Non-ortho Chlorobiphenyls in Fish and Sediments of the Estuary and Gulf of St.Lawrence

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1. Introduction

A few polychlorinated biphenyl (PCB) congeners have been shown to illicit toxic responses similar to those observed for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TeCDD). The PCBs that can assume a planar configuration, the non-ortho congeners 3,3',4,4'-TeCB (IUPAC No. 77), 3,3',4,4',5-PeCB (IUPAC No. 126), 3,3',4,4',5,5'-HxCB (IUPAC No. 169), are the most toxic[1]. These dioxin-like congeners are ubiquitous in the environment at similar or higher concentrations than the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)[2].

This study reports concentrations of non-ortho PCBs in two sediment cores and two species of bottom feeding fish of the Lower Estuary and the Gulf of St.Lawrence. Levels and the temporal trend of these compounds, as inferred from the dated sediment cores, are reported for the Laurentian Trough, the main zone of fine-grained sediment accumulation in the St. Lawrence Estuary. Levels of non-ortho PCBs in muscle, liver and gonads of cod (*Gadus morhua*) and Greenland halibut (*Reinhardtius hippoglossoides*) are presented. The data with accompanying values for sediment organic carbon content and tissue lipid concentration, permit the calculation of "biota-to-sediment accumulation factors" (BSAFs) for the non-ortho PCBs.

2. Methods

Sampling. In June 1992, sediments were collected using a box corer from two stations (23 and 24A), located at about 50 km apart, in the Laurentian Trough. Each core was immediately sliced on board into 25 slices of increasing thickness from the top of the core to about 40 cm depth. Aliquots of each sediment slice were transferred into solvent-cleaned glass jars for the analysis of non-ortho PCBs and in polypropylene vials for ^{210}Pb analysis, and then stored frozen at -20°C. Cod were captured by trawl in January 1993 in the Gulf of St.Lawrence and halibut were similarly caught in September 1993 in the St.Lawrence Estuary. Fish were wet-weighed and measured (total length) alive, transferred separately into plastic bags and then placed in a freezer at -20°C for later dissection. In the laboratory, two representative adult males of each species were analyzed for non-ortho PCBs. The muscle, liver and gonads were extracted from each semi-thawed fish, separately homogenized and transferred to clean glass jars.

Analysis. Sediment samples were air dried, spiked with labelled non-ortho congeners and extracted with toluene in a soxhlet apparatus. The extracts were first treated with activated Cu then cleaned on multi-layer column packed with H_2SO_4-silica, neutral silica and NaOH-silica and fractionated on a Florisil column as described by Harrad et al.[3]. Following homogenization, fish tissues were dried with Na_2SO_4, spiked with labelled non-ortho congeners and extracted with hexane-dichloromethane (1:1) mixture in a soxhlet apparatus. Lipids were removed by shaking the extracts with H_2SO_4-impregnated silica. After this treatment, the extracts were purified in the same way as the sediment samples. The final extracts containing the non-ortho PCBs were analyzed by high resolution gas chromatography (HRGC)- high resolution mass spectrometry (HRMS) using the isotope dilution method described by Kuehl et al.[4]. ^{210}Pb was determined for each sediment slice according to the technique of Eakins and Morisson[5], whereas sediment organic carbon was measured by combustion using a CHN analyzer. Lipid concentrations in fish tissues were determined according to the gravimetric method described by Bligh and Dyer[6].

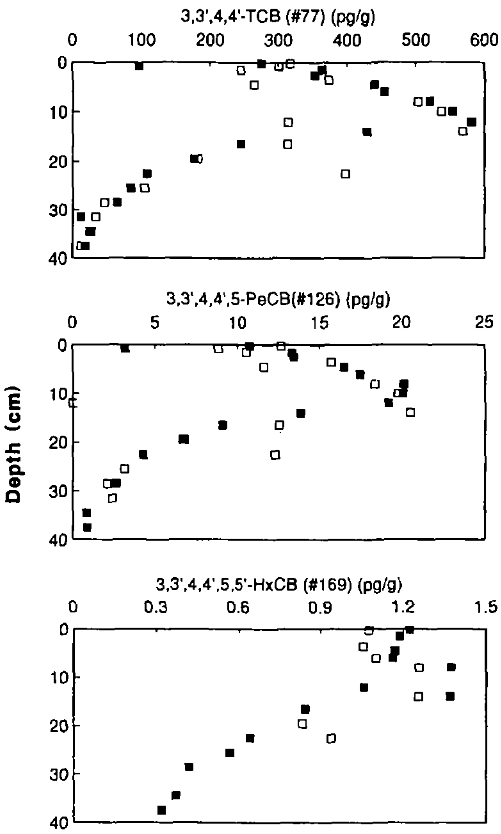

Figure 1. Depth distribution profiles of non-ortho PCBs at stations 23 (■) and 24A (□).

3. Results and discussion

Sediments. Sedimentary profiles of non-ortho PCBs from stations 23 and 24A are shown in Figure 1. Concentrations of non-ortho PCBs increase from the bottom of the cores, reach maximum values at about 10-15 cm depth and decrease sharply near the sediment surface. At both stations, maximum concentrations are 600 pg/g, 20 pg/g and 1.2 pg/g for congeners 77, 129 and 169, respectively. The subsurface maxima observed for these PCB congeners indicate that recent inputs to the St.Lawrence Estuary have decreased substantially. A two-zone diagenetic model of the ^{210}Pb distributions in the sediments[7] was used to determine sedimentation and mixing parameters in the cores. Based on the resulting sedimentation rate

