PERSISTENT ORGANIC POLLUTANTS IN SEA TROUT CAUGHT FROM FINNISH RIVERS EMPTYING INTO THE BALTIC SEA

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Abstract

Concentrations of persistent organic pollutants, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), biphenyls (PCB), polybrominated diphenylethers (PBDE), and organotin compounds (OT) were analysed in sea trout caught from seven rivers in Finland running to the Baltic Sea. Sea trout were divided into pools of small and large individuals. All the fish pools, excluding one pool from River Merikarvianjoki, had PCDD/F-PCB TEQ concentrations exceeding the maximum allowable concentration in fish (8 pg WHO-PCDD/F-PCB-TEQ/g fw) set by the European Commission of the European Community. A slight difference was seen in the WHO-PCDD/F-TEQ and WHO-PCB-TEQ concentrations between the pools of large fish and pools of small fish, attenuated by the small variation in size and age of the fish in pools. The concentrations of polybrominated diphenyl ethers as well as organotin compounds were low.

Introduction

The aim of the work was to examine the concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like and non-dioxin-like polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and organotin compounds (OTs) in sea trout (*Salmo trutta trutta*) caught in the most significant sea trout rivers in Finland. There are only few data, used for food monitoring, available from Finnish river fish and that comes from river lampreys, whose PCDD- and PCB-concentrations are high and most often exceed the EU maximum limits[1,2]. In addition to that there are few studies about the biomagnification of chlorinated by-products from pulp and paper and chlorophenol production[3,4]. Sea trout as well as salmon are assumed to contain high amounts of lipophilic environmental contaminants. In 2007, the total trout catch of professional fishermen in Finland was 68 tonnes from sea areas and 14 tonnes from lakes and rivers while that of recreational fishermen was 187 tonnes (in 2006) from sea areas and 767 tonnes from lakes and rivers[5].

Materials and methods

In 2008, seven main sea trout rivers (River Kymijoki, R. Vantaanjoki, R. Kemijoki, R. Iijoki, R. Aurajoki, R. Tornionjoki and R. Merikarvianjoki; Figure 1), were chosen as study areas. Two pooled samples were planned to be collected from each river; one from smaller and younger fish and one from larger and older fish. Each pooled sample consisted of three individual fish that were of about the same size. As an exception, fish for only one pool were caught from the rivers Aurajoki and Merikarvianjoki, and only one individual fish sample from the River Tornionjoki. Weight, length, age and gender of the fish were determined from individual samples before pooling.

Figure 1: Seven rivers from where sea trout were caught.

After homogenisation, the solid samples were freeze-dried and fat was extracted with a mixture of toluene and ethanol using an ASE (Accelerated solvent extractor, ASE 300) apparatus. The solvent was exchanged to hexane and the fat percentage was determined gravimetrically. The sample was then defatted on an acidic silica column. PCDD/Fs and PCBs were fractionated and purified on alumina and carbon columns. Analyses of 17 toxic PCDD/F congeners, 37 PCB congeners and 15 PBDE congeners were performed with HRGC/HRMS (VG70-SE250 or Autospec Ultima) using SIR with a resolution of 10,000 with DB-Dioxin and HP5-MS-columns. Internal ^{13}C–labeled standards were used to quantitate the concentration of analytes (pg/g or ng/g fw).

The OTCs analysed were monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT), triphenyltin (TPhT) and dioctyltin (DOT). OTCs were analysed from the freeze-dried sample by solvent extraction, ethylation with sodium tetraethylborate, and HRGC-HRMS analysis according to the tissue method developed by Ikonomou et al. with slight modifications[6,7]. Perdeuterated analogues of MBT, DBT, TBT, MPhT, DPhT, and TPhT were used as internal standards for the respective native 1H-compounds. Perdeuterated DPhT was used as an internal standard for DOT. The analysis was performed using an Autospec Ultima high resolution mass spectrometer operated in the selected ion monitoring mode. The column used was an HP-1 capillary column. All concentrations are reported as ng/g fw.

The Chemical Exposure Unit is an accredited testing laboratory (No T077) in Finland (current standard: EN ISO/IEC 17025). The scope of accreditation includes PCDD/Fs, non-*ortho* PCBs, PCBs, PBDEs and OT-compounds from food samples.

Results and Discussion

All fish caught from the rivers for sampling were one year old, except for the samples from the River Vantaanjoki pool of large fish and River Aurajoki, where the fish in pools were on average two years old. The weight of the individual sea trout in pools ranged from 0.9 kg (River Iijoki pool of small fish) to 6.0 kg (River Vantaanjoki pool of large fish).

Table 1: Sum concentrations of persistent organic pollutants in sea trout in seven Finnish rivers in 2008.

