Persistent organic pollutants in two species of white-blooded Antarctic fish

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Introduction

Persistent organic pollutants (POPs) are ubiquitous environmental chemicals and can be found even at very remote areas such as the Antarctic Ocean. Via long-range atmospheric transport (LRAT), global distillation processes and cold condensation POPs reach the Antarctic ecosystem and bioaccumulate in aquatic biota [1 – 3]. Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and former widely used pesticides such as γ-hexachlorocyclohexane (γ-HCH), hexachlorobenzene (HCB), and *p,p'*-DDT are lipophilic organic chemicals with high potential for bioaccumulation. Antarctic fish which hold high trophic positions, appear to exhibit low endogenous elimination rates for POPs and are therefore expected to show increasing levels of these chemicals with rising exposure to POPs and climate warming [4 – 8]. Therefore, two fish species of Antarctic icefish originating from the Southern Ocean around Elephant Island, were caught and analyzed for their levels of PCBs, PBDEs, HCB, HCHs, and DDTs in muscle tissue and ovaries. Additionally, toxic equivalents (TEQs) and bioanalytical equivalents (BEQs) were determined and compared. We used two species with different feeding habits and trophic web positions: the planktivorous *Champsocephalus gunnari* and the piscivorous *Chaenocephalus aceratus*.

Materials and methods

Two species of white-blooded icefish (*Channichthyidae*) were caught during a cruise with the research vessel *Polarstern* during March 13 to April 9, 2012, around Elephant Island and the South Shetland Islands. POPs were analyzed in muscle and ovary tissue of mature, female fish. All tissue samples were wrapped in aluminum foil and stored at -20°C until analysis. Muscle and gonad samples were defrosted, cut into small pieces and lyophilized at 33 Pa for 72 h until constant weight. Dried tissue of muscle or gonads was ground with anhydrous sodium sulfate and quartz sand to obtain a fine powder. The homogenate was extracted using a speed-extractor (E-914, Büchi, Switzerland) with a mixture of *n*-hexane/dichloromethane (1:1) as described by Hartmann [9]. After the evaporation of the solvents, the amount of lipids was determined gravimetrically. After the addition of $^{13}C_{12}$ labeled internal standards and dilution with *n*-hexane the solution was treated with 3 mL of oleum (7% SO_3 in conc. sulfuric acid). The suspension was centrifuged at 5'000 rpm for a few minutes and the *n*-hexane layer with the target analytes was collected; this extraction step was repeated twice. After evaporation of the solvents to 0.5 mL the extract was chromatographically purified on a multilayer mini silica gel column. The column was eluted with 5 mL *n*-hexane followed by 5 mL *n*-hexane/dichloromethane (1:1). Subsequently, the solvent was evaporated to 30 µL and the recovery standard ($^{13}C_{12}$ labeled PCB-70) was added. Quantitative determination of the target analytes was carried out by gas chromatography/high resolution mass spectrometry (GC/HRMS) at a mass resolution of 8'000 as described in the literature [10, 11]. The same extracts that were used for chemical analysis were used in the DR-CALUX bioassay for the determination of bioequivalent values (BEQs). The bioassay was performed by BioDetection Systems b.v. in Amsterdam (The Netherlands).

Results and discussion

All samples contained detectable levels of the target compounds. Most analyte concentrations and the TEQs and BEQs were clearly below levels in temperate species. Concentrations were about 15 to 110 times higher when calculated on a lipid weight basis compared to fresh weight basis. Our results revealed higher contaminant levels in ovary than in muscle tissues of both species. Overall, PCBs were the predominant group among all compounds measured in this study followed by the DDTs, PBDEs, HCB and γ-HCH (see Table 1 and Figure 1). Comparison with data from the literature points to higher PCB and DDT concentrations than those measured in icefish in the 1990ies.

Among the PCBs, PCB 153 contributed by 28% in muscle and by 26% in ovaries to all PCBs in both species. The second most abundant PCB were PCB 138 (26%) and 101 (21%). No significant difference in the PCB pattern of tissues, muscle and ovaries, and the two species of icefish was detectable (see Figure 2).
In the ovaries, levels of *p,p′*-DDE, *o,p′*-DDT, and *p,p′*-DDT were significantly higher in *C. aceratus* compared to those of *C. gunnari*. Moreover, DDT was significantly higher in muscle and ovaries of *C. aceratus* compared to *C. gunnari*. Among the DDTs, *p,p′*-DDE showed the highest concentration of up to 57% in muscle of *C. aceratus* (see Figure 1 and 2).

