Non- and mono-ortho substituted chlorobiphenyls in fish and marine mammals

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Abstract

Concentrations of the non-ortho substituted (planar) chlorobiphenyls (CBs) 77, 126 and 169 and the mono-ortho substituted CBs 105, 118 and 156 have been determined in freshwater fishes from the Netherlands and in marine fishes and some marine mammals from the southern North Sea. In contrast with other fish species a relatively strong metabolism for the CBs 77 and 126 was found to be present in yellow eel. A similar metabolism was found in marine mammals. The total amount of tetrachlorodibenzo-p-dioxin(TCDD)-equivalents due to PCBs is mainly determined by the CBs 77, 126, 169, 105, 118 and 156 with CB 126 as the main contributing CB in all organisms analysed.

Introduction

Based on their toxicity equivalency factors (TEFs)[1,2] and their concentrations in technical PCB mixtures [3,4], it was expected that the contribution of PCBs to the total amount of TCDD-equivalents due to PCBs (CB-TEQ) in organisms would be mainly determined by the non-ortho substituted (planar) CBs 77, 126 and 169 and the mono-ortho-substituted CBs 105, 118 and 156. Because of the relatively high PCB concentrations in freshwater fishes from the Netherlands[5], it was also expected that especially for the consumption of the lipid rich yellow eel (*Anguilla anguilla*) total amounts of TCDD-equivalents would be a cause for concern.
In order to verify these expectations, concentrations of non- and mono-ortho substituted CBs were determined in marine and freshwater fishes from the Netherlands. In order to obtain an impression of the bioaccumulation of these CBs through the food chain, some marine mammals from the southern North Sea were also analysed for these CBs.

Methods

Concentrations of the CBs 77, 126 and 169 were determined by a recently developed method[3]. With this method the planar CBs were separated from the remaining CBs by a porous graphitic carbon (PGC) HPLC column. For the final detection GC/MS with negative chemical ionisation was used. ^{13}C labeled CBs 77, 126 and 169 were used as internal standards. Concentrations of the CBs 105, 118 and 156 were determined together with the other CBs in a classical PCB analysis[6].
All fish or fish liver samples were pooled samples of 25-80 specimens, caught in 1990-1992. Two blubber samples were taken from a white beaked dolphin (*Lagenorynchus albirostris*) and a harbour porpoise (*Phocoena phocoena)* which were stranded alive at the

Dutch coast and kept alive for some days at an oceanarium. These samples were kindly supplied by Dr. R. Kastelijn of the Harderwijk oceanarium.

Results and discussion

Concentrations of planar CBs in all marine and freshwater fishes analysed except yellow eel (*Anguilla anguilla*) showed that CB 77 occurs in the highest concentrations, followed by CB 126, with only a minor contribution of CB 169 (Fig.1). In yellow eel CB 126 is the major planar CB, followed by CB 77 and CB 169. In the marine mammals dolphin and porpoise from the southern North Sea CB 169 is the major CB (dolphin) or almost equal in concentration to CB 77 (porpoise) (Fig.2). The average concentrations of CB 77 in marine and freshwater fishes and the average CB 126 concentrations in eel are around 100 ng/kg. The concentrations of planar CBs in fish liver and marine mammals are much higher: CB 77: upto 3700 ng/kg in cod liver southern North Sea, CB 169: upto 60.10^3 ng/kg in dolphin blubber from the southern North Sea.
When the concentrations of the CBs 77, 126 and 169 are expressed as ratios to CB 153, the patterns of these three ratios in all marine fishes and freshwater fishes, except in eels, come close to that in the technical PCB mixture Aroclor 1254 (Fig.3). Like marine mammals, eels show a completely different pattern. Supposing that CB 153 is not metabolized in fish, it may be concluded that for the CBs 77 and 126 a relatively strong metabolism is present in eel and also in marine mammals. This means that concentrations of planar CBs in eel from the Netherlands are about at the same level as concentrations of planar CBs in lean freshwater fishes. Due to its high fat content, and its unique life cycle in which lipophilic contaminants can not be released by spawning[7], total PCB concentrations in eel are much higher than in lean freshwater fishes in the Netherlands.
Using TEFs of the Dutch Working Group on TEFs (Van Zorge)[2], the contribution of the different non- and mono-ortho substituted CBs to the total amount of TCDD-equivalents due to PCBs can be calculated (Fig.4). It is shown that in all fish species, including eel, and in dolphin and porpoise CB 126 is the main contributer to the total amount of TCDD-equivalents due to PCBs. In eel CB 126 is followed by CB 156, in the other fish species and in the porpoise CB 77 is the second contributer, while in the dolphin this is CB 169. In marine mammals CB 126 was also reported as the highest contributing congener to the total amount of TCDD-equivalents by other authors, but different congeners were reported as the CB second contributer [8].
It may be expected that other mono-ortho substituted CBs, especially CB 157 (2,3,4,3',4',5' - hexa CB) and CB 167 (2,4,5,3',4',5' - hexa CB) have some contribution to the total amount of TCDD-equivalents due to PCBs, but based on their concentrations in the technical PCB-mixtures, their TEFs and the information about their occurrence in fish[9], this will probably not be more than a few percent.
Because of the metabolism of the CBs 77 and 126 in eel, most total amounts of TCDD-equivalents due to PCBs in eel from the Netherlands just stay below the Canadian tolerance level for fish consumption of 20 ng/kg. When this metabolism would have been absent, this tolerance level would have been exceeded in Dutch eel by about a factor 5-10.
The highest levels of non-ortho and mono-ortho substituted CBs in fishery products from the Netherlands are found in cod liver from the southern North Sea: total amounts of TCDD equivalents due to PCBs in these fish livers upto 210 ng/kg were measured.

