Study of dioxin and dioxin-like PCB levels in fatty fish from Sweden 2000-2002

Emma Ankarberg[1], Rickard Bjerselius[1], Marie Aune[1], Per Ola Darnerud[1], Lotta Larsson[1], Arne Andersson[1], Mats Tysklind[2], Sture Bergek[2], Katrin Lundstedt-Enkel[3], Lars Karlsson[4], Anna Törnkvist[1], Anders Glynn[1]

[1]Swedish National Food Administration, Research and Development Department, Uppsala
[2]Environmental Chemistry, Umeå University, Umeå
[3]Department of Environmental Toxicology, Uppsala University, Uppsala
[4]Institute of Freshwater Research, National Board of Fisheries, Älvkarleby

Introduction

The levels of PCDD/Fs and PCBs in fatty fish from the Baltic Sea area are still of major concern in Sweden, although the levels have decreased in Baltic Sea biota since the 1970. During later years this decrease seems to have leveled off, and at least dioxin levels in Baltic herring seem to be more or less the same during the last 10 years period. Harmonised EU maximum levels have been established for PCDD/Fs in fish and fishery products for human consumption, and the maximum level is 4 pg WHO-PCDD/F-TEQ/g fresh weight [1]. Certain fatty fish species in the Baltic Sea are shown to have levels of PCDD/Fs exceeding the maximum level. However, because of protective dietary advice, Sweden and Finland have an exemption from the Council regulation that allows national marketing of fish and fishery products that exceed the maximum level for PCDD/F. For dioxin-like PCBs, common EU maximum levels have not yet been established. However, during 2004 the Commission will review the present maximum levels for dioxins in the light of new data, with a particular aim to include dioxin-like PCBs. The Swedish National Food Administration (NFA) has undertaken a survey to analyse the concentrations of PCDD/Fs and dioxin-like PCBs in fatty fish in the Baltic Sea area. The study presents results from analyses of eel *(Anguilla anguilla)*, salmon *(Salmo salar)*, brown trout *(Salmo trutta)*, whitefish *(Coregonus lavaretus)*, herring *(Clupea harengus)*, sprat *(Sprattus sprattus)*, cod *(Gadus morhua callarias)* and vendace (roe) (from *Coregonus albula*) from several locations in the Baltic Sea.
This study reports the fifth part of the results from the analyses. The entire study is available on www.slv.se as interim reports 1-5.

Materials and Methods

The fish were caught during fall in 2000, 2001 and 2002. The sampling design was intended to cover areas in Sweden where fatty fish are caught on commercial basis as well as in areas where the public perform angling. For all fish species included in this study, analyses were carried out on muscle tissue or muscle tissue including skin (except vendace). For herring and sprat, the muscle including skin was analysed (i.e. edible part). All results presented here are from analyses of pooled samples. From all individuals equal amounts of tissue (in weight) were taken from the area around the dorsal fin. The tissue was pooled and homogenised.

17 PCDD/F congeners and the PCB congeners 28, 31, 52, 66, 74, 77, 81, 101, 105, 110, 114, 118, 126, 128, 138, 149, 153, 156, 157, 158, 167, 169, 170 and 180 were analyzeed. Only the levels of non-ortho and mono-ortho PCBs (i.e. the dioxin-like PCBs) are presented here.

PCDD/Fs and non-ortho PCBs

The PCDD/Fs and non-ortho PBCs (PCB congeners 77, 81, 126 and 169) were analysed according to a validated method at Umeå University, Sweden. In brief, the samples were homogenised with activated sodium sulphate and extracted with mixtures of actone/n-hexane and n-hexane/diethyl ether. The lipids were removed by treatment with sulphuric acid and the extract was then fractionated on a carbon column. The samples were quantified by isotope dilution technique using gas chromatography (GC) coupled with high resolution mass spectroscopy (MS).

