INVESTIGATION OF PCDDS, PCDFS AND SELECTED COPLANAR PCBS IN SCOTTISH FARMED ATLANTIC SALMON (*Salmo salar*)

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Introduction

Persistent organochlorine pollutants (POPs) have low solubilities in water and bioaccumulate in the food chain. POPs accumulate in the lipid compartment of the animal and within the aquatic food chain fatty fish may be contaminated with appreciable amounts of chlorinated hydrocarbons. Existing data on the levels of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs) consumed in the UK have been mainly derived from total diet surveys[1,2] and surveillance data for specific food types.[3] These data indicate organochlorine contamination of fish designated for human consumption, with mean concentrations of 25 pg/g lipid adjusted WHO-TEQ[4] for PCDD/Fs and PCBs in 12 UK salmon samples (sampled in 1995/6).[3, 5] The results from this investigation of PCDD/Fs and PCBs in farmed Scottish Salmon are in good agreement with recent reports, suggesting further PCDD/F and PCB investigations of farmed salmon and salmon feed, including feed fortified with fish oil and feed fortified with selected vegetable oils, are warranted.

Materials and Methods

Sites and sampling: Ten British salmon (*Salmo salar)* samples that enter the European fish market were analyzed for seventeen PCDD/Fs and seven non-*ortho* and mono-*ortho* PCBs. The samples were of variable age, both farm raised and wild, and were obtained from seven different Scottish sites, including retail suppliers, producers and Stirling University in Scotland, during January 1999. Random sampling was not possible, but unbiased representation of the situation of interest was achieved, by obtaining fish from the Northwest Scottish Highlands, the Western Scottish Highlands, the lowlands surrounding Stirling plus two wild fish from the Scottish border with England, and a Norwegian sample for which no information is available. The 'wild' fish may not have been genuinely wild, but were probably farm escapees. The fresh and frozen samples were wrapped in polyethylene bags and frozen immediately at -20^0C. Whole body weights of the fish ranged from 400g to 5.2kg, the fish ranged in age from 1 year to 3+ years. Table 1 gives sample details for the salmon.

Sample preparation: The samples were thawed, filleted, skinned and the epaxial muscle homogenized before being subdivided into smaller replicate portions of approximately 100 grams. The portions were weighed, stored in tightly sealed polythene bags and frozen at -20^0C. Two samples (Samples 213-11; 213-12) consisted of homogenized samples of two fish (from the same source and of the same age and size) to ensure similar sample quantities of tissue. The samples were packed in dry ice and transported directly to the US EPA/OPP laboratory the following day, where they were logged-in and stored at -60^0C prior to analysis. The samples were analysed for the seventeen PCDD/Fs which have toxic equivalency to 2,3,7,8-TCDD and the dioxin like coplanar PCBs 77, 105, 118, 126, 156, 157, and 169. All analyses were performed on a Kratos Concept high-resolution mass spectrometer using isotope dilution. The procedures used to analyze

the salmon samples were similar to those used to analyze for these compounds in beef fat as defined in U.S. EPA's Method 1613 and described by Ferrario et al.[6-8]

Results

The results were transcribed to an Excel spreadsheet for additional processing to derive Toxic Equivalent Factor contributions (TEF) values for each sample. All values were adjusted to the lipid content of the sample by dividing the whole weight concentration by the percent lipid in each sample. The percent lipid was determined according to Method 1613. The rounded result for each congener was multiplied by the appropriate International toxic equivalent factor (I-TEF)[9]and summed Toxic Equivalent contributions (TEQ) for all seventeen congeners and the non-*ortho* and mono-*ortho* PCBs. In cases where congeners were reported as non detects, lower bound TEQs were calculated by treating the result as if zero and upper bound TEQs by treating the result as if present at half of the limit of detection (LOD). Quality control (QC) samples were included in batches of samples analysed. Data were rounded to three decimal places for all analytes and are reported on a lipid adjusted basis (lwt) in Table 1 together with summaries of the TEQ results, and details of weight, age and lipid content for each sample analyzed.