Conclusions

- In yellow eel (*Anguilla anguilla*) a relatively strong metabolism is present for the CBs 77 and 126. Therefore the toxicity of PCBs in eel from the Netherlands is strongly reduced to levels around or below the Canadian tolerence level for fishery products.

- The highest levels of CB-TEQ in fishery products are found in cod liver from the southern North Sea.
- CB 126 is the major contributing CB to the CB-TEQ in fish and marine mammals.
- Despite a strong metabolism for the CBs 77 and 126 in dolphin and porpoise, the highest CB-TEQs are found in these animals.

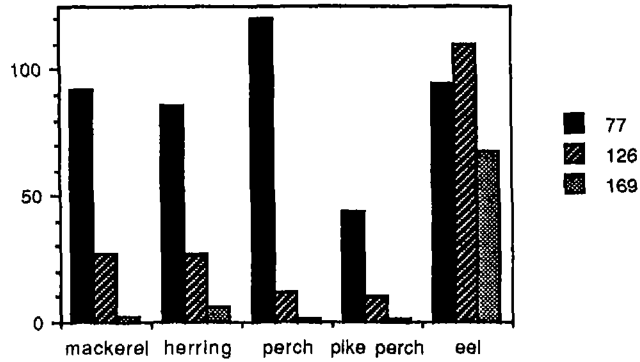

Fig.1: Planar CB concentrations in mackerel and herring from the southern North Sea, pike perch and perch from the Volkerak Lake (Rhine delta) and eel from the Rhine (ng/kg wet weight).

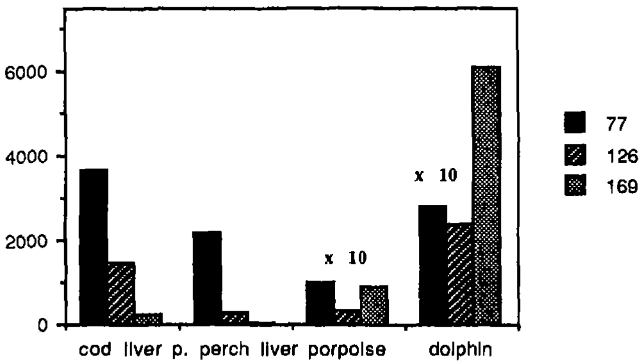

Fig.2: Planar CB concentrations in pike perch liver from the Hollands Diep (Rhine delta) and cod liver, porpoise blubber and dolphin blubber from the southern North Sea (ng/kg wet weight). Concentrations in porpoise and dolphin should be multiplied by 10.

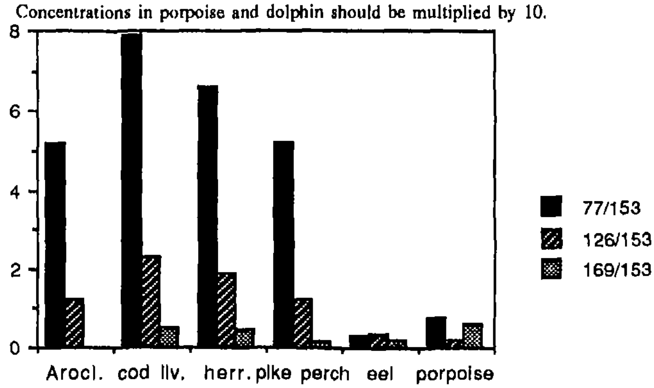

Fig.3: Ratios of planar CBs to CB 153 in Aroclor 1254, cod liver, herring, pike perch, eel and porpoise blubber.

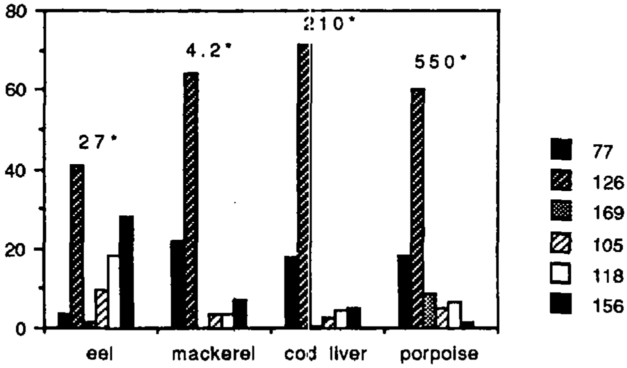

Fig.4: Contribution of the CBs 77, 126, 169, 105, 118 and 156 to the CB-TEQ (%). * : Total CB-TEQ.

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