Determination of Brominated Diphenyl Ethers in Fish Reference Materials.

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Introduction:

Brominated diphenyl ethers (BDPEs) are fire retardants used in the manifacutring of plastics, paints, textiles and electrical devices.[1] The annual production of BDPE in 1992 was 40,000 tons, and it continues to grow consistently. The extensive use of products containing BPDEs has resulted in the release of these compounds into the environment. BDPEs are lipophilic compounds and are shown to bio-accumulate through the food chain, and have been detected in both freshwater and marine organisms.[2]

In order to evaluate the global distribution, movement and fate of BDPEs in the environment, a sensitive, comprehensive, and interference free analytical method is required for their determination in complex environmental matrices. A number of procedures for the determination of BDPEs in the environment have been reported.[3] With the anticipation that a number of laboratories (in government, private sector, and academia) will engage in the BDPE analysis, there is a need to establish QA/QC guidelines. CRMs and RMs are an essential component of QA/QC programs, consequently there is a need to develop such materials for BDPEs. In 1992-1993 three CRMs based on fish tissue were produced for PCDDs, PCDFs, and co-planar PCBs determinations[4]. In this work we evaluated the feasibility of two tissue samples (Lake Ontario lake trout and Pacific herring) as the basis to develop CRMs for future round robin studies of BDPEs.

Material and Methods:

Homogenates of whole fish CRMs[4] in ampoules were vortexed to re-suspend the tissue and lipids. A 10 g aliquot of the homogenate was transferred qualitatively to large mortars; and 130 g of anhydrous Na_2SO_4 was added. The sample mixture was ground manually until a free-flowing mixture resulted. This mixture was transferred

into a large chromatography column and was spiked with the $^{13}C_{12}$-Tetra- through octa- chlorodiphenyl ether (CDPEs) surrogate mixture. The samples were eluted with 300 mL of DCM. Samples were concentrated by a combination of rotary evaporation and nitrogen evaporation prior to gel permeation chromatography (GPC). The GPC unit was an automated ABC Laboratories Autoprep model 1002A. The column was packed with 60 g of Bio Beads S-X3, 200-400 mesh (Bio-Rad Laboratories, Richmond, CA) in a 25 mm X 600 mm glass column. The elution solvent was 300 mL of DCM:hexane (1:1). Fractionation was accomplished with 3% deactivated silica gel columns; eluted with 140 mL of DCM. The sample was let evaporate to dryness at room temperature to minimize losses and 20 µL performance standard (100 pg/uL $^{13}C_{12}$ hexa-CDPE and tetra-BDPE) added for analysis.

High resolution GC/MS analyses of BDPEs was carried out on a VG AutoSpec-Q mass spectrometer connected to a Hewlett-Packard 5890 GC equipped with a CTC A200s autosampler. The GC injection port was configured for 1 uL on-column injections, with an initial temperature of 110 °C, held for 1 min, and ramped at 100 °C to 280 °C , and held there for 55 min. Gas chromatographic separation prior to MS was achieved using a 60 m X 0.25 mm X 0.25 µm Restek Rt_x5 capillary column.. The GC column was maintained at 110°C for 1 min, then ramped at 15 °C/min to 180°C , further ramped at 2°C/min to 280°C and held there for 60 minutes. Total run time was 90.7 min. Sample ionization was performed by electron impact (EI) at an electron voltage ranging from 30 to 40 eV depending on the optimization parameters of the instrument. Source temperature was 270 °C and the resolving power of the analyzer was 10000. The mass spectrometer was operated in SIM mode using a total of 8 descriptors to analyze the 24 BDPE congeners. Quantitation of samples was by internal standard method using an Excel spreadsheet, using EPA 8290 QA/QC protocols .

Custom standard solutions were purchased from Cambridge Isotope Laboratories and comprised analytical, surrogate spiking, and performance Standards. CIL also, provided individual standard solutions for the purpose of checking BDPE purity for individual congeners and determining relative retention times.

Results and Discussion:

A dioxin-like HRGC/HRMS based analytical method was developed for the determination of congener specific brominated diphenyl ether (BDPE) compounds in biota samples. This methodology was based on the 24 commercially available congeners. The recoveries for the internal standards ranged between 65% and 120%.

Experimental results in the form of total ion chromatogram of the 24 congener standard and Lake Ontario lake trout are presented in Figure 1. As it is illustrated in Figure 1 the number of congeners in the standard was not sufficient to match all of the congeners in the sample; consequently an average response factor was used to estimate the concentrations of each homologue group.