The concentration of lipid found in the samples ranged from 3.43% to 14.7%. The immature (smolt) fish are fed lower levels of oils, and tend to store lower levels of lipid in the flesh compared to mature fish and this is reflected in the lipid content of the samples,- with one unusual exception (Sample 213-10). Whether this fish had a similar dietary lipid intake to the other fish sampled is not known, but it has been observed that there can be marked variation in flesh lipid content within fish fed the same dietary oil level such that certain individual fish utilize high-energy diets but deposit little lipid in their flesh while others tend toward greater adiposity.[10]

All fish contained detectable levels of certain PCDD/Fs. Levels varied between samples, generally increasing with age, and showing a skewed distribution for the PCDD/Fs resulting from a minority of relatively high values. The main dioxins and furans detected were 2,3,7,8 TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF and to a lesser extent 1,2,3,7,8-PeCDF. Apart from one fish (Sample 213-10) which had been frozen a year previously, the highest levels of PCDD/Fs and PCBs were observed in the oldest fish, 3 years + as expected.

The 2,3,7,8 TCDD concentrations ranged from 0.51 pg/g lwt in the post smolt fish, around a year old, (Sample 213-12) to 1.09 pg/g lwt in the most mature fish, over 3 years of age, (Sample 213-05), and 1.39 pg/g lwt in a supermarket sourced fish (Sample 213-10). This is equivalent to 0.03 pg/g wwt in the post smolt to 0.15 pg/g wwt in the most mature fish, and 0.05pg/g wwt in the same supermarket fish. The latter fish had the lowest lipid content of all the samples including the post smolts. The 1,2,3,7,8-PeCDD concentrations ranged from 0.8 pg/g lwt to 4.16 pg/g lwt.

All the selected coplanar PCBs were detected, and they were quantitatively the dominant contaminants. The consistent congener patterns were markedly higher than one would expect from the range of sources of the samples, unless they were fed on similarly sourced feeds. The highest PCB concentration detected in all samples was PCB 118 ranging from 31900 pg/g lwt (1093 pg/g wwt: Sample 213-10) to 14800 pg/g lwt (1380 pg/g wwt: Sample 213-07). The highest total lipid adjusted PCB concentration was 45100 pg/g (Sample 213-10), but the lipid adjusted TEQ contribution for this fish was 24.0 pg/g, lower than the lipid adjusted TEQ contribution for one of the largest fish (Sample 213-05) at 24.8 pg/g. On a wet weight basis the largest fish PCB TEQ remained high at 3.40 pg/g, but was reduced for Sample 213-10 to 0.82 pg/g due to the lower lipid content in the fish tissue. The summed concentration of selected PCBs is the sum of concentrations of the congeners measured and is an underestimate of the total PCB concentration as other isomers were present which were not measured. The data was disaggregated by both age and whether the fish was farmed or wild and while significant age related differences were observed between the 2 year old + fish and 1 year olds, there was no statistically significant difference between the farmed and wild fish (or farm escapees).

Discussion

The results from this study are in good agreement and of a similar order of magnitude to the values for Salmon reported in the recent MAFF study with surprisingly high detections of PCB congeners.[5] Previous reports have detected significant levels of PCDD/Fs and PCBs in fatty fish such as herring and salmon.[11-14] The potential contribution to the human diet of PCBs and PCDD/Fs from farmed Scottish salmon will vary according to the age of the fish, whether the individual fish had a predisposition to adiposity, or not, the frequency of consumption, portion size, cooking practices and the age of the consumer. The possible contribution to dietary intakes of organochlorines from farmed Salmon could be significant for high consumers, but national extrapolations cannot be made on the basis of this study due to the relatively small sample size.

