

NON-DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN FARMED AND WILD FISH

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Introduction

There is currently renewed interest in non-dioxin-like (NDL) polychlorinated biphenyls (PCBs) following the recent review of their toxicity by the European Food Safety Authority (EFSA) and proposals by the European Commission to set limits for them in food¹.

Previous surveys in the United Kingdom (UK) by the former Ministry of Agriculture, Fisheries and Food confirmed that NDL PCBs are present in freshwater and marine fish, but the main interest at the time was in the dioxins and dioxin-like PCBs in those samples^{2,3}. The UK government received a large number of enquiries from those people who eat large amounts of fish and were concerned about the presence of PCBs and other contaminants, and there was special interest in any distinction between farmed and wild salmon. The previous survey was not designed to distinguish the types of salmon.

Methods and materials

Samples

In the current survey, 28-60 samples of each of a number of fish and shellfish species and some fish products, purchased in 2003-2004, were processed into single composite samples for each species or product. In the case of Atlantic salmon (*Salmo salar*), sea bass (*Dicentrarchus labrax*), UK turbot (*Psetta maxima*) and halibut (*Hippoglossus hippoglossus*), separate composites comprising farmed and wild fish were prepared. In addition, composite samples of farmed fresh water eels (*Anguilla spp*), gilthead sea bream (*Sparus aurata*) and sea trout (*Salmo trutta*), and wild Alaskan salmon (*Oncorhynchus spp*), were prepared. In the case of farmed and wild Atlantic salmon, herring (*Clupea harengus*), mackerel (*Scomber scombrus*) and farmed trout (*Oncorhynchus mykiss*), the composites comprised 30 samples, and the remaining samples of these species, plus four of organic salmon and six of organic trout, were analysed individually. Further details of the sampling are given elsewhere⁴.

Analysis

All the samples were analysed by the Central Science Laboratory. This laboratory has taken part in a number of inter-laboratory trials, including several rounds of "Dioxins in Food" and FAPAS. ¹³C₁₂ labelled ortho-substituted PCBs (IUPAC numbers 28, 52, 101, 118, 138, 153, 180 and 194) were added as internal standards. NDL PCBs were analysed using gas-chromatography low-resolution mass spectrometry⁵. A total of 40 NDL PCB congeners (PCBs 18, 28, 31, 33, 41, 44, 47, 49, 51, 52, 56/60, 61/74, 66, 87, 99, 101, 110, 128, 129, 138, 141, 149, 151, 153, 170, 180, 183, 185, 187, 191, 193, 194, 201, 202, 203, 206, 208 and 209) were targeted.

Results and discussion

For the fish species detailed above, Table 1 shows the results for selected NDL PCB congeners analysed in the composites and the ranges and weighted means in the samples analysed individually. The weighted means take account of the concentrations in both the composites and individual samples, allowing for the numbers of fish comprising the composites. Concentrations of the remaining congeners were lower and sometimes below the

Table 1: Concentrations of non-dioxin-like PCBs ($\mu\text{g}/\text{kg}$) in composite and individual samples