The concentration of BDPEs in Lake Ontario lake trout and Pacific herring are presented in Figure 2. Lake Ontario lake trout had higher levels of BDPEs than Pacific herring. Lake Ontario lake trout is at the top of the food web and represented a naturally contaminated sample. Pacific herring was collected from the northern tip of Vancouver Island, represented a relatively clean sample. The higher concentrations of the BDPEs in the lake trout can be attributed the differences in their habitat and

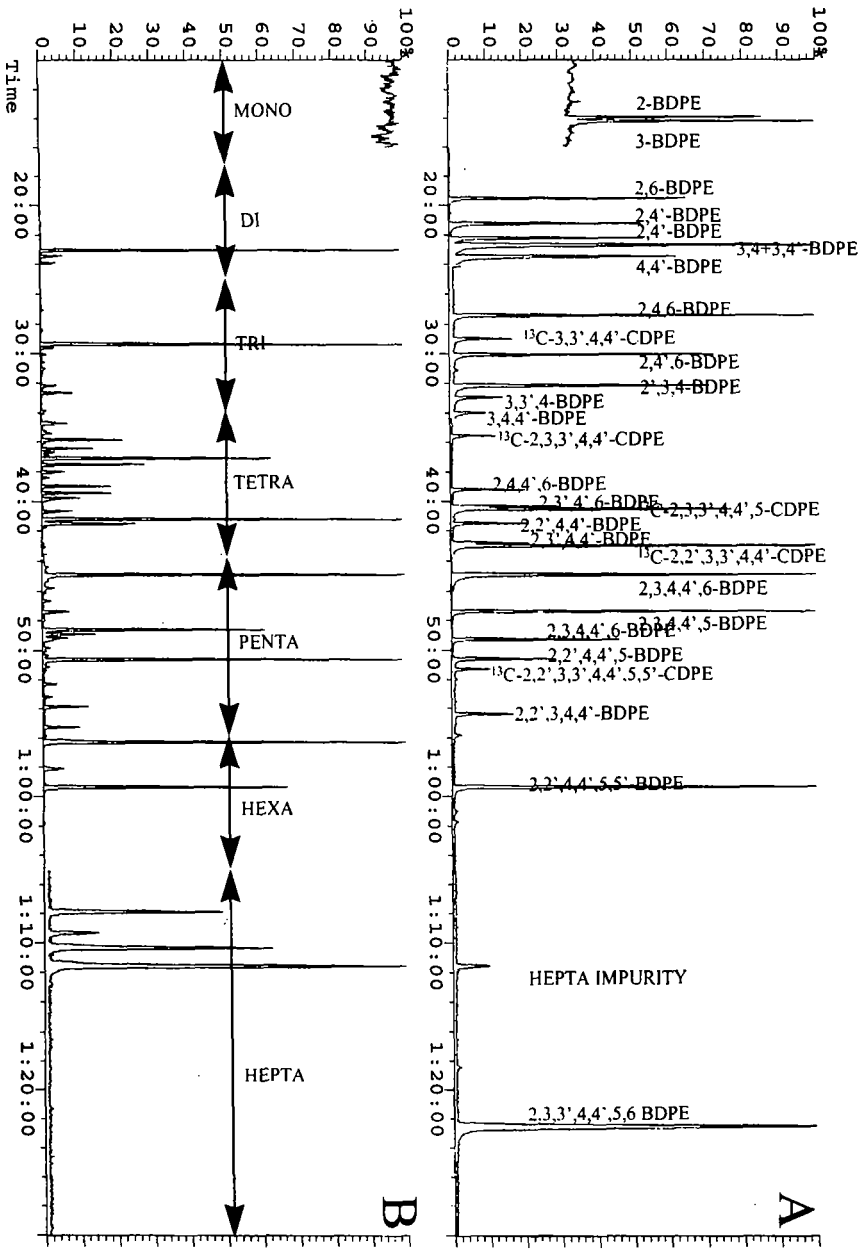
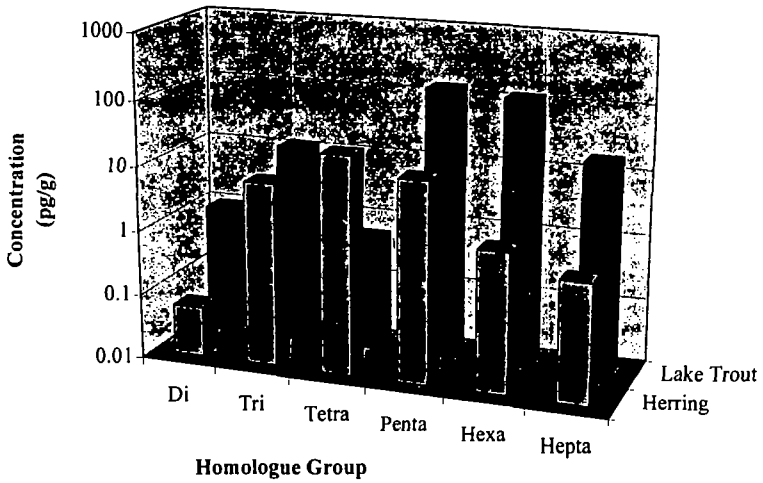


Figure 1. TIC of BDPE congeners with ^{13}C CDPEs used as internal standard (A) and Lake Ontario lake trout (B).

differences in trophic levels. Similar results were observed for the concentrations of PCDDs, PCDFs, and PCBs.[4]

In summary significant levels of BDPEs were found in both Lake Ontario lake trout and Pacific herring; and sufficient quantities of these materials are commercially available (CIL) for a round-robin study.

Figure 2. Concentration of Brominated Diphenyl Ethers (pg/g) in Pacific Herring (RCRM2) and Lake Ontario Lake Trout (BCRM)



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