POLYCHLORINATED BIPHENYLS, POLYCHLORINATED-DIBENZODIOXINS AND -DIBENZOFURANS IN MACKEREL ICEFISH AND MARBLED ROCKCOD FROM THE KERGUELEN ISLANDS (ANTARCTICA)

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Introduction

Polychlorinated biphenyl (PCBs), polychlorinated-dibenzo-*p*-dioxins (PCDDs), polychlorinated-dibenzofurans (PCDFs) and chlorinated pesticides (HCB, *p,p'-P,P'-DDE*) are industrial chemicals or by-products that exhibit several common properties such as high lipophilicity (increasing with chlorination), high resistance to degradation by acids, bases, heat and hydrolysis. The characteristics that led to their wide use in industry and agriculture also cause them to accumulate in ecosystems. Moreover, they elicit toxic responses in organisms including humans[1]. They have already been detected in Antarctic organisms[2, 3,4], but to our knowledge this is the first study on the presence of persistent organic pollutants in marbled rockcod and mackerel icefish from the Kerguelen Islands.

The Kerguelen Islands lie within an Antarctic Convergence where upwelling cold water from the Antarctic mixes with the warmer waters of the Indian Ocean. The sea water surrounding the Kerguelen Islands is ice-free.

The aim of this study was to evaluate the accumulation of certain persistent organic pollutants (POPs) such as PCBs, *p,p'-DDE* and hexachlorobenzene (HCB), polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) in mackerel icefish (*Champsocephalus gunnari*) and marbled rockcod (*Notothenia rosii*) collected at the Kerguelen Islands. The determination of POP body burden in these commercial fish species is important in assessing the eventual risk for humans, therefore the relative 2,3,7,8-tetrachlordibenzo-*p*-dioxin toxic equivalents (TEQs) were calculated. Both fish species are rather long-lived, they can accumulate contaminants over an estimated maximum lifespan of 12-13 years. Both feed on krill, planktonic and benthic crustaceans, mollusks, bony fish while the marbled rockcod may also feed on young mackerel icefish too[5, 6]. Risk by fish consumption involves not only humans but other fish and marine mammals that feed on icefish and rockcod as well. The contaminant load is passed down the from prey to predator giving rise to the biomagnification process.

Materials and Methods

Marbled rockcod and mackerel icefish were collected November 30-December 1 2000 aboard the French trawler Kerguelen De Tremarec using a bottom trawl bag. The bag was cast at a depth of 125-126 m for marbled rockcod and 180-187 m for mackerel icefish. Liver and muscle samples of both species and whole icefish were analyzed following the method described elsewhere[7]. Briefly, homogenized tissues were Soxhlet extracted with methylene chloride/n-hexane. Clean up and lipid removal was accomplished by multi-layer (acidic) silica gel column chromatography. A portion of the final extract was used for the determination of *ortho*-substituted PCBs, *p,p'-DDE* and HCB. Remaining extracts were subjected to activated carbon impregnated silica gel column chromatography fractionation to separate non-*ortho* coplanar PCBs, PCDDs and PCDFs. Concentrations of individual congeners were measured against the corresponding standards. Gas chromatograph with electron capture detector (GC-ECD) and GCQ plus ion trap mass spectrometer from ThermoFinnigan was used[8].

Results and Discussion

HCB, p,p'-DDE, SPCB

Average concentrations of POPs are listed in Table 1. HCB and *pp'-DDE* concentrations were quite low, ranging from 0.003±0.005 ng/g wet wt in the muscle of icefish to 0.087±0.064 ng/g wet wt in the liver of rockcod. PCBs ranged from 0.671±0.791 ng/g wet wt to 3.731±3.338 ng/g wet wt in muscle and liver of the icefish. PCB levels of 166±28 ng/g wet wt and 327±90 ng/g wet wt are reported in the liver of Mediterranean *L. boscii* and *P. blennoides*[9], respectively. HCB, *pp'-DDE* and PCBs values are very low compared to other areas; Sinkkonen *et al*. found 8.4-23.3 ng/g lipid wt of HCB, 24.7-67.3 ng/g lipid wt of *pp'-DDE* and 78.1-286.7 ng/g lipid wt of SPCB in Arctic cod liver from Vestertana Fjord[10]. In Mediterranean species, DDTs were 99.3±16.7 ng/g wet wt in the liver of *Lepidorhombus boscii* and 131±30 ng/g wet wt in the liver of *Phycis blennoides*[9].

