Contribution of PCDD/PCDFs, Planar and Ortho Substituted PCB Congeners to the Total TCDD-Equivalent Concentration in Fish Fillet from the St-Lawrence River.

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The aquatic environment is known to be contaminated by polychlorinated hydrocarbons such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs). Because these contaminants exist in environmental and biological samples as complex mixture of congeners, the concept of toxic equivalents (TEQs) for all 2,3,7,8 substituted PCDD/PCDF has been introduced in the early 80's to simplify the risk assessment and regulatory control. The relative potency of the PCDDs and PCDFs are expressed as a proportion relative to 2,3,7,8-TCDD and are referred to as Toxic Equivalency Factor (TEF). In Canada, accepted TEFs values are those proposed by NATO[1].

Recently, the WHO-European Centre for Environment and Health[2] has published consensus TEFs values for the 3 planar, 8 mono-ortho and 2 di-ortho substituted PCBs. Consensus TEF values for planar PCBs is #77=0.0005, #126=0.1 and #169=0.01, while TEFs values for the 8 mono-ortho PCB congeners range between 0.00001 and 0.0005 and for di-ortho congeners #170=0.0001 and #180=0.00001.

The St-Lawrence river in Québec (Canada) is contaminated by complex mixtures of polychlorinated hydrocarbons and pesticides. The major sources of contaminants are the Great Lakes, the tributaries and several industrial and municipal effluents along the river. Over 30 fish species are caught by recreational fisherman along the St-Lawrence river. Acceptable level of PCDD/PCDF in fish fillet for human consumption, proposed by the Ministry of Environment of Québec and Ontario, is 15 pg/g of 2,3,7,8-TCDD-EQ, while acceptable level of total PCBs is 2 mg/kg.

The objective of this study was to evaluate the contribution of planar, mono-ortho and di-ortho PCBs to the total 2,3,7,8-TCDD-Equivalent concentration in fish fillet from 5 species collected in the St-Lawrence river, using the TEFs values proposed by WHO.

Materials and Methods:

Sample collection. In the Montréal area, 14 brown trout (*Salmo trutta*), 8 rainbow trout (*Salmo gairdneri*), 7 chinook salmon (*Oncorhynchus tshawytscha*) were collected by fisherman. Six copper redhorse (*Moxostoma hubbsi*), a species mostly extinct, were collected in the Richelieu river but this fish species is believed to migrate to the St-lawrence river. In the Quebec area, 4 american eel (*Anguilla rostrata*) were collected by commercial fishing trap. From all individual species, fillet were dissected out and homogeneised in commercial stainless steel blender.

Analytical Methods. Samples (25 g fillet) were dryed with sodium sulfate (125 g), blended in a fine powder and spiked prior to extraction with a mixture of nine $^{13}C_{12}$ labelled 2,3,7,8-substituted PCDD/PCDF, the three $^{13}C_{12}$ planar PCBs and three $^{13}C_{12}$ mono-ortho substituted PCBs. Sample was extracted in a glass column with 650 ml of hexane/methylene chloride (50/50)[3]. Fractionation of PCBs, planar PCBs + mono-ortho and PCDD/PCDF was performed on alumina column according to Sakai[4]. An additional cleanup was performed on the PCDD/PCDF fraction on a carbon column. Each fraction was evaporated to dryness and 50 μl of internal standards was added prior to analysis.

Quantification. Planar PCBs and PCDD/PCDF were analysed by HRGC/HRMS (VG AutospecQ). The HRMS was operated in electron impact mode (EI) with 34 eV ionizing energy, 260 °C source temperature. Analytes were monitored in selected ion monitoring mode at a static resolution of 10000 (10 % valley). All the results were corrected for the recovery rates of the $^{13}C_{12}$ surrogates and detection limits were around 0.2 pg/g wet weight. Mono and di-ortho PCBs were analysed by HRGC/LRMS on a ion trap detector Varian Saturn II. Results were not corrected for recovery rates and detection limits were around 20 pg/g wet weight.