	Sum of PCDD/Fs (pg/g fw)[1]	**Sum of PCBs (ng/g fw)**[2]	**Sum of PBDEs (ng/g fw)** [3]	**Sum of OTCs (ng/g fw)**[4]
River Kymijoki small	27.1	123	2.0	11.2
River Kymijoki large	27.1	91	2.2	6.7
River Vantaanjoki small	11.6	98	2.0	11.8
River Vantaanjoki large	14.1	118	2.5	12.2
River Aurajoki	19.1	184	4.5	10.3
River Kemijoki small	10.7	161	2.9	11.4
River Kemijoki large	12.5	158	2.9	9.7
River Iijoki small	11.9	73	2.6	9.8
River Iijoki large	14.2	170	3.4	9.4
River Tornionjoki	14.2	164	3.3	10.1
River Merikarvianjoki	8.6	79	2.2	9.1

[1] Sum of 17 toxic 2,3,7,8-chloro substituted PCDD/F congeners; [2] Sum of 37 PCB congeners: 18, 28/31, 33, 47, 49, 51, 52, 60, 66, 74, 77, 81, 99, 101, 110, 105, 114, 118, 122, 123, 126, 128, 138, 141, 153, 156, 157, 167, 169, 179, 180, 183, 187, 189, 194, 206, 209; [3] Sum of 15 PBDE congeners: 28, 47, 66, 71, 74, 77, 85, 99, 100, 119, 138, 153, 154, 183, 209; [4] Sum of OT compounds: MBT, DBT, TBT, MPhT, DPhT, TPhT, and DOT.

The sum of PCDD/F- and PCB-TEQ concentrations was below the maximum allowable total concentration of 8 pg WHO-TEQ/g fw[1] only in the sea trout from River Merikarvianjoki (Figure 2).

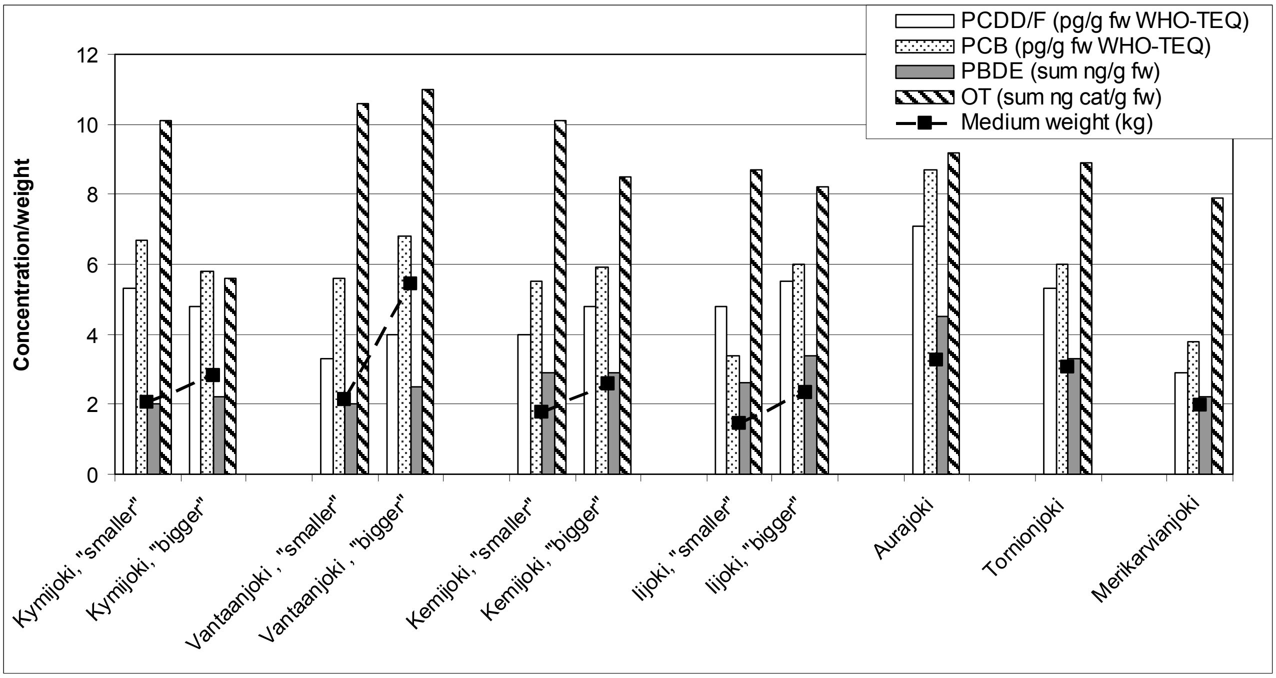

Figure 2. Concentrations of certain organic pollutants in sea trout caught from Finnish rivers

In the other sea trout the maximum allowable concentration was exceeded, the range being 8.2-15.8 pg WHOPCDD/F-PCB-TEQ/g fw. The highest TEQ and sum PBDE-concentrations were found in the fish from River Aurajoki where the sea trout caught were on average 2 years old.