Fingerprints and composition of isomer-specific PCB classes are also described; the most abundant congeners were PCB185 > PCB > PCB99 > PCB170 in the tissues of the marbled rockcod and PCB101 > PCB185 > PCB 170 in the tissues of the mackerel icefish. Low-chlorinated congeners (tri-, tetra-CBs) showed concentrations ranging from <0.001-1.146 ng/g wet wt. Hepta-CBs were higher in rockcod (40-50 % ca.) while penta-CBs were higher in icefish (20-45% ca.). The composition pattern is similar to that of the Kanechlor technical mixture.

The liver somatic index (LSI) versus the PCB concentration was determined to evaluate correlation between contaminant load and the organisms' health status ($p < 0.05$).

PCB concentrations were plotted against the specimens' sex and age (Figures 1-2). In icefish, values tend to be generally higher in males than in females while no important differences were detected in rockcod. The sex-based differences in icefish can be traced to the female metabolism in ovogenesis during which female icefish might eliminate part of the body burden. HCB, *pp'-DDE* and PCB concentrations similarly decreased with age; in particular, POPs seem to decrease starting from age 3 years, that is, when they are sexually mature. On the other hand, icefish may also be able to detoxify POPs through gill respiration[11].

Dioxin-like compounds and TEQs

Concentrations of dioxin-like POPs are shown in Table 1. Most toxic mono- and non-*ortho* substituted PCBs ranged from below detection limit (0.001 ng/g wet wt) to 0.29 ng/g wet wt and 0.539 pg/g wet wt, respectively, in the liver of icefish. A wide ranging accumulation pattern of PCDDs/DFs were observed in the liver and muscle of the two species. In fact, both PCDDs and PCDFs were higher in the muscle (67.549 and 1.136 pg/g wet wt, respectively) of rockcod than in the liver (21.797 and 0.594 pg/g wet wt, respectively), while the opposite observed was in icefish (39.959 pg/g wet wt of PCDDs and 0.658 pg/g wet wt of PCDFs in the muscle; 933.359 pg/g wet wt of PCDDs and 110.610 pg/g wet wt of PCDFs in the liver).

Data on contaminant levels were used to analyze the relative contribution of mono- and non-*ortho* PCBs, PCDDs and PCDFs to total TEQs. Calculated concentrations of total TEQs were 38.034 pg/g wet wt and 13.762 pg/g wet wt in the liver and muscle of icefish, 1.798 pg/g wet wt and 1.355 pg/g wet wt wt in the liver and muscle of rockcod. TEQs are reported to be 77 pg/g wet wt in bluefin tuna and 82 pg/g wet wt in shark from the Mediterranean Sea [12].

Table 1. Concentration (average±standard deviation) of persistent organic pollutants in the tissues of Antarctic fish (Nr=*Notothenia rossii*, Cg=*Champsocephalus gunnari*, bb= body burden).

	Nr liver	Cg liver	Nr muscle	Cg muscle	Cg bb
N	13	12	12	11	9
HCB (ng/g wet wt)	0.075±0.070	0.015±0.032	0.026±0.070	0.003±0.005	0.007±0.013
p,p'-DDE (ng/g wet wt)	0.087±0.064	0.027±0.024	0.019±0.026	0.010±0.014	0.007±0.007
ΣPCBs (ng/g wet wt)	3.358±1.503	3.731±3.338	1.202±1.268	0.671±0.791	0.935±0.915
Tri-CBs	0.220	1.146	0.101	0.059	0.110
Tetra-CBs	0.000	0.674	0.104	0.048	0.079
PentaCBs	0.051	0.701	0.143	0.297	0.264
Hexa-CBs	0.608	0.415	0.146	0.088	0.098
Hepta-CBs	1.228	0.608	0.420	0.130	0.249
Octa-CBs	0.381	0.104	0.170	0.009	0.100
Nona-CBs	0.084	0.040	0.056	0.000	0.007
Mono-*ortho* PCBs	0.150	0.290	0.100	0.040	nd
Non-*ortho* PCBs (pg/g ww)	0.206±0.040	0.539±0.631	0.126±0.166	0.019±0.010	nd
ΣPCDDs (pg/g wet wt)	21.797	933.359	67.549	39.959	nd
ΣPCDFs (pg/g wet wt)	0.594	110.619	1.136	0.658	nd
$\Sigma TEQ_{(PCBs+PCDDs+PCDFs)}$ (pg/g wet wt)	1.798	38.034	1.355	13.762	nd

