditions were modified slightly for the sludge. Samples were spiked with ^{13}C labeled TBBPA (100 μ l at 150 pg/ μ l) and extracted at 150°C and 1500 psi (10.3 MPa). Sludge extracts were first applied to the silica/sulfuric column and then derivatized overnight.

Initial analyses were accomplished utilizing a Hewlett Packard 5989A mass spectrometer coupled with a Hewlett Packard 5890 Series II gas chromatograph equipped with a Hewlett Packard 7673A automatic sampler. Splitless injections (2 μ l) were made onto a 30 m J&W Scientific DB-5ms column (0.25 mm i.d.; 0.25 μ m film thickness) with helium as the carrier gas at a constant flow of 1.3 ml/min. Initial temperature was 80°C, held for 1.5 minutes and ramped at 20°C/minute up to 240°, 2°/minute to 294°, then ramped at 10°/minute to a final temperature of 310°C and held for 5 minutes. The injector and detector temperatures were set at 250 and 200°C respectively. Analyses of the sediments and sludge were run for confirmation and subsequently quantified using a Micromass Ultima GC/high resolution MS in electron ionization (EI) mode under similar operating conditions. Splitless injections (1 μ l) were made onto a 60 m Restek Rtx-5 column (0.25 mm i.d.; 0.25 μ m film thickness) with helium as the carrier gas at a constant flow of 1.2 ml/min. The initial temperature was 80°C, held for 1 minute and ramped at 20°/minute to 240°, then 8°/minute to 310°C and held for 19 minutes. TBBPA in sediment was determined using a five-point external standard calibration curve. Levels in sludge were determined based on the response of ^{13}C TBBPA internal standard. Ions from the $[\text{M}-\text{CH}_3]^+$ clusters for native (558.7590 and 556.7609) and ^{13}C labeled (568.8012 and 566.8032) MeTBBPA were monitored in selected ion recording mode.

Results and Discussion

Very little is known about levels of TBBPA in the Canadian environment. The focus of this study was to determine levels of TBBPA in sediments and sludge from the Great Lakes region. Published methods were examined and various clean-up techniques were explored to improve recoveries. A method was developed for the determination of TBBPA in sediment using Accelerated Solvent Extraction (ASE). Extraction recoveries were $95 \pm 1\%$ from spiked celite using DCM ($n = 2$). Clean-up was achieved in two stages using micro-columns to minimize contact with acid. Recoveries of methylated TBBPA from 3 cm silica/5% sulfuric acid were $37 \pm 9\%$, but improved to $97 \pm 10\%$ with the bi-layer column. Derivatized TBBPA eluted in the second fraction. Although sulfur did not interfere with the analysis, removal decreased instrument maintenance and down time. Sulfur was removed using silica/silver nitrate. This step was performed after derivatization, as non-derivatized TBBPA was very poorly recovered. Although alternate derivatization techniques were explored, the final method used methylation to reduce the polarity of the two hydroxy groups. For this reason it is not possible to quantify dimethyl-TBBPA

(MeTBBPA) and TBBPA separately. Therefore levels reported from this study represent the sum of TBBPA and MeTBBPA. MeTBBPA may be present either due to microbial methylation of TBBPA or from releases of MeTBBPA, also produced commercially. Overall the method recovery was greater than 80%.



The method was applied to Detroit River suspended sediments, as this region has been identified as an Area of Concern due to high concentrations of contaminants in the sediments (PAHs, heavy metals). TBBPA was detected at all eight Detroit River stations sampled. Levels were lowest in southern Lake St. Clair (0.60 ng/g, Site A); and highest downstream from a sewage treatment plant (1.84 ng/g, Site B) and downstream from the mouth of the Rouge River (1.82 ng/g, Site C). Levels were also elevated in the Trenton Channel (1.30 and 1.31 ng/g, Sites D and E). At the outflow of the Detroit River, Sites F and H, the concentration of TBBPA was almost 3 times higher on the western than the eastern side (1.49 and 0.60 ng/g respectively). Station H levels were very similar to the upstream site (0.61 ng/g, Site G) and Lake St. Clair (0.60 ng/g, Site A). Levels of TBBPA and MeTBBPA were reported in Swedish sediment upstream (34 and 24 ng/g) and downstream (270 and 1500 ng/g) from a plastics factory using TBBPA^{ix}. The figure

opposite illustrates the trend in the Detroit River data, which compares favourably with other classes of contaminants that have shown a strong association with human activities in the watershed. Levels of TBBPA (ng/g) are shown alongside TEQs in pg/g for dioxin-like PCBs (DL-PCBs) and PCDD/Fs^x.

Sludge samples were collected at treatment plants from southern Ontario communities within the Thames River watershed and the method was applied with minor modifications. A retention time shift in both the MeTBBPA and performance standard peak was confirmed in the sediment samples using HRMS. Therefore it was decided to utilize the increased selectivity and sensitivity of HRMS in electron ionization mode for the sludge samples. This permitted the use of ¹³C labeled TBBPA as an internal standard. Although the sample size required was much smaller (~1.0 g); sludge has more organic matter than sediment, therefore extracts were applied to silica/sulfuric acid columns prior to derivatization. TBBPA was detected in all seven Ontario sludge samples (14.3 to 43.8 ng/g d.w.) including both raw and digested sludges. A survey of Canadian sewage sludge reported levels of TBBPA up to 46.2 ng/g d.w.^{xi}. An earlier Swedish study reported similar levels of TBBPA (31 and 56 ng/g d.w.), while MeTBBPA was below detection in the two sludge samples. A subsequent, more extensive study on sludge from Sweden

showed similar levels of TBBPA ranging from below detection up to 220 ng/g w.w. . There was considerable variation among plants with the highest concentrations of TBBPA associated with plants that received wastes from the electronics industry . Variation may reflect differences in general exposure and/or the type of waste stream (domestic or industrial) entering the plant. As noted the highest concentration of TBBPA from the Detroit River study was downstream from a sewage treatment plant. If wastewater treatment plants are a major source of TBBPA, sludge that is removed during treatment would be expected to have much higher levels than the discharged effluent. Sludge is an inevitable byproduct of sewage treatment. Better treatment removes more solids which generates more sludge. Chemicals that do not volatilize or decompose during treatment tend to concentrate in the sludge^{xii}.

To date there is only one published report on levels of TBBPA in Canada . To address this absence of information, a method for the determination of TBBPA in sediment and sludge was developed and applied to Detroit River suspended sediments and sewage sludge from Ontario. Ongoing work is being done on Lake Ontario bottom sediments and sewage sludge from the United States. Sources of TBBPA in sludge should be investigated as there are concerns regarding the application of sludge to agricultural lands. Determining levels of TBBPA in the environment is an important first step in identifying potential sources and subsequently ways to limit its release into the environment.

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