Mono-ortho-PCBs

The analyses of and the mono-ortho PCBs (PCB congeners 105, 114, 118, 156, 157 and 167) were performed according to a validated method at NFA, Uppsala, Sweden [2, 3]. The samples were extracted with mixtures of acetone/n-hexane and n-hexane/diethyl ether. After evaporation the lipid content was gravimetrically determined and the lipids were then removed by treatment with sulphuric acid. The PCBs were separated from most of the chlorinated pesticides by fractionation on a silica gel column. Finally, the samples were quantified on a GC equipped with dual capillary columns and dual electron capture detectors (ECD).

The PCDD/DF and PCB levels are expressed in pg WHO-TEQ/g fresh weight according to the WHO TEFs for human risk assessment [4]. In calculating the WHO-TEQ values, the upper-bound level has been used for non-detects.

Results and Discussion

The Swedish maximum limit (ML) for PCBs in foodstuffs of animal origin is expressed as the concentration of the congener PCB 153 (for fish, the ML in Sweden is set to 100 µg/kg fresh weight; SLV FS 1993:36, reprint 1998:40). In this study the levels of PCB 153 were all below the ML (min = 0.7 µg/kg fresh weight in a 3.4 year old pooled cod sample from the Baltic proper and max=53.6 µg/kg fresh weight in a 12 years old pooled male herring sample from Gotland; data not shown). A correlation analysis of sum dioxin-like PCB-TEQ (expressed in pg/g fresh weight) and the dominating non-dioxin like PCB 153 (expressed in µg/kg fresh weight) reveals a relatively strong correlation coefficient of $r = 0.94$ (Spearman, $p>0.001$) with a ratio of approximately ¼.

The contribution of the dioxin-like PCBs to the total TEQ (i.e. PCBs + PCDD/Fs) is significant but shows also a large intra-species variation. The PCB-levels range between 31-86% of the total TEQ value. In brown trout, salmon, sprat and especially in eel, the contribution of PCBs to the total TEQ value exceeds 50%. In herring, the largest contribution to the total TEQ comes from the PCDD/Fs. This large contribution of PCDD/Fs to the total TEQ in herring is consistent, regardless of catching location.

For comparison, in the 16 year old silver eel caught at the Västervik location, the contribution from the dioxin-like PCBs to the total TEQ was as high as 80 % while the corresponding contribution from the 4-6 year old herring caught at Piteå archipelago only was 34 %. Despite this, the levels of dioxin-like PCBs in herring are the highest among the samples studied (10-15 pg/g fresh weight in herring from Bålsön, Västra Banken and SE of Gotland). Also, in other fatty fish analysed, the PCB TEQ levels were considerably higher (max 6-8 pg/g fresh wt.) as compared to the lean cod (one pooled sample; 0.3 pg/g fresh wt.).

The dioxin-like PCB congener 126 contributes most to the sum TEQ of dioxin-like PCBs. The contribution is on average 71 % (min 53 % and max 81 %) and the correlation is highly significantly correlated with the sum dioxin-like PCBs in the analysed fish samples ($r = 0.99$, Spearman, $p>0.001$). Thus, despite the large variation in age, catching area and species in the material, the PCB126-TEQ vs. sum PCB-TEQ ratio is highly consistent.

It is important to note that the concentration of environmental organic contaminants can vary considerably in individuals from the same location, depending on factors such as age, fat content, size, etc [5]. Earlier investigations have shown that levels of POPs in fish from a single location can vary from year to year and season to season [6]. Also, the fat content of fatty fish can vary greatly from individual to individual, within the same species, depending on what time of year they are caught. Variations may be due to the fish having spawned (lower fat levels), or to the fish having been caught during a foraging period (higher fat levels). Since the PCBs accumulate in the fish fat, a reduction of fat content will have a great impact on the TEQ levels. To avoid this, the TEQ levels in this study are expressed as pg/g fresh weight.

The results presented in this study can only be seen as representative of the sampling occasion in question.

