

Determination of Co-Planar Polybrominated-chlorinated Biphenyls in Fish from Great Lakes: Preliminary Results and Analytical Challenges

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Introduction:

Recently the occurrence of polybrominated chlorinated biphenyls (PXBs) in biota collected from various global regions was reported by Ohta et al.¹ There are several routes of formation for PXBs. Nakano et al.² reported formation of co-planar PXBs (Co PXBs) during the manufacturing process of Fe₃Cl. Several studies have documented the formation of Co-PCBs along with PCDD/Fs during incineration processes.^{3,4} Similarly, the formation of PXDD/Fs with the inclusion of brominated compounds in the feed stock should facilitate the de novo synthesis of Co-PXBs via thermal reactions.

The introduction of a second type of halogen into the polychlorinated biphenyl moiety increases the number of possible congeners from 209 to 9180. Currently there are a limited number of PXBs standards commercially available of which all are co-planar. To determine the occurrence of PXBs in the North American environment an isotope dilution HRGC/HRMS method was developed. The concentrations of five Co-PXBs in fish extracts from the non ortho/mono ortho fraction as identified in MOE Method 3418⁵ were analyzed. Fish from the Laurentian Great Lakes were analyzed in this investigation. Since the number of possible congeners is not limited to the congeners covered in this study there are several analytical challenges that can present themselves when dealing with such complex mixtures of compounds. Even at $m/\Delta m \geq 10\ 000$ the potential for interferences from other compounds and/or other homologue groups exists.

Experimental:

Three monobromotetrachlorobiphenyl (4'-Bromo-2,3,3',4-tetrachloro, 4'-bromo 2,3',4,5 tetrachloro and 4'-Bromo-3,3',4,5-tetrachlorobiphenyl), a tribromodichlorobiphenyl (3',4',5'-tribromo-3,4-dichlorobiphenyl) and a monobromopentachlorobiphenyl (4'-Bromo-3,3',4,5,5'-pentachlorobiphenyl) congeners were custom synthesized by Cambridge Isotope Laboratories. ¹³C analogues were also available but only the native compounds were incorporated into this preliminary assessment. Recoveries were based on ¹³C PCBs (¹³C CB-156, 157 and 189) that had been added at the beginning of the extraction process. ¹³C CB-138 was used as an instrument performance standard.

All biota samples were extracted at the Ontario Ministry of Environment using MOE method 3418. Briefly, approximately 5 g of sample was spiked with 15 congeners of ¹³C₁₂-PCDD/Fs and 12 congeners of ¹³C₁₂ - DLPCB surrogates prior to extraction. Each sample was acid digested overnight using concentrated HCl and extracted with hexane the following day. Fractionation and cleanup of the samples were accomplished using sequential columns based on sulfuric acid/silica, alumina and 5% PX21-Amoco Carbon Silica.

Gas chromatographic (Hewlett Packard 6890) separation was accomplished using an RTX Dioxin (60mx0.25mm, 0.15µm film thickness) connected to HRMS (Micromass, Autospec Ultima). The chromatographic conditions were as follows: initial temperature 120°C, initial held 1.5minutes, raised to 220°C at 20 °C/min, raised to 320°C @2.5°C/min, held for 15 min. The injection temperature and transfer line temperature were held at 280°C and 260°C respectively. The mass spectrometer was operated in electron ionization mode at $m/\Delta m \geq 10\ 000$.

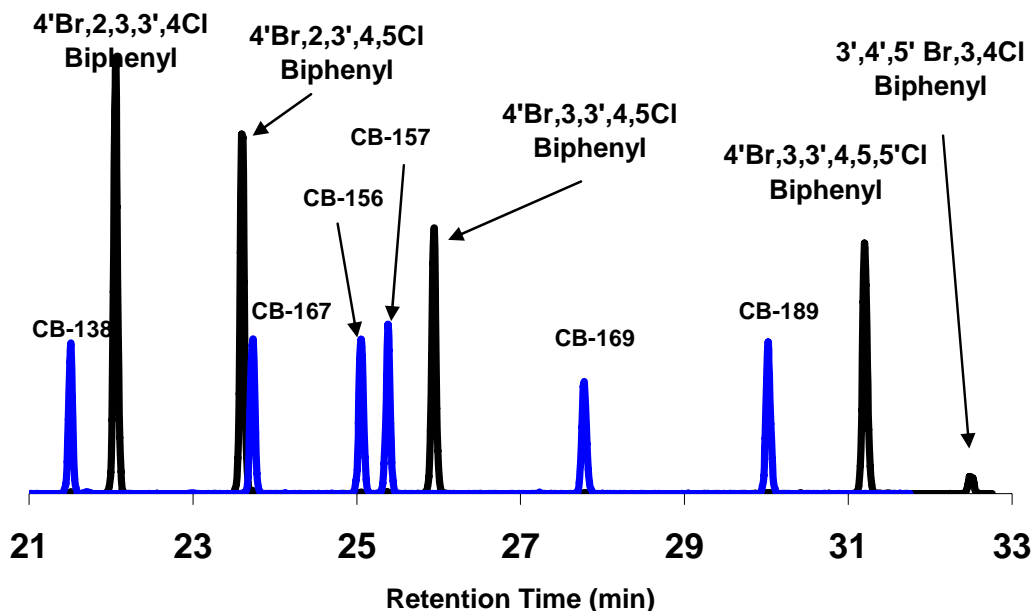


Figure 1. Chromatogram of five Co-PXB congeners along with $^{13}\text{C}_{12}$ -Co-PCBs used as internal standards in this study.