Results and Discussion:

Polychlorinated dioxins and furans have been detected in all 40 samples (figures 1-5). Most congeners detected were 2,3,7,8 substituted congeners. This behavior is in good agreement with Stalling[5] and Brochu[3] . 2,3,7,8-TCDD was the major dioxin congener and 2,3,4,7,8,-PeCDF and 2,3,7,8-TCDF were the most important furans. In brown trout and rainbow trout, furans concentrations were always three times higher than dioxins. Whittle[6] has reported similar ratios between PCDF/PCDD for lake trout from Lake Ontario. This behavior is related to the historical production of chlorophenol and losses of these contaminants from waste dump sites into Lake Ontario. PCDD/PCDF concentrations found in chinook salmon species were at least six times higher than those found in trout samples. Level of PCDD/PCDF found in american eel were lower than chinook salmon but higher than trout. Interestingly, levels in copper redhorse were the lowest one among the 5 species.

Planar PCBs #77 and #126 have also been detected in all 40 samples with concentrations ranging from 17 to 1920 pg/g (wet weight) and 13 to 2050 pg/g (wet weight), respectively (figures 1-5). Concentrations of PCB #169 are the lowest of the three non-ortho substituted PCBs (ND to 164 pg/g wet weight). Concentrations of PCB #77 detected in brown trout, rainbow trout and copper redhorse are always higher than PCB #126 by a factor ranging from 3.6 to 17. According to several authors[7),8),9)], similar ratio of PCB #77 over PCB #126 would be obtained (4.8 - 18) by

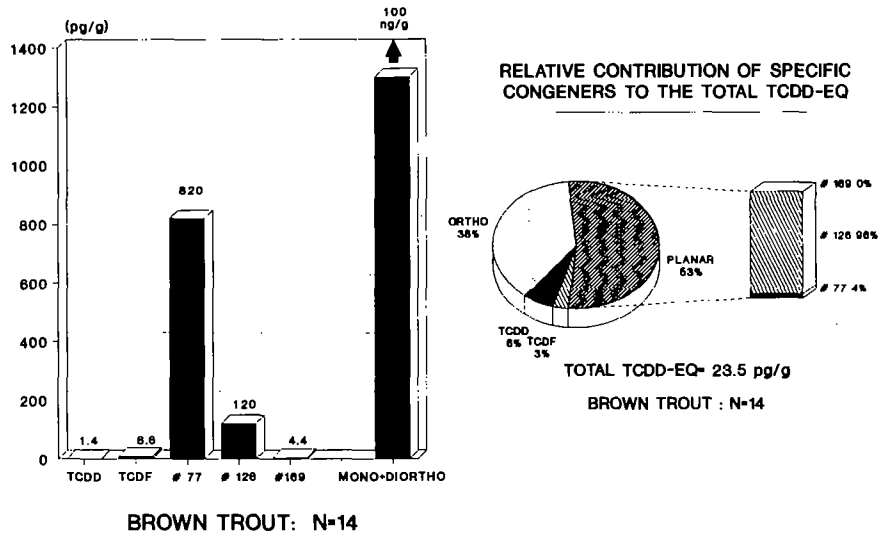
mixing technical Aroclor 1254 and 1260 in a ratio of 2:1. Such ratio of Arochlor is in good agrement with Nimi[10] for the lake Ontario salmonids. Thus, the input of planar PCB from Aroclor mixture is apparently unchanged for these three fish species.

Ratio of a selected PCB congener to a reference PCB congener as a tool to indicate metabolism is used frequently. Congener #153 is often used as reference PCB because it is always present in high concentration and it is assumed that this congener is not metabolized in fish[8]. Ratio of planar PCB #77 and PCB#126 over PCB #153 in a mixture of Aroclor 1254:1260 (2:1) are 0.0017 and 0.00036 respectively. These same ratio are 0.014 and 0.0020 for the brown trout, 0.027 and 0.0024 for the rainbow trout and 0.017 and 0.0025 for the copper redhorse. These ratio indicate bioaccumulation of these planar PCBs by a factor of around 6-10 for PCB #77 and PCB #126.

Planar PCBs patterns for chinook salmon and american eel differ, PCB #126 being the most abundant followed by PCB #77 and PCB #169. The same distribution was also reported by Smith[11] in chinook salmon and Boer[7] in yellow eel from Netherland. Mean ratio of PCB#77 and PCB#126 over PCB#153 are 0.002 and 0.0027 for the chinook salmon. These ratios indicate that the input of PCB #77 is similar to the Aroclor mixture but, on the other hand, PCB #126 is bioaccumulated by a factor of 6 like the brown trout, rainbow trout and the copper redhorse. For the american eel, PCB #77 ratio (0.0003) is about 6 times lower than the technical mixture. However PCB #126 ratio is 0.0023 which indicate a bioaccumulation of this congener by a factor of 6 like other species.