Table 1. WHO-TEQ levels of 17 dioxins and furans and 10 dioxin-like PCB congeners (pg/g fresh weight) in fish muscle, fish muscle + skin and fish roe from 67 pooled fish samples caught along the Swedish east and south coast from fall 2000 to fall 2002. Y = yellow eel, S = silver eel. NA = Not analysed. F = female, M = male. B. trout = Brown trout.

Species (Gender)	Age[*] (years)	Mean weight (g)	Fat (%)	Location caught	No. indiv. in pool	Non-ortho PCB-TEQ	Mono-ortho PCB-TEQ	Sum PCB-TEQ	**PCDD /F-TEQ**	Tot TEQ	**% PCB of tot TEQ**
Eel Y (f)	NA	339	13.5	Baltic proper[a]	19	2.2	0.9	3.1	0.7	3.8	**82**
Eel Y (f)	NA	369	17.1	Baltic proper[b]	21	2.9	1.2	4.1	0.7	4.8	**85**
Eel Y (f)	NA	360	14.1	Baltic proper[c]	20	1.7	0.6	2.3	0.7	3	**77**
Eel Y (f)	NA	391	18.7	Baltic proper[d]	20	2.7	1.0	3.8	0.6	4.4	**86**
Eel S (f)	16 (11-22)	1088	24.0	Baltic proper[e]	20	4.4	1.8	6.2	1.5	7.7	**81**
Eel S (f)	10 (7-20)	661	19.6	Baltic proper[f]	10	2.7	0.8	3.6	1.0	4.6	**78**
B. trout (m)	3 (2-4)	3642	2.7	Bothnian Bay[g]	5	3.6	1.5	5.1	3.8	8.9	**57**
B. trout (f)	3.8 (3-6)	2890	2.9	Bothnian Bay[g]	5	4.0	1.8	5.8	4.8	10.6	**55**
B. trout (m)	2.5 (2-3)	4100	3.9	Bothnian Sea[h]	5	2.8	1.0	3.8	3.5	7.3	**52**
B. trout (f)	2.2 (2-3)	3067	4.4	Bothnian Sea[h]	5	3.5	1.3	4.8	4.6	9.4	**50**
B. trout (m)	1.3 (1-2)	3525	4.1	Bothnian Sea[i]	4	2.9	1.1	4.0	3.8	7.8	**51**
B. trout (f)	1.8 (1-3)	2950	3.3	Bothnian Sea[i]	4	2.6	1.2	3.8	3.9	7.7	**49**
B. trout (m)	2.6 (2-4)	7620	3.0	Baltic proper[j]	5	4.5	1.4	5.9	2.9	8.8	**67**
B. trout (f)	2.2 (2-3)	5880	3.3	Baltic proper[j]	5	4.3	1.3	5.6	2.6	8.2	**68**
Salmon (m)	1.2 (1-2)	3426	2.9	Bothnian Bay[g]	5	4.2	1.1	5.3	3.1	8.4	**63**
Salmon (f)	1.8 (1-2)	6462	3.4	Bothnian Bay[g]	5	5.4	2.2	7.6	7.8	15.4	**49**
Salmon (m)	1.4 (1-2)	4547	2.5	Bothnian Bay[h]	5	3.8	1.4	5.2	4.8	10	**52**
Salmon (f)	2 (2)	6039	3.3	Bothnian Bay[h]	5	4.3	1.7	6.0	5.3	11.3	**53**
Salmon (m)	1.6 (1-3)	4760	4.0	Bothnian Sea[i]	5	3.6	1.2	4.8	3.7	8.5	**56**
Salmon (f)	1.4 (1-2)	3800	3.9	Bothnian Sea[i]	5	3.6	1.2	4.8	3.9	8.7	**55**
Salmon (f)	1 (1)	3950	9.5	Baltic proper[k]	5	4.4	1.3	5.7	3.1	8.8	**65**
Salmon (m)	1 (1)	3840	11.5	Baltic proper[k]	5	4.7	1.4	6.1	3.8	9.9	**62**
Salmon (m)	2 (2)	8060	3.2	Baltic proper[j]	5	5.7	1.5	7.2	3.8	11	**65**
Salmon (f)	2.2 (2-3)	8500	2.7	Baltic proper[j]	5	6.3	1.7	8.0	3.7	11.7	**68**
Herring(mix)	1 (1)	18	5.9	Bothnian Bay[l]	7	0.5	0.4	0.8	0.9	1.7	**47**