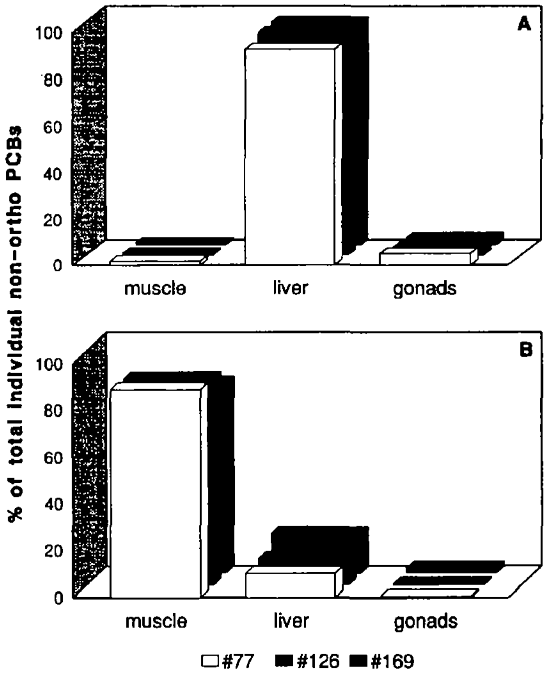

Figure 2. Relative distribution of non-ortho PCBs in muscle, liver and gonads in cod (A) and halibut (B).

and the thickness of the mixed zone in the cores, the model indicates that non-ortho PCBs first appeared in the late 1950's and reached maximum levels in the 1980's. As a direct consequence of mixing processes, some of the contaminants in the surficial sediments are derived from the more concentrated subsurface material. This suggests that recent inputs of non-ortho PCBs to the St.Lawrence Estuary have decreased even more significantly over the last decade than indicated by the sedimentary profiles.

Fish. Non-ortho PCB congeners are detected in all the analyzed tissues of both fish species. The relative distribution of non-ortho PCB congeners in the muscle, liver and gonads is consistent within each fish species but very different between the two (Figure 2). Non-ortho

Table 1. BSAFs for non-ortho PCBs in cod and halibut exposed to Lower Estuary / Gulf of St. Lawrence sediments. Data are given as mean values (± standard deviation).

non-ortho congener	BSAFs Cod (*G. morhua*) (n=2 ♂)	BSAFs Greenland halibut (*R. hippoglossoides*) (n=2 ♂)
77	0.033 (±0.009)	0.144 (±0.028)
126	0.047 (±0.018)	0.049 (±0.010)
169	1.14 (±0.46)	0.432 (±0.025)

PCBs in cod are mainly found in the liver (>90%) whereas these compounds are principally located in the muscle (>80%) of halibut. A strong correlation ($r^2 > 0.98$) is observed between the distribution of the non-ortho PCB congeners and the distribution of lipids among fish tissues for both species. These results clearly show that lipids play a major role in the distribution of non-ionic organic contaminants in these fish species. Concentrations of non-ortho PCBs in fish (sum of the three tissues normalized to lipid concentrations) decrease from the least (# 77) to the most (# 169) chlorinated congener by a factor of about 10 for cod and 80 for halibut. The same trend is observed in sediments but the decrease is by a factor of about 600. This significant difference in non-ortho PCB concentration range can be explained by either metabolisation of congener # 77 or bioconcentration (defined as an accumulation to a concentration higher than that found in the external environment) of congener # 169.

BSAF. A commonly used parameter that relates the concentrations of non-ionic contaminants in fish or benthic organisms to contaminant concentrations in surface sediments is the "biota-to-sediment accumulation factor" (BSAF)[8-11]. BSAF is defined as:

$$BSAF = \frac{C_{Lipid}}{C_{Organic\ Carbon}}$$

where BSAF is unitless, C_{Lipid} is the concentration of contaminant in lipid of pooled fish tissues (muscle, liver and gonads) in ng of contaminant/g of lipid, and $C_{Organic\ Carbon}$ is the concentration of contaminant in the top 5 cm of surface sediment organic carbon reported in ng of contaminant/g of organic carbon. BSAFs are also used in equilibrium models which assume that a state of equilibrium exists for the distribution of chemicals between water, sediments and organisms in the aquatic environment.

Recognizing that the number of fish and sediment samples are limited in the current study, an estimate of the transfer of the PCB congeners in the food-chain can still be made using the analytical results of these compounds. Table 1 presents the average BSAFs for cod and halibut exposed to Lower Estuary/Gulf of St.Lawrence sediments. The similar BASF values for both species suggest that these bottom feeding fish are comparably exposed to the non-ortho PCBs in sediments. BSAFs for dioxin-like congeners in marine fish are basically nonexistent. However, congener # 77 and # 126 BASF values are within the 0.03-0.2 range reported for 2,3,7,8-TeCDD in a variety of fish species from Lake Ontario[11]. BSAF values for congener # 169 are closer to 1, and fit in the low end of the range of 1 to 5 generally found for non-ionic organic compounds, including PCBs, in aquatic invertebrates[8-10,12]. The low BSAF values calculated for congeners 77 and 126 suggest that cod and halibut may possess the ability to metabolize and/or excrete these specific compounds, a capacity already observed for other fish species[9,13].

4. Conclusion

The most toxic PCBs, the non-ortho congeners, were all detected in the Laurentian Trough sediments. The sedimentary records of these compounds clearly indicate that inputs to the St.Lawrence Estuary have diminished considerably in recent years. Non-ortho PCBs were also found in tissues (muscle, liver and gonads) of the two marine fish (cod and Greenland halibut) investigated. For both species, a strong correlation was obtained between the distribution of non-ortho congeners and the lipid distribution of fish tissues. Similar BSAF values for these compounds in cod and halibut suggest that the two species may be comparably exposed to these contaminants in sediments and possess the ability to metabolize and/or excrete the less chlorinated non-ortho PCBs.

5. References

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