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References

1. MAFF (1995). Food Safety Information Sheet. 71, MAFF, London. UK.
2. MAFF (1996). Food Surveillance Information Sheet. 89, MAFF, London. UK.
3. MAFF (1999). Food Safety Information Sheet. 184, MAFF, London. UK.
4. Kutz, F.W., Barnes, D.G., Bottimore, D.P., Greim, H., & Bretthauer, E. W. (1990) Chemosphere. 20, 751-757
5. Parsley, K., Wright, C & Thorpe, S. (1999) Report FD 97/66 MAFF, London.
6. Ferrario, J., Byrne, C., McDaniel, D., Dupuy, A., Harless, R. (1996) Analytical Chemistry 68, 647-652.
7. Ferrario, J., Byrne, C., Dupuy, A. (1997) Chemosphere, 34, 2351-2466
8. Ferrario, J., Byrne, C., Dupuy, A. , Winters, D.L., Lorber, M. & Anderson, S. (1998) Organohalogen Compounds, 35, 29-32
9. Van den Berg, M., Birnbaum, l., Bosveld, A.T.C., Brünstrom, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S. W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X., Liem, A.K.D., Nolte, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillit, D., Tysklind, M., Younes, M., Wærn, F., Zacharewski, T. (1998). Env. Health. Persp. 106, 775-792
10. Bell, J. G., McEvoy, J., Webster, J. L., McGhee, F., Millar, R. M., & Sargent, J. R. (1998) J. Agric. Food. Chem 46, 119-127
11. Vuorinen, P.J., Vartiainen, T., & Keinänen, M. (1997) In 7th Nordic symposium on organic pollutants. (Vartiainen, Terttu, & Komulainen, Hannu Eds.), Kuopio University Publications C. Natural and Environmental Sciences 68.
12. Becher, G., Jensen, A.J., Zubchenko, A., Haug, L.S., Hvidsen, N.A., Johnsen, B.O., & Kashin, E. (1998) Organohalogen Compounds 39, 427-430
13. Atuma, S.S., Aune, M., Bergh, A., Wicklund-Glynn, A., Darnelund, P.O., Larsson, L., Olsson, M., and Sandström, O. (1998). Organohalogen Compounds, 39, 153-156
14. Bergqvist, P-A., Hjelt, M., & Rappe, C. (1990) In Water Pollution research report 24: Transport of organic micropollutants in estuaries, marine and brackish waters. Proc. of a workshop "Organic Micropollutants in the Aquatic environment" (Wahlberg, C., Minderhovd, A., & Angeletti, G. Eds.) Commission of the European Communities, Directorate-General for Science, Research and Development, Brussels.

Table 1 : PCDDs, PCDFs and selected coplanar PCBs in Scottish Atlantic Salmon: Lipid Adjusted (pg/g, ppt)