An expected difference could be seen in the variations of PCDD/F- and PCB-WHO TEQ concentrations between the pools of large and small fish, but the difference was not significant because the difference in the size and age of sea trout between the large and small pools was quite modest. The only river where the PCDD/F- and PCB-WHO TEQ concentration was higher in small sea trout than in large sea trout was River Kymijoki. This might be explained by the modest difference in fish sizes between the small (median weight 2.1 kg) and large (median weight 2.8 kg) sea trout.

When comparing the sea trout TEQ results from two of the most northern rivers, River Tornionjoki and River Iijoki, it can be seen that PCDD/Fs contributed to total TEQ more than in the other rivers. This is in line with the previous study on Baltic herring in where it was observed that PCDD/F contribution to total TEQ increased when going north in the Baltic Sea[2].

The difference in PBDE concentrations between the small and large sea trout was quite small, and overall, the concentrations were quite low without any areal differences.

The dominating PCDD/F congeners found in the sea trout were as expected 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF (Figure 3). Some differences in the congener distributions between the different sampling sites were seen as the proportion of these two congeners varied in different sampling sites. The dominating PCDD/F congener was the same each time in fish pools from the same area. PCB congeners PCB138 and PCB153 were the dominating PCB congeners throughout the samples. PBDEs were dominated by congeners BDE47 followed by BDE100 and BDE99 in all the studied samples.

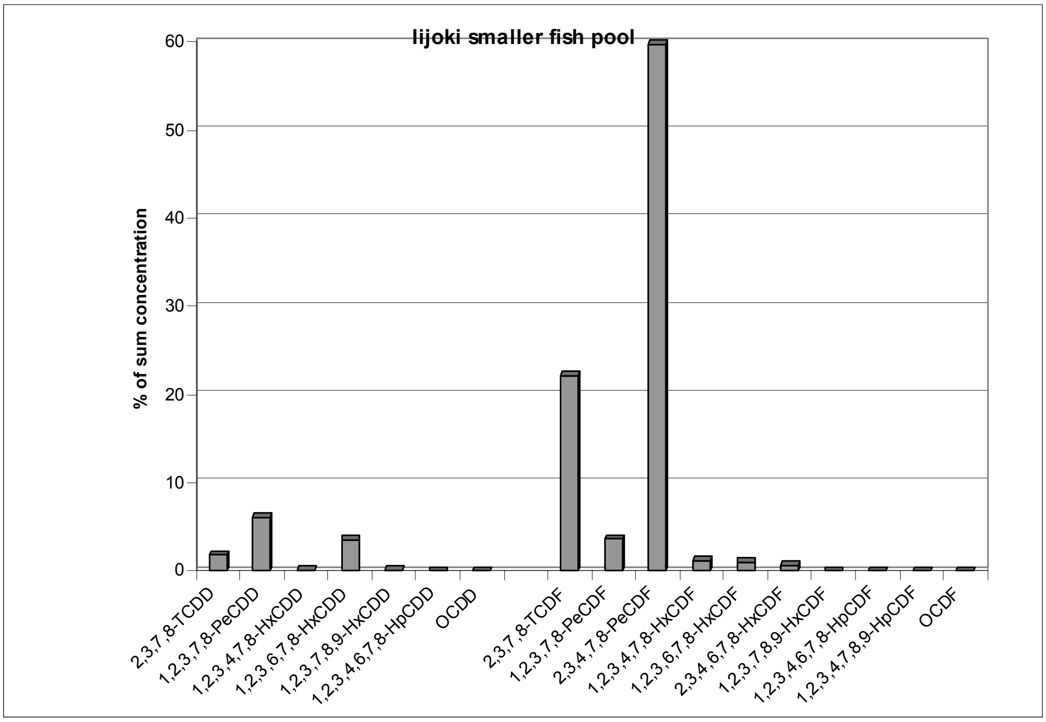

Figure 3. Typical PCDD/F congener distribution in sea trout samples.

Due to immunotoxic similarities, a group Tolerable Daily Intake (TDI) of 250 ng/kg body weight has been set by EFSA for TBT, DBT, TPhT and DOT[8]. The sum of these OTCs varied between 5.6 and 10.1 ng/g fw (upperbound concentrations). These concentrations are comparable to concentrations measured recently in uncontaminated areas of the Baltic Sea[9]. For humans, fish is the main source of OTCs[10], and with the present concentrations it can be said that the TDI value will not be exceeded by consuming sea trout.

The results have led to discussions about risk management measures for sea trout regarding dioxin and PCB concentrations. It has been decided that the consumer will be informed of this data together with dietary advice on sea trout consumption. Sea trout will be classified in the same category as Baltic salmon, which in Finland is recommended to be eaten only 1-2 times a month (100 g portions).

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