Congener		Concentrations (microgram/kg fresh weight)							
Fish Species (No in composite) [No of samples]:	Farmed salmon (30)	Farmed salmon [30]		Wild salmon (30)	Wild salmon [30]		Farmed Trout (30)	Farmed Trout [28]	
	Comp- osite	Range	Weighted Mean	Comp- osite	Range	Weighted Mean	Comp- osite	Range	Weighted Mean
PCB28	0.5	0.2-0.7	0.5	0.3	0.03-0.8	0.3	0.2	0.1-0.4	0.2
PCB52	1.5	0.8-2.1	1.4	1.0	0.08-2.4	0.9	0.7	0.4-1.1	0.7
PCB66	1.1	0.5-1.5	1.1	0.7	0.06-2.2	0.7	0.5	0.3-0.9	0.5
PCB99	1.5	0.8-2.1	1.5	0.9	0.09-2.3	0.8	0.6	0.3-1.0	0.6
PCB101	2.5	1.4-3.9	2.5	1.7	0.2-4.0	1.6	1.0	0.6-1.7	1.0
PCB110	1.9	0.8-3.7	2.0	0.9	0.08-3.6	0.8	0.6	0.5-1.7	0.8
PCB138	5.5	2.5-7.3	5.1	3.0	0.2-7.3	2.7	1.9	1.0-3.5	1.9
PCB149	3.1	1.1-3.8	2.7	1.6	0.1-3.9	1.4	1.1	0.5-1.6	1.0
PCB151	1.0	0.4-1.1	0.9	0.5	0.04-1.2	0.5	0.4	0.2-0.4	0.4
PCB153	5.7	2.6-7.6	5.3	3.2	0.2-7.7	2.9	1.9	1.0-3.6	2.0
PCB170	0.7	0.3-1.2	0.7	0.4	0.01-1.1	0.4	0.3	0.1-0.9	0.3
PCB180	1.4	0.7-2.1	1.4	0.9	0.03-2.1	0.8	0.5	0.3-1.1	0.5
PCB183	0.5	0.2-0.7	0.4	0.3	0.02-0.6	0.3	0.2	0.09-0.3	0.2
PCB187	1.9	0.7-2.5	1.7	1.1	0.05-2.3	1.0	0.7	0.3-1.1	0.7
Σ PCBs 28, 52, 101, 138, 153 and 180	17	8.3-24	16	10	0.6-24	9.1	6.2	3.4-11	6.4
Σ 40 PCBs	37	18-48	35	21	2.0-53	20	14	7.2-23	14
Congener		Concentrations (microgram/kg fresh weight)							
Fish Species (No in composite) [No of samples]:	Herring (30)	Herring [30]		Mackere 1 (30)	Mackere 1 [30]		Organic salmon [4]	Organic trout [6]	
	Comp- osite	Range	Weighted Mean	Comp- osite	Range	Weighted Mean	Range	Range	
PCB28	0.6	0.2-1.1	0.5	0.2	0.1-2.5	0.3	0.3-0.5	0.2-0.3	
PCB52	1.5	0.5-3.6	1.3	0.9	0.3-11	0.9	0.8-1.6	0.5-0.7	
PCB66	1.3	0.4-4.4	1.2	0.6	0.2-14	0.9	0.7-1.6	0.3-0.6	
PCB99	1.8	0.6-5.5	1.6	1.3	0.2-28	1.5	0.9-1.5	0.4-0.6	
PCB101	2.9	1.2-9.1	2.9	2.2	0.2-44	2.4	1.6-2.7	0.8-1.1	
PCB110	3.9	1.1-12	3.6	1.4	0.3-25	1.6	0.9-1.4	0.5-0.6	
PCB138	6.9	2.3-20	6.7	4.5	0.8-95	5.5	3.5-4.9	1.4-2.0	
PCB149	3.9	1.1-9.9	3.6	2.7	0.5-57	3.4	1.8-2.4	0.6-1.0	
PCB151	1.0	0.3-2.3	1.0	0.7	0.2-16	0.9	0.5-0.9	0.2-0.3	
PCB153	6.7	2.1-21	6.6	4.9	0.8-105	6.0	3.7-5.2	1.5-2.1	
PCB170	0.9	0.2-2.7	0.8	0.6	0.1-11	0.8	0.6-0.7	0.2-0.4	
PCB180	1.6	0.4-5.4	1.5	1.2	0.2-17	1.3	1.1-1.4	0.4-0.6	
PCB183	0.5	0.07-1.9	0.5	0.4	0.03-7.1	0.5	0.2-0.5	0.1-0.2	
PCB187	2.2	0.4-7.2	2.1	1.9	0.3-41	2.4	1-1.8	0.4-0.7	
Σ PCBs 28, 52, 101, 138, 153 and 180	20	7.6-60	19	14	2.8-275	16	11-16	4.7-6.6	
Σ 40 PCBs	43	15-128	41	28	6.4-548	20	23-35	4.7-6.6	