Samples	TEF[9]	213-02	213-04	213-05	213-06	213-07	213-08	213-09	213-10	213-11	213-12
Source		L.Tain (f)	L.Tain (f)	L.Tain (f)	R.Allen (w)	L.Leven (f)	Norway	R.Devon (w)	Retail (f)	S. L.A (f)	S L.B (f)
Approx age of fish		3+ yrs	3+ yrs	3+ yrs	2 yrs	2+ yrs	2+ yrs	2 yrs	2 yrs	1 yr	1 yr
% lipid		12.13	14.7	13.69	7.71	9.3	13.73	12.14	3.43	4.04	5.39
Sample Wt (g)		99.8	99.7	100	100.8	102.1	100.9	100.1	100.9	99	100.9
Whole weight WWt(g)		59.88	49.85	50	98.78	81.68	50.45	60.06	98.88	97.02	98.88
Lipid adjusted LWt(g)		7.26	7.33	6.84	7.62	7.6	6.93	7.29	3.39	3.92	5.33
Congener											
2,3,7,8-TCDD	1	0.68	0.64	1.09	0.61	0.53	0.63	0.87	1.39	0.61	0.51
1,2,3,7,8-PeCDD	1	1.27	1.32	2.06	1.06	1	1.28	1.42	4.16	1.2	0.8
1,2,3,4,7,8-HxCDD	0.1	-0.17	-0.17	-0.18	-0.16	-0.16	0.17	-0.17	0.85	-0.32	-0.23
1,2,3,6,7,8-HxCDD	0.1	0.26	0.28	0.43	-0.16	-0.16	0.3	0.22	1.39	-0.32	-0.23
1,2,3,7,8,9-HxCDD	0.1	-0.17	-0.17	-0.18	-0.16	-0.16	-0.18	-0.17	-0.37	-0.32	-0.23
1,2,3,4,6,7,8-HpCDD	0.01	-0.17	-0.17	-0.18	-0.16	-0.16	-0.18	-0.17	-0.37	-0.32	-0.23
OCDD	0.0001	0.69	0.68	0.73	0.66	0.66	0.72	0.69	1.47	1.28	0.94
2,3,7,8-TCDF	0.1	17.85	15.39	27.42	11.87	12.57	15.95	18.02	48.52	15.15	12.92
1,2,3,7,8-PeCDF	0.05	1.52	1.18	2.69	0.88	1.04	1.4	1.65	5.65	1.34	0.99
2,3,4,7,8-PeCDF	0.5	5.8	4.37	10.63	3.97	4.22	5.02	6.51	13.95	4	3.75
1,2,3,4,7,8-HxCDF	0.1	-0.17	-0.17	0.18	-0.16	-0.16	-0.18	-0.17	0.68	-0.32	-0.23
1,2,3,6,7,8-HxCDF	0.1	-0.17	-0.17	0.16	-0.16	-0.16	-0.18	0.13	0.78	-0.32	-0.23
2,3,4,6,7,8-HxCDF	0.1	0.16	0.19	0.29	-0.16	0.12	0.25	0.19	1	0.24	-0.23
1,2,3,7,8,9-HxCDF	0.1	-0.17	-0.17	-0.18	-0.16	-0.16	-0.18	-0.17	-0.37	-0.32	-0.23
1,2,3,4,6,7,8-HpCDF	0.01	-0.17	-0.17	-0.18	-0.16	-0.16	-0.18	-0.17	-0.37	-0.32	-0.23
1,2,3,4,7,8,9-HpCDF	0.01	-0.17	-0.17	-0.18	-0.16	-0.16	-0.18	-0.17	-0.37	-0.32	-0.23
OCDF	0.0001	0.69	0.68	0.73	0.66	0.66	0.72	0.69	1.47	1.28	0.94
Upper-bound TEQ	**Fat (0.5 LOD)**	6.83	6.06	11.51	5.01	5.06	6.23	7.56	18.21	5.62	4.7
Lower-bound TEQ	**Fat (0 LOD)**	6.75	5.97	11.45	4.89	4.96	6.16	7.48	18.13	5.42	4.53
PCB 77	0.0001	190	288	536	528	235	280	243	622	360	601
105	0.0001	5970	6360	7220	6960	4040	5660	6230	9240	469	5090
118	0.0001	21400	22400	23000	24200	14800	17100	25100	31900	16400	17200
126	0.1	108	130	203	126	64.7	140	113	183	81.2	84.1
156	0.0005	1890	2530	2260	2180	1030	1950	2330	2440	129	1350
157	0.0005	535	679	657	599	337	444	677	690	359	398
169	0.01	22.3	20.8	28.5	16.7	15.2	20.9	24.4	30.1	15.1	12.4
TEQ of 7 PCBs		14.67	17.36	24.82	17.02	9.05	17.63	15.88	23.99	11.06	11.49

Non Detects and Limit of detection (LOD) indicated by minus sign, Values underlined indicate that the values are not within the ion ratio range for QA/QC

L= loch; R= river; SLA= Stirling Loch A; SLB= Stirling Loch B; (w)=wild; (f)= farmed