PCDDs, PCDFs and dioxin-like PCBs in Greenland Shark (Somniosus microcephalus)

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Introduction

The Greenland Shark (*Somniosus microcephalus*) is the largest fish and the only shark known to inhabit the cold Arctic waters [1]. This fish species feeds throughout the marine food chain but is mainly a top predator [2]. The usual size of these sharks is 2-5 meters but there have been reports of individuals up to 7 meters. Like other fish Greenland Sharks grows slowly during their whole life and the growth rate has been estimated to be around 0.5 cm/year [3]. This gives Greenland Sharks a possible life span of 100 years or more. An earlier study on Greenland Sharks has revealed a wide range of different contaminants and has also suggested a poor metabolism [2].

The long life span, occupation of a high trophic level and a suggested slow metabolic rate makes the Greenland Shark a perfect sentinel for organic contaminants in the Arctic environment.

In this study polychlorinateddibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) have been determined in Greenland Shark muscle and liver.

Material and Methods

Chemicals: All ^{13}C-labelled internal standards used were delivered by Cambridge Isotopes Laboratories (Andover, USA) or Wellington laboratories (Guelph, Canada). Solvents and chemicals used were of the highest commercial grade available. Carbon AX 21 from AMOCO (USA) and SephadexLH 20 from Fluka.

Instruments: Measurements were made by high resolution gas chromatography together with high resolution mass spectrometry (HRGC/HRMS) on a HP 5890 II GC (Agilent, USA) coupled with a VG-AutoSpec MS (Micromass) or a Finnigan MAT 95 XL. For gas chromatographic separation a DB 5 column (60 m, 0.25 mm ID and 0.1 µm film) was used. The mass spectrometer was run in electron impact (EI) mode with a resolution of 10 000. Two isotope masses were measured for each component. The quantification was carried out by the use of internal/external standard mixtures (isotope dilution method) using a five-point calibration curve.

Samples: Between 2001 and 2003 Greenland Sharks have been collected from the area around Iceland. All sharks were accidentally caught in trawls or entangled in long lines. For this study muscle and liver from ten sharks, all females in size 3.6-4.8 meters have been used.

Analysis: In short 15 g of muscle and 3 g of liver were spiked with a mixture of ^{13}C-labelled internal standards (17 2,3,7,8 substituted PCDDs/Fs, 4 non-*ortho* PCBs and 8 mono-*ortho* PCBs), mixed with sodium sulfate and column extracted with cyclohexane:dichloromethane (DCM). The lipid content was determined gravimetrically and separation of the planar compounds (PCDDs, PCDFs and non-*ortho* PCBs) from lipids and non-planar compounds (*ortho*-PCBs) were done on an active carbon column. Clean up of the forward phase (*ortho*-PCBs and lipids) included a multilayer column consisting of different layers of sulfuric acid/silica gel and potassium/silica gel and a Sephadex column. The reversed phase (PCDDs, PCDFs and non-*ortho* PCBs) were cleaned up on a combined column consisting of two columns. The first one was packed with sulfuric acid/silica gel and put on top of an aluminum oxide column. After evaporation of solvents ^{13}C-labelled 1,2,3,4- TCDD was added as recovery standard to both fractions.

Toxic equivalents (TEQs) for PCDDs/Fs and dioxin-like PCBs have been calculated according to toxic equivalency

factors (TEFs) established by the World Health Organisation (WHO) [4] for humans and mammals.

Quality control: The ERGO laboratory has successfully taken part in control studies organised by WHO and is a certified dioxin laboratory. For this study one blank sample and one control sample from a fish oil pool used for quality control at Ergo were run with each batch of ten samples. Additionally 6 control samples from this control fish oil pool were analysed separately.

Results and Discussion

This is the first report on PCDDs/Fs and dioxin-like PCBs in Greenland Shark. Concentrations of PCDDs, PCDFs, dioxin-like PCBs and TEQ values found in Greenland Shark muscle and liver are summarised in Table 1.