For γ-HCH, no difference was noticeable between the tissues of the two icefish when considered on the lipid weight basis. HCB concentrations (ng/g lw) were higher in muscle and ovaries of *C. aceratus* than in *C. gunnari* (see Figure 1). In case of the PBDEs, the pattern was dominated in both icefish by BDE 47 (59% in muscle, 54% in ovaries), followed by BDE 99 with approximately 20% and BDE 100 with approximately 12% (see Figure 2). This pattern is in line with the BDE congener distribution found in fish around the globe and is similar to the composition of the technical pentabromo diphenyl ether product [10, 12, and 13].

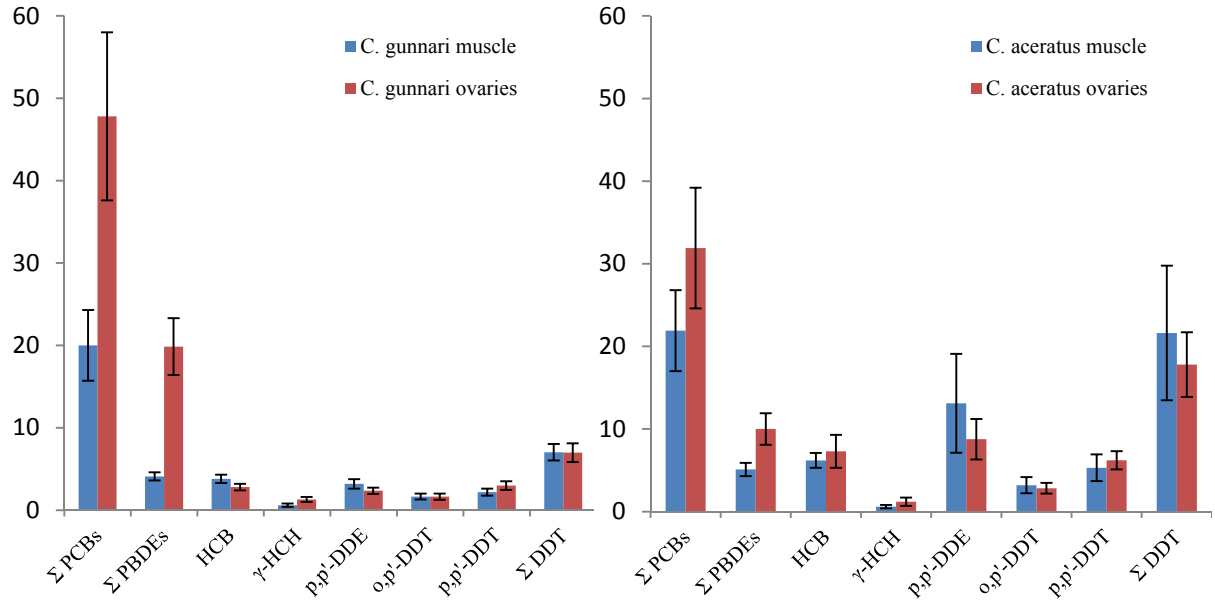

Figure 1: Mean concentrations (± sem) of Σ PCBs (28, 52, 101, 138, 153 and 180), Σ PBDEs (28, 47, 99, 100, 153, 183 and 197), HCB, γ -HCH, and Σ DDT (*p,p′*-DDE, *o,p′*-DDT and *p,p′*-DDT) in muscle and ovaries of the two icefish *C. gunnari* (n=11) and *C. aceratus* (n=10) in ng g^{-1} lipid weight.

Table 1: Mean levels of organic contaminants in tissues of two Antarctic icefish species in ng g^{-1} lw. TEQs and BEQs reported in pg g^{-1} fw.

	C. gunnari muscle	*C. gunnari* ovaries	*C. aceratus* muscle	*C. aceratus* ovaries
Lipid content %:	2.13	6.93	1.45	2.64
TEQ	0.47	0.07	0.16	0.53
BEQ	0.20	5.14	0.15	0.57
Σ PCBs	20.04	47.82	21.91	31.87
Σ PBDEs	4.08	19.85	5.01	10.03
HCB	3.82	2.84	6.22	7.37
γ-HCH	0.59	1.25	0.58	1.18
p,p'-DDE	3.19	2.36	13.11	8.76
o,p'-DDT	1.65	1.64	3.20	2.83
p,p'-DDT	2.19	2.98	5.31	6.21