Herring (m)	2.5 (2-3)	25	5.5	Bothnian Bay[l]	14	0.7	0.3	1.0	1.4	2.4	**42**
Herring (f)	2.5 (2-3)	24	5.0	Bothnian Bay[l]	14	0.6	0.2	0.8	1.1	1.9	**42**
Herring(mix)	5 (4-6)	32	4.6	Bothnian Bay[l]	6	1.4	0.6	2.0	3.8	5.8	**34**
Herring (m)	2.5 (2-3)	27	4.5	Bothnian Sea[m]	15	0.9	0.4	1.3	2.5	3.8	**34**
Herring (f)	2.5 (2-3)	25	4.7	Bothnian Sea[m]	15	0.7	0.3	1.0	2.0	3	**33**
Herring (m)	4.5 (4-5)	33	5.7	Bothnian Sea[m]	10	1.2	0.5	1.7	3.8	5.5	**31**
Herring (f)	4.5 (4-5)	35	3.7	Bothnian Sea[m]	10	1.0	0.5	1.5	3.5	5	**30**
Herring (m)	5 (4-6)	55	10.9	Bothnian Sea[n]	9	3.5	1.6	5.1	10.1	15.2	**34**
Herring (f)	5 (4-6)	62	11.1	Bothnian Sea[n]	9	4.6	1.5	6.2	10.4	16.6	**37**
Herring (m)	8 (7-9)	98	15.5	Bothnian Sea[n]	6	6.9	3.2	10.0	19.7	29.7	**34**
Herring (f)	8 (7-9)	98	14.3	Bothnian Sea[n]	6	7.5	2.4	9.9	17.2	27.1	**37**
Herring (m)	5.5 (5-6)	92	14.2	Bothnian Sea[o]	10	7.1	3.5	10.5	20.9	31.4	**33**
Herring (f)	5.5 (5-6)	86	10.9	Bothnian Sea[o]	8	5.8	2.5	8.3	18.9	27.2	**31**
Herring (m)	8 (7-9)	93	13.3	Bothnian Sea[o]	9	6.9	3.6	10.5	22.9	33.4	**31**
Herring (f)	8 (7-9)	87	11.5	Bothnian Sea[o]	9	5.1	2.3	7.5	16.8	24.3	**31**
Herring (m)	5 (4-6)	40	9.0	Baltic proper[p]	9	3.5	1.3	4.8	6.8	11.6	**41**
Herring (f)	5 (4-6)	40	7.8	Baltic proper[p]	9	2.8	0.8	3.6	4.6	8.2	**44**
Herring (m)	7.9 (7-9)	114	11.0	Baltic proper[p]	8	4.7	1.4	6.1	6.7	12.8	**48**
Herring (f)	7.8 (7-9)	86	9.6	Baltic proper[p]	6	3.3	0.9	4.2	5.3	9.5	**44**
Herring (m)	5 (4-6)	32	7.3	Baltic proper[q]	9	2.8	0.6	3.4	4.7	8.1	**42**
Herring (f)	5 (4-6)	33	8.0	Baltic proper[q]	9	2.7	0.8	3.4	4.5	7.9	**43**
Herring (m)	7.9 (7-9)	111	13.3	Baltic proper[q]	8	5.6	1.9	7.5	9.9	17.4	**43**
Herring (f)	8 (7-9)	119	15.4	Baltic proper[q]	8	6.0	1.9	7.8	10.3	18.1	**43**
Herring (m)	12 (12-13)	234	11.5	Baltic proper[q]	4	9.7	4.5	14.2	10.8	25	**57**
Herring (f)	12 (12-13)	175	11.1	Baltic proper[q]	4	4.6	2.1	6.7	7.2	13.9	**48**
Herring (m)	5 (4-6)	41	3.8	Baltic proper[r]	9	1.0	0.4	1.4	1.7	3.1	**45**
Herring (f)	5 (4-6)	41	5.3	Baltic proper[r]	9	1.3	0.4	1.7	1.9	3.6	**47**
Herring (m)	7.3 (7-9)	89	6.5	Baltic proper[r]	6	1.8	0.6	2.3	2.9	5.2	**44**
Herring (f)	7.6 (7-9)	98	5.8	Baltic proper[r]	5	1.7	0.5	2.1	2.6	4.7	**45**
Herring (m)	3.5 (3-4)	103	11.2	W Bornholm	10	1.7	0.5	2.3	2.0	4.3	**53**
Herring (f)	3.5 (3-4)	88	9.5	W Bornholm	10	1.7	0.5	2.3	1.9	4.2	**55**
Sprat (mix)	4.9 (4-7)	21	7.1	W Bornholm	14	3.2	0.7	3.9	2.7	6.6	**59**

