Dioxin and PCB concentrations in Baltic salmon have decreased remarkably during the 2000s'

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Introduction

Wild fish are the major source of dioxins (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) for humans in the Baltic region. The physical properties of the sea, shallowness, large drainage area and long residence time contribute to the fact that the Baltic Sea is globally among the most polluted sea areas[1].

Although the levels of PCDD/Fs and PCBs have declined from the 1970s' their concentrations in Baltic herring (*Clupea harengus membras*) and salmon (*Salmo salar*) still exceed the established maximum levels set by the European Commission for food [2]. Finland and Sweden have, however, a derogation to the European Commission regulation, allowing them to place on their markets Baltic herring and salmon even though they exceed the maximum allowable concentrations of PCDD/Fs and/or PCBs. The derogation has specific conditions such as informing the consumers and especially vulnerable sections of the population on dietary recommendations in order to prevent the possible health risks. Additionally, European Commission recommends to monitor the presence of PCDD/Fs and PCBs in fish and fishery products from the Baltic region.

Previously, we have studied these hazardous substances in two projects concentrating on Baltic fish in 2002 and 2009. The present project was launched in 2016 to gain up to date information on the levels of dioxins, PCBs, PBDEs and perfluorinated alkyl substances (PFAAs) in Baltic fish. Altogether 101 composite samples will be collected from several fishing grounds off western coasts of Finland according to the subdivisions (SDs) and statistical rectangles of the International Council for the Exploration of the Sea (ICES), and 15 samples from three Finnish lakes with commercial fishery. This paper reports the results of the environmental contaminants of Baltic salmon species.

Materials and methods

Of the total of 101 Baltic fish samples to be analyzed in the project, eight pooled Baltic salmon samples from 24 individual salmons in two length categories were caught from ICES SDs 30, 31 and 32 (Figure 1).

Figure 1: Baltic Sea with ICES Sub-divisions

Analysis was carried out on salmon muscle with scraped subcutaneous lipids following the requirements laid down by the legislation[3]. Extraction, clean-up and analysis were done according to an accredited (T077, accreditation by FINAS according to EN ISO/IEC 17025) method at National Institute for Health and Welfare, Kuopio, Finland. PCDD/F-, PCB- and PBDE-samples were freeze dried and fat was extracted with ethanol-toluene in Accelerated Solvent Extractor (Dionex ASE 300). The solvent was then exchanged to hexane and the lipid content was determined gravimetrically. Samples were defatted on an acidic multilayer silica column and purified and fractionated by alumina and carbon columns. PCDD/Fs, PCBs and PBDEs were analyzed with HRGC/HRMS (Autospec Ultima) using selected ion monitoring mode with a 10,000 resolution. PCDD/Fs and PCBs and PBDEs were separated on a DB5 MS column (60 m x 0.25 mm x 0.25 µm). For BDE209 column was ZB-5MS Plus (6 m, ID 0.18 mm, 0.18 µm).

PFAAs were extracted from freeze-dried fish samples twice with 2 mL of 20 mM ammonium acetate in methanol. Prior to instrumental analysis, the extracts were filtered with 0.2 µm syringe filter. The PFAAs were analyzed using liquid chromatography (Dionex, Ultimate 3000 RSLC) negative ion electrospray tandem mass spectrometry (Thermo Scientific, TSQ Quantum Discovery Max).

The samples were analyzed for the seventeen toxic PCDD/Fs, twelve dioxin-like PCBs (PCB 77, 81,105,114, 118, 123, 126, 156, 157, 167,169, 189) , six non-dioxin-like PCBs (PCB 28, 52, 101, 138, 153, 180), fifteen PBDEs (BDE 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 138, 153, 154, 183, 209) and thirteen PFAAs (PFHxS, PFHpS, PFOS, PFDS, PFHxA , PFHpA, PFOA, PFNA , PFDA, PFUnA, PFDoA, PFTrA, PFTeA).

All the results are expressed on a fresh weight (fw) basis. PCDD/F and PCB TEQs were calculated using the WHO 2005 TEFs [4].

Results and discussion

Concentrations of PCDD/Fs, PCBs, PBDEs and PFAAs in the pooled salmon samples are represented in Table 1.