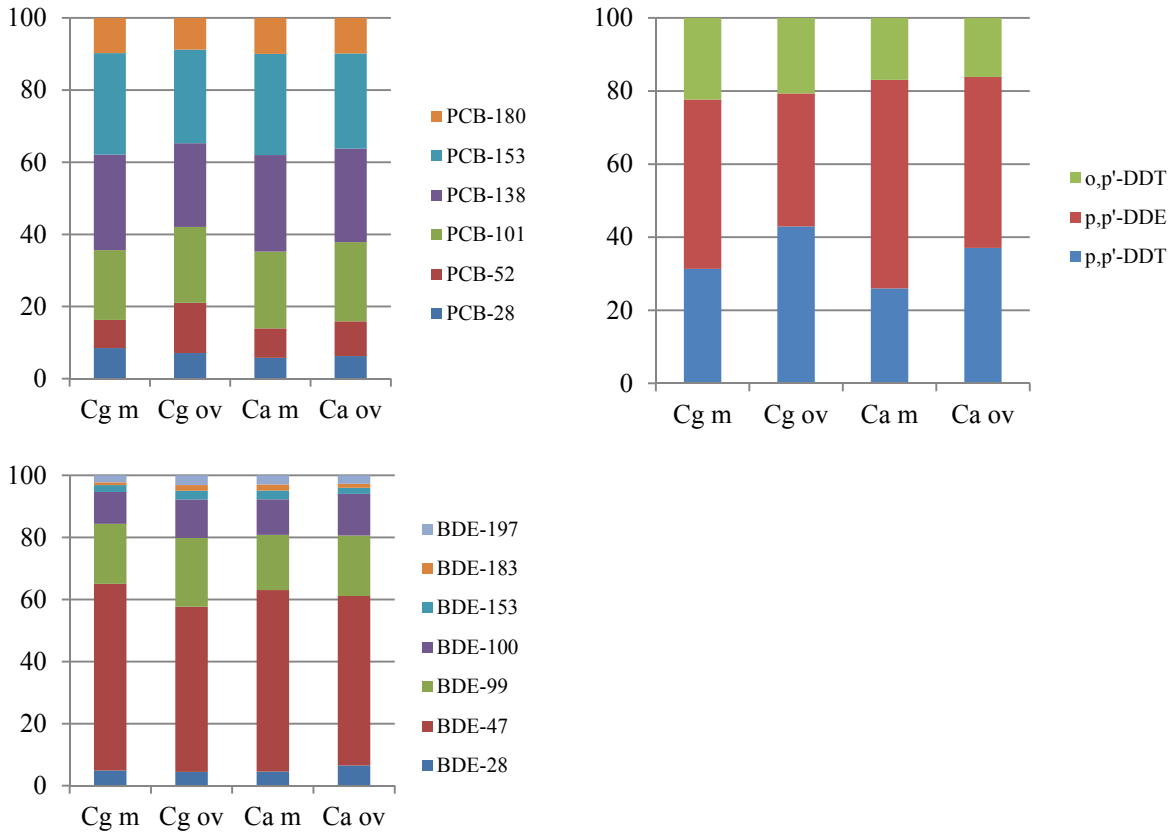

Figure 2: Congener composition (percentage) of PCBs, DDTs and BDEs in muscle (m) and ovaries (ov) of *C. gunnari* (Cg) and *C. aceratus* (Ca).

Long-term observations of POP levels in Antarctic biota are scarce. Similar studies as the present work were published by Weber and Goerke [5, 14]. From 1987 to 1996, these authors reported an increase of PCB 153 and PCB 180 levels in *C. aceratus* but not in *C. gunnari*. In the present study, we found three times higher concentrations of the same PCB congeners in the tissues of our two icefish species than in the previous study from 1996 published by Weber and Goerke [5]. In contrast, the HCB levels show a declining trend from the 1987 study to our current measurements. A similar pattern of stable and declining HCB levels by up to 2.5% per year has also been observed in Arctic biota since the late 1980ies [15]. In *C. aceratus*, levels of *p,p′*-DDE had already increased from 1987 to 1996, and the values we measured in both tissues of *C. aceratus* were almost twice as high as in 1996 [5, 15]. On the other side *p,p′*-DDE concentrations in *C. gunnari* remained at similar levels from 1987 over 1996 to the present study. Despite this, overall DDT levels were increasing from 1987 to 1996 in both icefish species, and the herein presented values are also slightly higher than those in 1996, suggesting an increasing trend of DDTs in icefish in the Antarctic region of Elephant Island and South Shetland Islands. Conclusively, PCB and DDT concentrations tend to rather increase than decrease in tissues of *C. aceratus* and *C. gunnari* from Antarctica. Additionally, worldwide climate change contributes to an increased volatilization of POPs, and via long range atmospheric transport these toxic contaminants reach even very remote regions like the Low and High Antarctica. Concurrently, accelerated melting of glaciers and ice masses in the Antarctica may contribute to increased release of stored POPs and thereby lead to a progressive contamination of the Southern Ocean and its biota.

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