Species (Gender)	Age* (years)	Mean weight (g)	Fat (%)	Location caught	No. indiv. in pool	Non-ortho PCB-TEQ	Mono-ortho PCB-TEQ	Sum PCB-TEQ	**PCDD /F-TEQ**	Tot TEQ	**% PCB of tot TEQ**
Sprat (mix)	2.5 (2-3)	18	10.6	W Bornholm	16	3.2	0.7	3.8	2.4	6.2	**61**
Sprat (mix)	5 (2-8)	9	9.1	Baltic proper[s]	22	3.2	0.7	3.9	3.6	7.5	**52**
Whitefish(m)	5.2 (4-6)	409	1.4	Bothnian Bay[g]	5	0.4	0.2	0.7	0.7	1.4	**50**
Whitefish (f)	4.6 (4-7)	509	1.7	Bothnian Bay[g]	5	0.8	0.4	1.2	1.1	2.3	**52**
Whitefish(m)	4.3 (3-5)	290	1.0	Bothnian Sea[h]	10	1.0	0.5	1.5	1.7	3.2	**47**
Whitefish (f)	4.9 (3-6)	379	1.2	Bothnian Sea[h]	7	1.0	0.5	1.5	1.9	3.4	**44**
Whitefish(m)	4.3 (3-6)	314	1.2	Bothnian Sea[t]	7	0.5	0.2	0.7	1.0	1.7	**41**
Whitefish (f)	4.3 (3-6)	358	1.2	Bothnian Sea[t]	10	0.5	0.2	0.7	0.8	1.5	**47**
Vendace roe	NA	22	12.2	Bothnian Bay[u]	74	1.1	0.3	1.4	2.2	3.6	**39**
Cod (mix)	3.4 (3-5)	1224	0.6	Baltic proper	11	0.2	0.1	0.3	0.2	0.5	**60**

[a] Kvädöfjärden, [b] Marsö, [c] Sturkö, [d] Valjeviken, [e] Västervik, [f] Karlshamn, [g] R. Lule älv, [h] R. Ångermanälven, [i] R. Dalälven, [j] R. Mörrumsån, [k] N. of Gotland, [l] Piteå archipelago, [m] Ångermanälven, [n] Bålsön, [o] Västra Banken, [p] Landsort, [q] SE Gotland, [r] Utlängan, [s] E Gotland, [t] Öregrundsgrepen, [u] Luleå archipelago.
*For Brown trout and Salmon, age represents the number of years in the sea (after two-three years in the river)

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