Table 1. Baltic salmon samples and their PCDD/F-TEQ, PCB-TEQ, indicator-PCB, PBDE and PFAAs concentrations in 2016. Each sample represents three individuals.

	ICES-subdivision	Mean length, cm	Mean weight, kg	Mean age, years	Mean fat %	WHO 2005 PCDD/F TEQ, pg/g fw	WHO 2005 PCB TEQ, pg/g fw	Indicator-PCBs,sum ng/g fw	PBDEs ng/g fw	PFAAs, sum (PFOS) ng/g fw
Bothnian Sea	30	79	6.1	1.7	16.2	5.4	4.6	52.6	3.3	2.6 (2.2)
Bothnian Sea	30	100	11.7	2.7	10.4	2.9	4.3	37.9	2.9	3.2 (3.2)
Bothnian Bay	31	84	5.5	2.0	16.1	3.7	5.2	46.5	3.4	3.7 (3.7)
Bothnian Bay	31	97	9.4	1.7	15.4	3.7	4.5	42.9	3.0	4.4 (4.4)
Gulf of Finland, west	32	72	3.5	1.3	14.5	3.6	4.6	42.5	2.6	3.2 (3.2)
Gulf of Finland, west	32	94	8.0	2.3	12.6	4.2	5.9	48.6	3.6	5.8 (5.4)
Gulf of Finland, east	32	69	3.4	1.3	14.6	3.7	5.1	46.8	3.3	4.1 (4.1)
Gulf of Finland, east	32	95	9.5	2.3	14.1	3.0	3.4	39.8	2.0	2.9 (2.9)

According to our results, six out of eight samples exceeded the EU maximum level for PCDD/Fs (3.5 pg TEQ/g fw) and all samples exceeded the maximum level for the sum of PCDD/Fs and PCBs (6.5 pg TEQ/g fw). The non-dioxin-like PCBs (indicator-PCBs), however, did not exceed the EU maximum level (75 ng/g fw). So far, no maximum levels have been set for PBDEs or PFAAs by EU.

The PCDD/F and PCB concentrations in Baltic salmon decreased considerably from the levels of 2002 [5] and 2009 [6] (Figure 2). A similar decrease has also been observed in the Swedish coast in the 2000's [7,8]. In 2009, our results were only a bit higher than the Swedish results from the Bothnian Sea and Bothnian Bay in 2010 [7], and our 2016 results were little lower than reported in the latest publication of Swedish monitoring of PCDD/Fs and PCBs in 2013 in Baltic Sea salmon [8] . Taken together, the PCDD/F and PCB levels in salmon caught from the Baltic Sea are still decreasing.

The decrease in PCDD/Fs and PCBs in salmon varied between 54% (Gulf of Bothnia) and 57% (Eastern Gulf of Finland) from 2002 and between 0% (Western Gulf of Finland) and 39% (Eastern Gulf of Finland) from 2009 to 2016. The overall decrease in the total TEQ concentration from all sampling sites was 58% during 2002−2016, and 21% during 2009−2016.

The levels of PBDEs slightly decreased, but instead a slight increase in the concentration of perfluoro-octane sulfonate (PFOS, the major PFAAs homologue detected in 2016) was observed between 2009–2016. The PBDEs including BDE-209 and PFOS were only analyzed in 2009 and 2016, and 13 PFAAs in 2016, only.