Concentrations of PCDDs, PCDFs and non-*ortho* PCBs were lower in muscle than in liver but showed a similar pattern. The furans were present in higher concentrations than the dioxins and the pattern was dominated by the lower chlorinated congeners (tetra- to hexa-substituted compounds). 2,3,7,8-TCDF was the most abundant congener with a median value of 4.4 pg/g lipid in muscle and 190 pg/g lipid in liver.

Of the non-*ortho* PCBs, CB-77 and CB-126 were found in the highest concentrations. Mono-*ortho* PCB concentrations and pattern was very similar in both muscle and liver samples, the most abundant congener was CB-118 followed by CB-105.

Table 1: Concentrations of PCDDs, PCDFs (pg/g lipid) and dioxin-like PCBs (ng/g lipid) in Greenland Shark muscle (n=10) and liver (n=10). TEQ values are given in pg WHO-TEQ/g lipid.

	Muscle		**Liver**	
	median	range	median	range
Lipid (%)	16	13-22	55	36-72
Concentration (pg/g lipid)				
PCDDs	2.5	0.35-7.0	47	8.8-180
PCDFs	8.7	0.58-24	330	39-1400
PCDD/Fs	11	0.93-30	370	47-1600
Concentration (ng/g lipid)				
non-*ortho* PCBs	0.26	0.05-0.99	5.4	0.97-23
mono-*ortho* PCBs	560	190-1600	690	170-1600
WHO-TEQs (pg/g lipid)				
PCDDs	1.3	0.32-4.4	31	6.8-110
PCDFs	1.1	0.12-3.4	52	5.4-210
PCDD/Fs	2.5	0.44-7.5	82	12-330
non-*ortho* PCBs	7.5	0.91-28	280	36-1100
mono-*ortho* PCBs	73	28-210	95	25-220
Total TEQs	87	29-230	490	73-1600

Total TEQ concentrations in muscle were about five times lower than in liver samples (Figure 1a). The mono-*ortho* PCBs contributed with 88% of the total in muscle, followed by the non-*ortho* PCBs (Figure 1b). In liver that had higher concentrations of PCDDs/Fs and non-*ortho* PCBs the major contribution to the total came from the non-*ortho* PCBs with 61% (Figure 1b). The large contribution from the non-*ortho* PCBs is due to high concentrations of the most toxic PCB congener, CB-126. Liver concentrations of non-*ortho* PCBs in this study are higher than values found in fish and marine mammals from the Greenland environment [5].

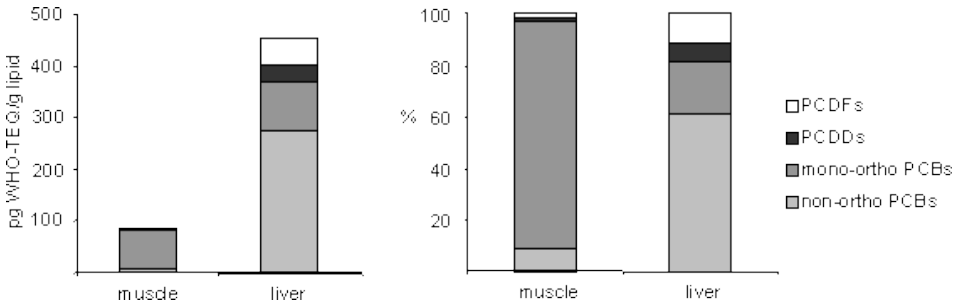

Figure 1: (a) Median WHO-TEQ concentrations and (b) comparison of TEQ compositions in Greenland Shark muscle (n=10) and liver (n=10).

Comparing the TEQ values for Greenland shark to other fish species from the same waters in the North Atlantic shows than muscle values for PCDD/Fs and non-*ortho* PCBs are in the same range but higher values for mono-*ortho* PCBs [6]. Liver TEQ values on the other hand are much higher.

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