SIMULTANEOUS DETERMINATION OF CHLORINATED AND BROMINATED DIPHENYL ETHERS IN BIOTA

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Introduction:

Chlorinated diphenyl ethers (CDPE) are a group of halogenated contaminants. Their chemical structure consists of two phenyl rings attached with each other via an ether bond. Like PCBs there are 10 positions for chlorine substitution which results in 209 possible congeners. Structural similarities of CDPEs to PCBs, PCDDs, and PCDFs have resulted in similar physical and chemical properties. For example: Log K_{ow} of 5.78 and 5.82 were reported for PCB-77 and CDPE-77 respectively (1). CDPEs have been used as heat exchangers, flame retardants, plasticisers, lubricants, and hydraulic fluids (2). They are widely used as intermediates in chemical reactions, as such they have been reported as an impurity in chlorophenols, and phenoxy acids, and not surprising they are known to be present in chemical effluents. CDPEs are widespread contaminants, and have been shown to bio-accumulate in fish, marine mammals, birds, and humans (3-7). In the past CDPEs were considered as an interference in the determination of PCDFs, and the majority of the literature on CDPEs deals with separation and elimination of this interference (8).

Although CDPEs are classified as toxic pollutants by the US-EPA there is limited information on the toxicity of CDPEs Chiu et. al. (9) showed similar levels of toxicity between CDPEs and PCBs. Several CDPEs have been shown to induce MFO in trout. Safe(10) suggested that mono and non-ortho substituted CDPEs and PCBs have the same TEF values. Bioavailability of CDPEs in contaminated sediments was studied using both benthic organisms and semipermeable membrane devices (11). CDPEs were determined in sediments and fish from Lake Ontario, Canada, in the early 1980's (12). Thirteen congeners were found in fish from Whitby Harbour, Ontario, Canada at levels ranging from not detected (0.005 ppm) to 0.0679 ppm. These were the highest levels found when compared to other sites in Lake Ontario that contained sub-ppm levels or non-detectable CDPE concentrations.

Similar to BDPEs, CDPEs are common global contaminants, consequently an effective, and reliable method for routine determination of CDPEs is required. Last year we reported on a method for the determination of brominated diphenyl ethers (13). A refined method to determine these two groups of contaminants (CDPEs & BDPEs) simultaneously would enhance the capability of the laboratory and will result in a faster turn around time. In this presentation the results obtained from using simultaneous analysis method for CDPEs and BDPEs are discussed and concentrations of CDPEs in fish CRMs are presented.

Material and Methods:

Homogenates of whole fish CRMs (14) 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) with the compounds of interest being collected in the last 150mL. Fractionation was accomplished with 3% deactivated silica gel columns; eluted with 140 mL of DCM. The sample was evaporated 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.

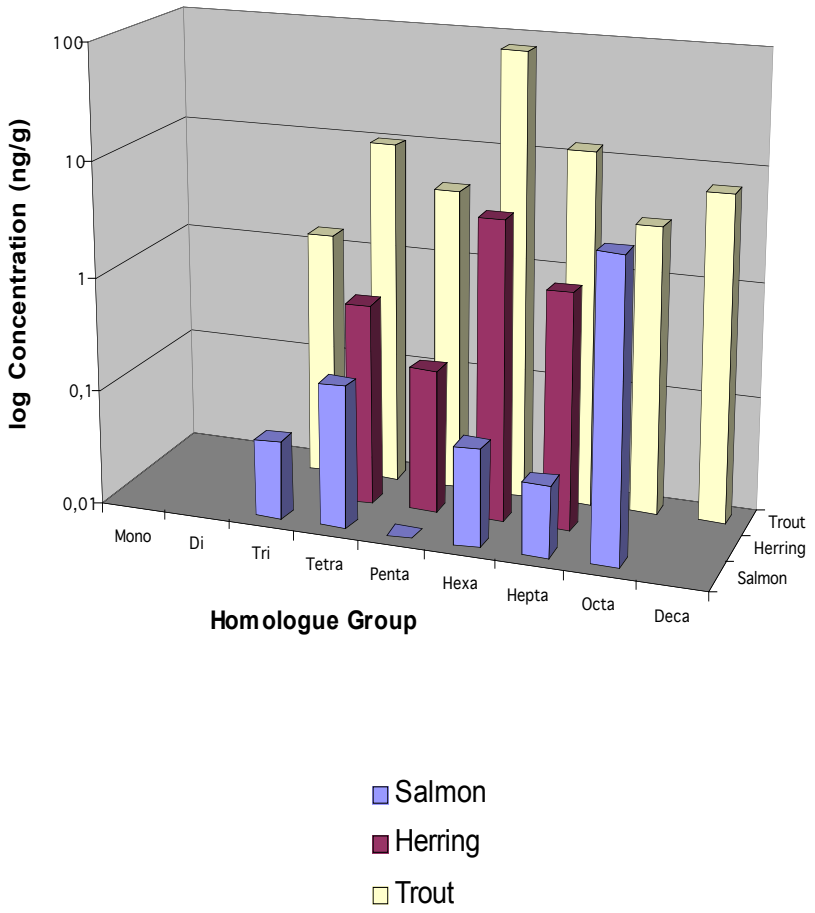
High resolution GC/MS analyses of CDPEs and BDPEs were carried out on a VG AutoSpec-Q mass spectrometer connected to a Hewlett-Packard 5890 GC equipped with a CTC A200s autosampler. Separate analytical runs were made for each from the same cleaned up extracts. The GC injection port was configured for 1 uL on-column injections, with an initial temperature of 160 ^{o}C, held for 1 min, and ramped at 100 ^{o}C/min to 280 ^{o}C , and held 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. For BDPEs the GC column was maintained at 110^{o}C for 1 min, then ramped at 15 ^{o}C/min to 180^{o}C , further ramped at 2^{o}C/min to 280^{o}C and held there for 60 minutes. Total run time was 90.7 min. For CDPEs the temperature program was the same with the exception that the hold time was only 10 min. resulting in a total run time of 65.70 min. Sample ionization was performed by electron ionization (EI) at an electron voltage ranging from 30 to 40 eV depending on the optimization parameters of the instrument. Source temperature was 270 ^{o}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 23 BDPE congeners and 9 SIM descriptors to analyze the 18 CDPEs. Quantitation of samples was performed by an internal standard method using VG2020 and an Excel spreadsheet following 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 CDPE purity for individual congeners and determining relative retention times.