Table 2: Concentrations of non-dioxin-like PCBs ($\mu\text{g}/\text{kg}$) in composite samples of other species

Fish Species (No in composite)	Farmed sea bass (60)	Wild sea bass (60)	Farmed halibut (60)	Wild halibut (60)	Farmed turbot (60)	Wild turbot (60)	Farmed bream (60)	Farmed eels (60)	Farmed sea trout (60)	Alaskan salmon wild (60)
	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site	Compo- site
PCB28	0.2	0.4	0.3	0.1	0.1	0.1	0.2	0.2	0.3	0.08
PCB52	0.6	1.1	0.9	0.4	0.4	0.4	0.6	0.4	0.8	0.2
PCB66	0.4	1.3	0.7	0.3	0.3	0.3	0.5	0.4	0.6	0.1
PCB99	0.8	2.4	1.1	0.7	0.6	0.8	0.8	0.7	0.8	0.2
PCB101	1.3	3.2	1.7	0.9	0.9	1.1	1.0	0.8	1.4	0.3
PCB110	0.9	2.1	1.4	0.4	0.6	0.7	0.8	0.9	1.0	0.2
PCB138	2.7	8.2	4.1	2.2	2.2	3.1	2.8	2.8	2.9	0.4
PCB149	1.5	3.2	1.8	0.6	1.1	1.3	1.3	1.1	1.7	0.3
PCB151	0.5	1.1	0.7	0.3	0.3	0.4	0.4	0.3	0.5	0.09
PCB153	2.8	9.6	4.3	2.7	2.5	3.7	2.9	2.7	2.9	0.5
PCB170	0.4	1.3	0.6	0.4	0.3	0.5	0.4	0.5	0.4	0.05
PCB180	0.7	2.7	1.1	1.0	0.7	1.0	0.8	1.0	0.7	0.1
PCB183	0.3	1.0	0.4	0.2	0.3	0.3	0.3	0.4	0.2	0.05
PCB187	0.9	3.7	1.3	0.6	0.9	1.2	0.9	1.2	0.9	0.2
Σ PCBs 28, 52, 101, 138, 153 and 180	8.3	25	12	7.3	6.7	9.5	8.2	7.9	9.0	1.6
Σ 40 PCBs	17	49	25	13	14	18	17	17	19	3.6

limit of determination. Also presented are the sum of the 'ICES 6' indicator PCBs (the original 'ICES 7' congeners excluding PCB-118, which is dioxin-like) and the sum of all 40 congeners. All of the results for these and the remaining samples can be found in the analytical report for the survey⁶. Values for means, $\Sigma 6$ and $\Sigma 40$ are *upper bound* figures.

Nearly all of the congeners analysed were present at concentrations above the limit of determination in all the samples reported in this paper. For those species where some individual samples were analysed, comparison of the concentrations in the composites with those of the weighted means indicates that the values were usually fairly similar. However, in the case of mackerel there was one sample in which the concentrations of all the NDL PCBs were very high (around seven times those in the sample with the next highest concentrations). This sample also contained very high levels of dioxins and dioxin-like PCBs. The concentrations of most of the congeners in the mackerel composite are notably lower than the means of the values in the individual samples (data not shown). This suggests that none of the fish contributing to the composite contained such high concentrations. Levels in the organic salmon and trout samples were similar to those in the conventionally farmed samples.

In most of the samples, the most abundant congener was PCB 153, followed usually by PCBs 138 and 101. The six indicator PCBs (PCBs 28, 52, 101, 138, 153 and 180) together accounted for 39-51% of the sum of the 40 congeners analysed. Except for the outlying mackerel sample mentioned above, the concentrations are all well within the maximum limit of 75 $\mu\text{g}/\text{kg}$ being proposed by the European Commission for these congeners in fish and fishery products. Since the concentrations of dioxins and dioxins plus dioxin-like PCBs in this single mackerel sample⁷ already exceeded relevant limits, whilst none of the concentrations in any of the other samples analysed did so, the proposed limits for NDL PCBs would not have provided any additional protection.