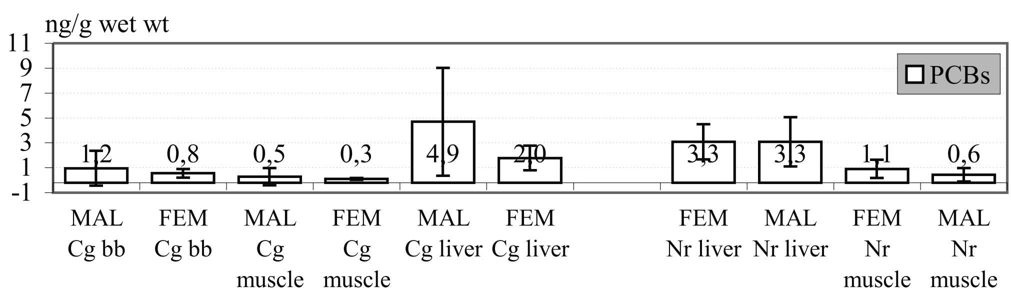

Figure 1. ΣPCBs in liver and muscle of mackerel icefish (Cg=*Champsocephalus gunnari*) and marbled rockcod (Nr=*Notothenia rossii*) plotted against sex.

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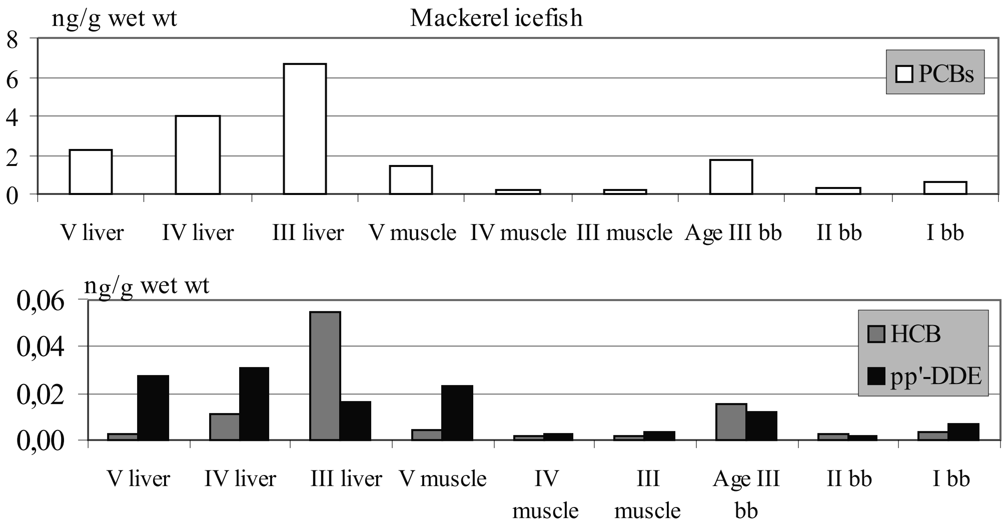

Figure 2. ΣPCBs in liver, muscle and homogenates of mackerel icefish plotted against age.

Table 2. Age class and sexual maturity in mackerel icefish (Kock *et al.*, 1997).

Age class	lenght (cm)	age (year)	Sexual maturity
I	15-16	1+	immature
II	18-19	2+	immature
III	26-27	3+	mature
IV	28,5-30	4+	mature
V	33-34	5+	mature

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