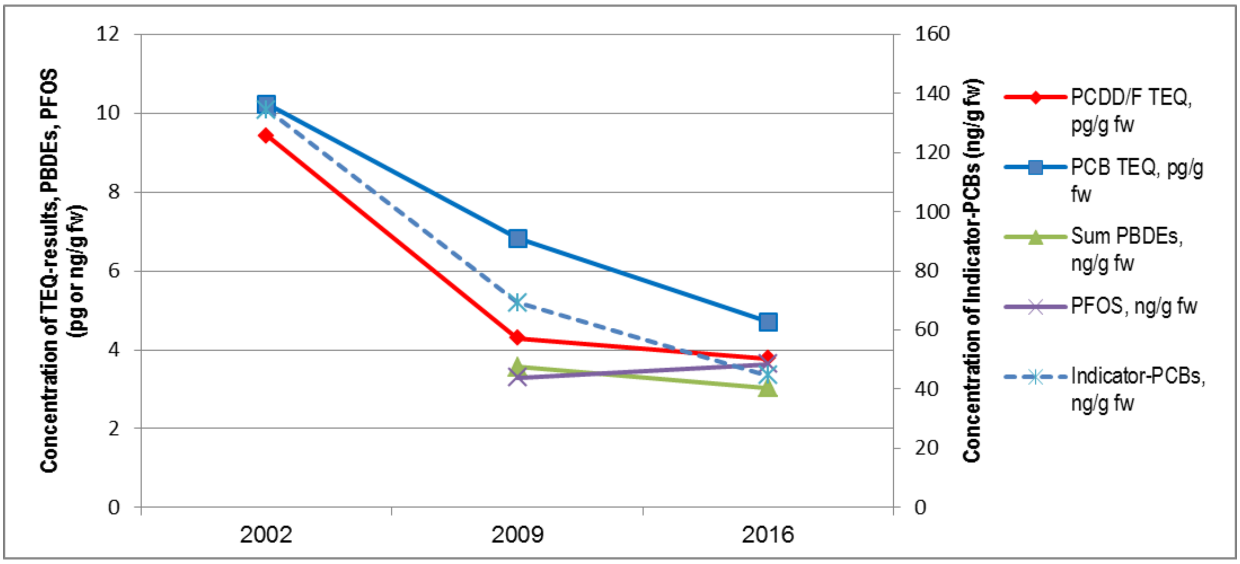

Figure 2. Mean PCDD/F-PCB, PBDE and PFOS concentrations in Baltic salmon in 2002-2016

The age of the salmon varied to some extent between the sampling years 2002–2016, which probably affects the concentrations of persistent organic compounds. When the age of the caught salmon was standardized to the concentration of 2nd sea-year salmon the decrease of the total PCDD/F-PCB-TEQ concentration was 45 % from the year 2002 and 27 % from the year 2009 (Figure 3), i.e. a bit slighter than without age standardization.

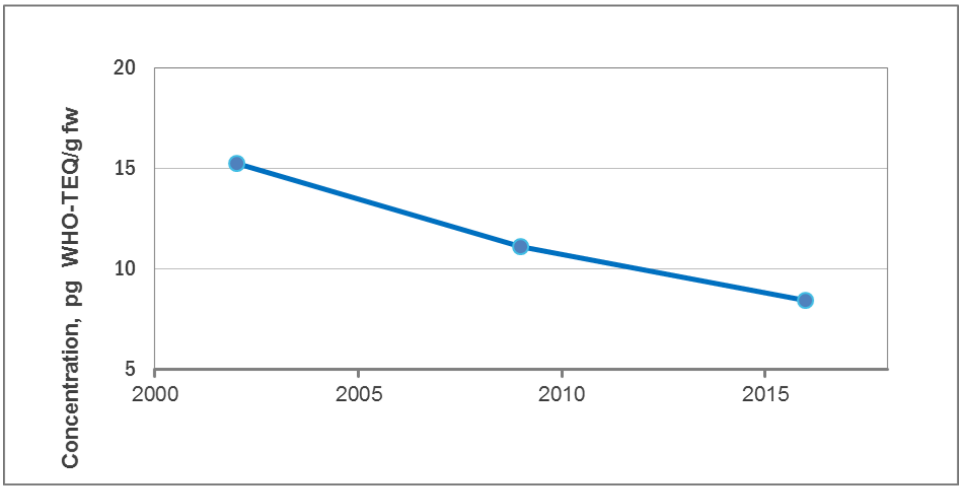

Figure 3. Age standardized PCDD/F-PCB-sum-TEQ concentrations in Baltic salmon in 2002-2016.

PCDD/F and PCB levels in Baltic salmon are rather high, particularly in the Gulf of Bothnia, and most of the studied samples still exceeded the maximum allowable levels set by the EU. The dietary advice on Baltic salmon consumption is thus still necessary. However, the concentrations are continuously decreasing, mostly due to the inhibitory actions taken on their formation, manufacturing and use.

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