Of the non-indicator congeners, PCB 149 was generally the most abundant and PCBs 99, 110 and 187, and sometimes PCB 170, were also significant, often being more abundant than PCBs 28 or 52. In combination,

PCBs 99, 110, 149 and 187 constituted 17-28% of the sum of the concentrations of the 40 congeners present. This suggests that, if non-dioxin-like PCBs regulation is to be meaningful, account should perhaps be taken of these congeners as well as of the ICES 6 congeners. Concentrations of other NDL PCBs, especially the more highly chlorinated congeners, were lower.

In the case of Atlantic salmon, the values for the sums of the ICES 6 congeners and of all 40 congeners analysed were both significantly higher in farmed than in wild fish ($\tau=0.05$). Concentrations of PCBs in farmed halibut were higher than in the wild fish whereas, in the case of sea bass and UK turbot, the higher concentrations were reported in the wild fish. These follow the same pattern as seen for dioxins and dioxin-like PCBs. Herring and mackerel, which are wild, contained the high reported levels of NDL-PCBs. The highest reported levels of Σ 40 NDL PCBs were composites samples of other wild fish species included in the same survey – sardines/pilchards (*Sardina pilchardus*) [47 $\mu\text{g}/\text{kg}$ fresh weight] and dogfish (*Squalus spp*) [39 $\mu\text{g}/\text{kg}$ fresh weight]. In general it is therefore unwise to draw any significant inference regarding the relative concentrations in farmed and wild fish.

There is currently no Tolerable Daily Intake for non-dioxin-like PCBs. The Food Standards Agency's current advice on fish consumption was formulated to balance the nutritional benefits against the risks from the presence of dioxins and dioxin-like PCBs, brominated flame retardants and heavy metals⁸. No modification to the advice was considered necessary on the basis of the NDL PCB contents.

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1. European Food Safety Authority *Opinion of the Scientific Panel on contaminants in the food chain [CONTAM] related to the presence of non dioxin-like polychlorinated biphenyls (PCB) in feed and food* 2005; EFSA-Q-2003-114, available at www.efsa.europa.eu/EFSA/efsa_locale-1178620753812_1178620803980.htm.
2. Ministry of Agriculture, Fisheries and Food *Dioxins and PCBs in farmed trout in England and Wales. Food Surveillance Information Sheet* 1998; 145 available at <http://archive.food.gov.uk/maff/archive/food/infosheet/1998/no145/145trout.htm>.
3. Ministry of Agriculture, Fisheries and Food *Dioxins and PCBs in UK and imported marine fish. Food Surveillance Information Sheet* 1999; 184 available at <http://archive.food.gov.uk/maff/archive/food/infosheet/1999/no184/184diox.htm>.
4. Mortimer D. N., Gem M., Rose M., Fernandes A., White S., Knowles T. G. *Organohalogen Comp* 2006; 68: 616.
5. Fernandes A., White S., Dsilva K., Rose M. *Talanta* 2004; 63: 1147.
6. White S., Fernandes A., Petch S., Rose M. *Survey of dioxins and PCBs in farmed and wild fish and shellfish* 2005; *FD 05/06*. Central Science Laboratory, Sand Hutton, York.
7. Food Standards Agency *Dioxins and dioxin-like PCBs in farmed & wild fish and shellfish* 2006; 03/06 available at www.food.gov.uk/multimedia/pdfs/foodsurvey0306.pdf.
8. Food Standards Agency. *FSA issues new advice on oily fish consumption. News Release* 2004; R913-44 available at www.food.gov.uk/news/pressreleases/2004/jun/oilyfishadvice0604press.