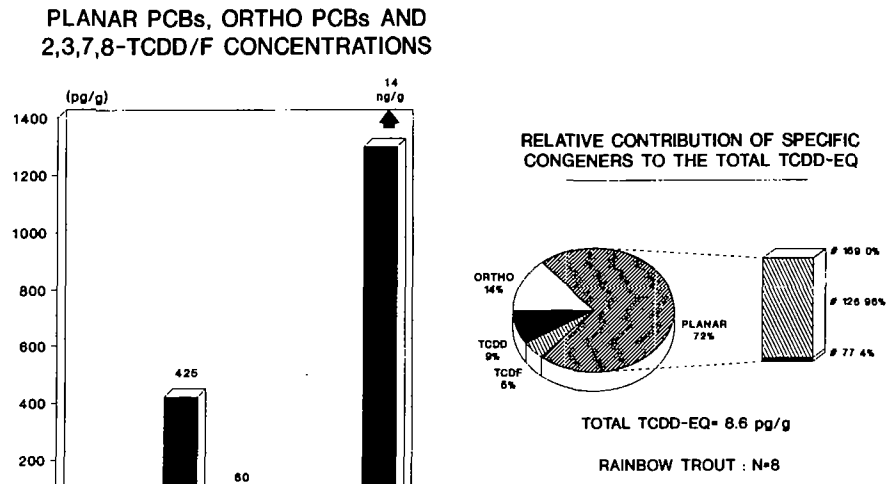
Figure #1

PLANAR PCBs, ORTHO PCBs AND 2,3,7,8-TCDD/F CONCENTRATIONS



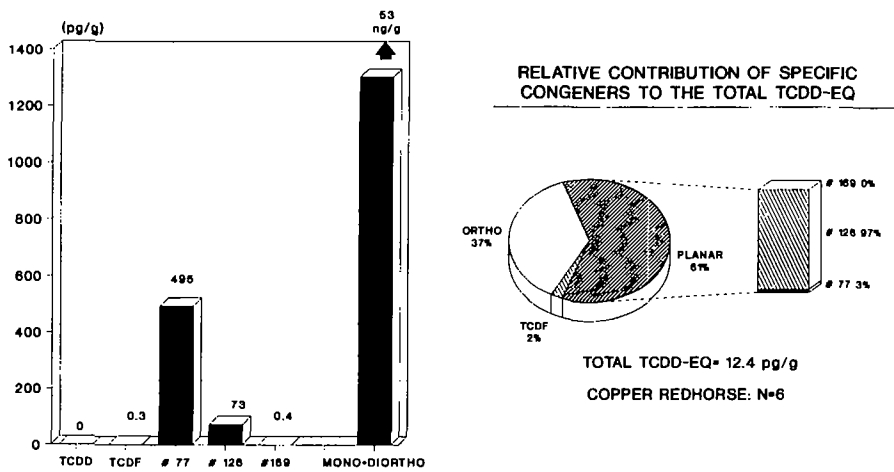
BROWN TROUT: N=14

Figure #2



RAINBOW TROUT : N=8

Figure #3



COPPER REDHORSE: N=6

Figure #4

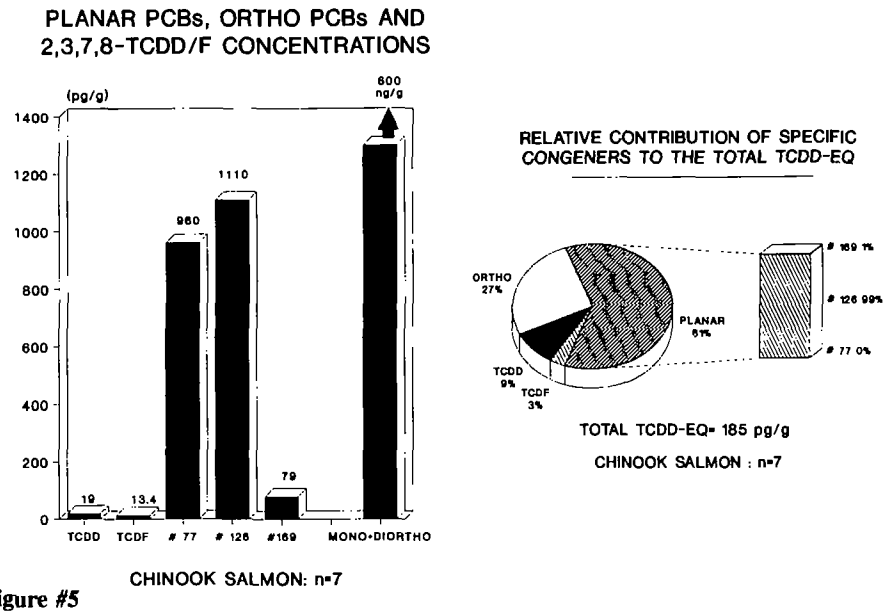
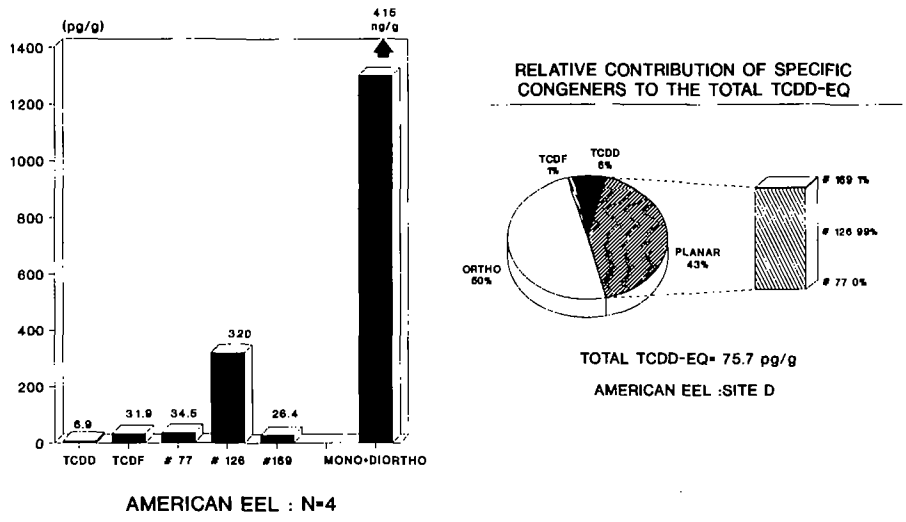


Figure #5



The concentration of mono and di-ortho substituted PCBs are always 100 times higher than planar PCBs. Pattern distribution of these congeners is very similar in all species analysed. Mono-ortho substituted PCB #118 is the most abundant congener followed by PCB #105, #156 and #157. Di-ortho substituted PCB #180 is the major congener of its class in all species, followed by PCB #170. Highest levels of mono and di-ortho substituted congeners are found in chinook salmon, while the lowest levels were detected in rainbow trout.

TCDD-EQUIVALENT:

If only 2,3,7,8 substituted PCDD/PCDF congeners are considered in the calculation of the total TCDD-EQ, chinook salmon would be the only species with TCDD-EQ levels slightly higher than the fish consumption limit of 15 pg/g and also the only species with total PCB concentration over 2 μg/g.

Using TEFs values proposed by the WHO, planar PCBs contribute to more than 43 % of the total TCDD-EQ in all species. More than 95 % of the contribution of planar PCBs is related to PCB #126. From these new TCDD-EQ concentrations, only rainbow trout and copper redhorse are slightly under the acceptable level of 15 pg/g TCDD-EQ. TCDD-EQ concentrations in chinook salmon become more than 10 times higher than proposed acceptable level while those for american eel are 5 times higher and brown trout are 2 times higher.

CONCLUSIONS:

- Relatively high levels of planar PCB #77 and #126 are measured in all fish analysed, with only a minor contribution of PCB #169.
- Contribution of planar PCBs to the total TCDD-EQ concentration is more than 43 % for all samples at all sites.
- From TEFs values proposed by WHO, PCB #126 contributed to more than 95 % of the planar PCB-EQ.
- Contribution of PCBs to the total TCDD-EQ is more than 85 %.

References:

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