Results and Discussion:

Our dioxin-like HRGC/HRMS based analytical method was extended to include the determination of congener specific chlorinated diphenyl ether (CDPE) compounds in biota samples. This methodology was based on the 18 commercially available congeners. The recoveries for the internal standards ranged between 77 and 107% for the hexa- and hepta- surrogates. The number of congeners in the standard was not sufficient to match all of the congeners present in the sample; consequently an average response factor was used to estimate the concentrations of each homologue group.

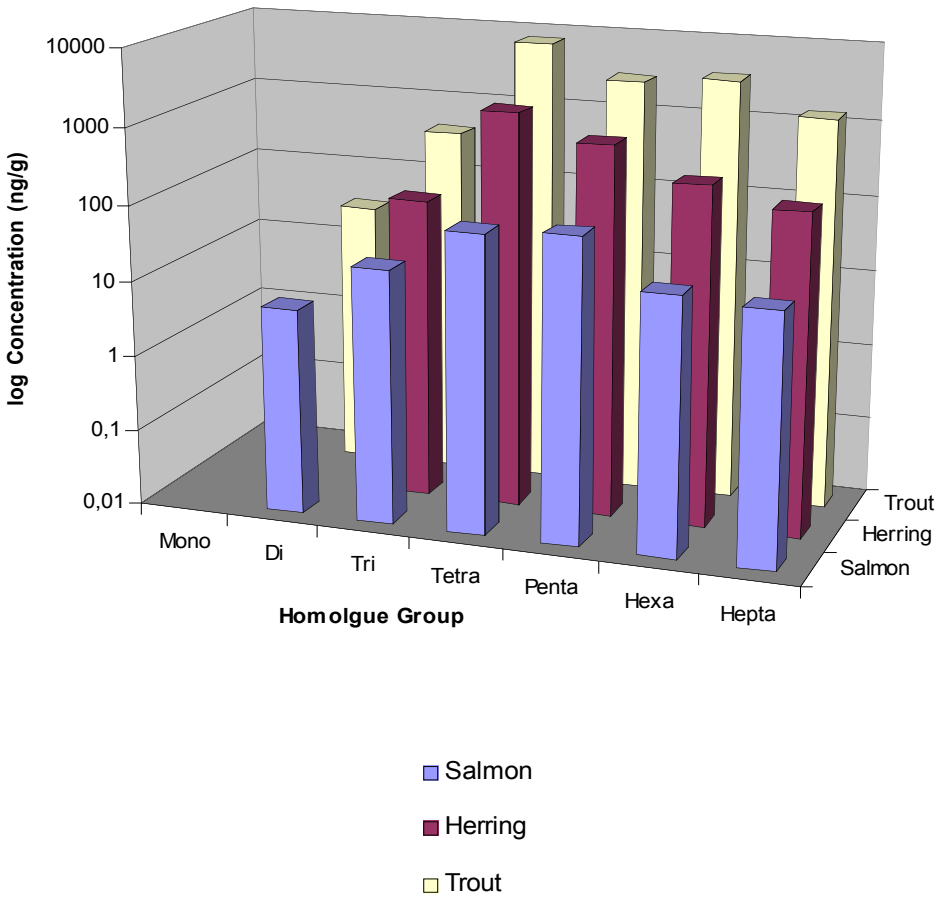
Figure 1: CDPE Concentration (ng/g lipid) in Salmon, Herring, and Trout



The concentration of CDPEs in Lake Ontario lake trout, sockeye salmon, and Pacific herring CRMS are presented in Figure 1. The CRM BDPE results are shown in Figure 2. The levels of CDPEs are 3 orders of magnitude lower than the BDPEs in the same sample. Lake Ontario lake trout had highest levels of CDPEs followed by herring and then salmon, which has the lowest concentrations.These latter two matrices also had fewer congeners and at much lower concentrations. For the lake trout samples the most abundant congeners were the 2,2',4,4',5-penta CDPE followed by the deca-, 2',4,4',5-tetra, 2,2',3,3',4,4',5-hepta and the 2,4,4'-tri CDPE. Lake Ontario lake trout is at the top of the food web and represented a naturally contaminated sample. Also there is a known local source of CDPEs located at Whitby Harbour on Lake Ontario. Pacific herring was collected from the northern tip of Vancouver Island representing a relatively clean sample and the salmon was also collected from British Columbia. The higher concentrations of the CDPEs in the lake trout can be attributed to the differences in their habitat and differences in trophic levels. Similar results were observed for the concentrations of PCDDs, PCDFs, and PCBs.

In summary this method is capable of determining BDPEs and CDPEs simultaneously which results in less preparation steps and faster turnaround time. CDPEs as well as BDPEs were found in Lake Ontario lake trout, sockeye salmon and Pacific herring; indicating that CDPEs can be included for the interested participants in a BDPE/CDPE round robin study using these commercially available CRMs.

Figure 2: BDPE Concentration (ng/g lipid) in Salmon, Herring, and Trout



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