Results and discussion:

A typical chromatogram of these compounds is presented in Figure 1. A major challenge in this type of analysis is the vast number of congeners which are all impossible to be obtained commercially, and their subsequent separation on any type of gas chromatographic column. This study focused on the five Co-PXB congeners that are presently commercially available. Preliminary results for Co-PXBs are presented in Table 1. 4'-MoBr-3, 3',4,4',5,5'-PeCB was present in all samples, 4'-MoBr-2,3,3',4-TeCB were not detectable in two channel catfish and brown trout, and 4'-MoBr-2, 3',4,5-TeCB was detected in 9 out of 22 samples. Similar to the results from other studies, the levels of Co-PXBs are lower than Co-PCBs. Consideration should be given to the fact that the number of possible PXB congeners is significantly higher than that of PCBs and that this study focuses on only five congeners. In general, the levels of PXBs observed in fish from Lake Ontario are lower than the values reported by Ohta et al.¹

During the course of this study two additional unidentified peaks were observed in the monobromopentachlorobiphenyl mass functions which had ion ratios that were within the minimum criteria for PXBs. The possibility of interference from PCDD/Fs was investigated by injecting a mixed standard and comparing the accurate mass. Further investigation using extended SIR revealed four mass peaks for the second large eluting unknown indicating the possible presence of a tri-halogenated compound. Subsequent investigation into matching accurate mass indicated that this was not the case. Consequently, the search parameters were broadened with the removal of the halogen restriction and two additional compounds that matched the criteria, monobromo, tetrachloro biphenyl and tribromodibenzofuran, were identified. Further investigation into the identification of the unknown peaks including accurate mass determination for the halogen cluster in both of these peaks and retention time comparison with authentic brominated dibenzo furans and CO-PCBs are planned.

Fish Species	Sampling Location	4'-bromo-2,3,3',4-TeCB	4'-bromo-2,3',4,5-TeCB	4'-bromo-3,3',4,5,5'-PeCB
Carp	Whitby Harbor	0.18		4.0
Carp	Whitby Harbor	28		54
Carp	Whitby Harbor	6.4		
Carp	Whitby Harbor	3.8		30
Brown Bullhead	Whitby Harbor	1.98		12
White Sucker	Whitby Harbor	2.2		55
Whitefish	Upper Bay of Quinte		3.0	33
Whitefish	Upper Bay of Quinte	10	4.7	42
Channel Catfish	Upper Bay of Quinte			17
Channel Catfish	Upper Bay of Quinte		0.84	12
Whitefish	Lake Ontario	7.7		54
Channel Catfish	Hamilton Harbor	6.4		20
Channel Catfish	Hamilton Harbor	6.6	2.0	23
Channel Catfish	Hamilton Harbor	16	5.7	49
Channel Catfish	Hamilton Harbor	6.4	2.8	25
Channel Catfish	Hamilton Harbor	4.4		20
Carp	Upper Niagara River	2.9	1.1	3.3
Rainbow Trout	Lake Ontario, Credit River	1.6		9.4
Rainbow Trout	Lake Ontario, Credit River	2.1		16
Brown Trout	Lake Ontario, Credit River			12
Coho	Lake Ontario, Credit River	3.6	1.5	11
Chinook	Northwestern	3.6	1.5	12

Table 1. Co Planar PXB Concentrations in Fish from Laurentian Great Lakes in Canada (all values in pg/g).

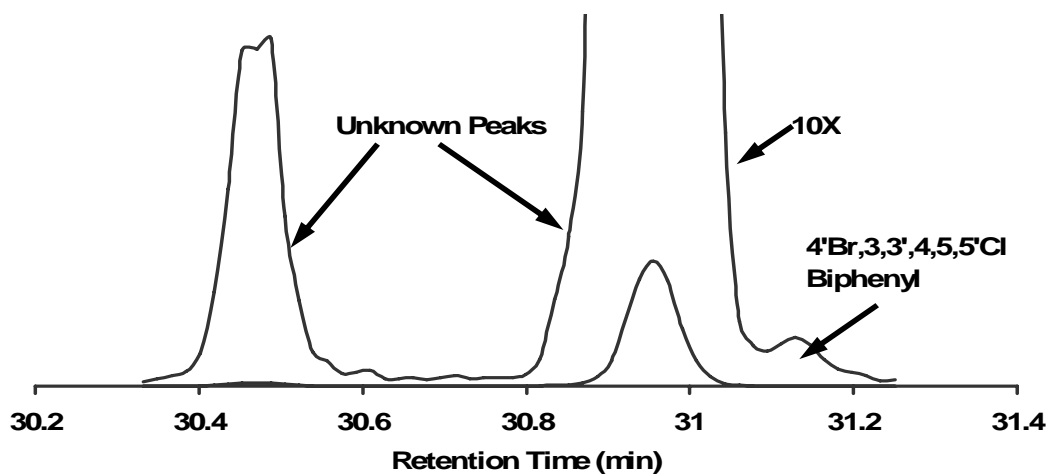


Figure 2. Chromatogram of 4'Br, 3,3',4,4,5,5'Cl biphenyl along with two major unknown peaks.

To the best of our knowledge this is the first report on the occurrence of PXBs in the North American environment. The occurrence of these compounds in biota from higher trophic levels such as marine mammals from other locations such as the Arctic, St Lawrence Estuary will be investigated.

Acknowledgements:

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