NON-DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN FISH AND SHELLFISH

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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 and the proposals by the European Commission to set limits for them in food[1].

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 such people who eat large amounts of fish concerned about the presence of PCBs and other contaminants, and there was special interest in the difference between farmed and wild salmon. The previous survey was not designed to distinguish the types of salmon.

Methods and materials

Samples

In one survey 28-60 samples of each of a number of fish and shellfish species and some fish products were purchased in 2003-2004 were processed into single composite samples for each species or product. These included fresh Greenland Turbot (*Reinhardtius hippoglossoides*), sprats (*Sprattus sprattus*), whitebait (various species), dogfish (*Squalus spp*) and sardines (*Sardina pilchardus*); and herring rollmops (*Clupea harengus*), canned mackerel (*Scomber scombrus*), canned sardines (*Sardina pilchardus* and/or *Sprattus sprattus*), canned pilchards (*Sardina pilchardus*) and canned salmon (various species). Further details of the sampling were given elsewhere[4]. In other surveys samples of smaller numbers of fish products and of farmed shellfish, shellfish from UK waters were obtained during 2005-06. These included canned red (*Oncorhynchus nerka*) and pink (*Oncorhynchus gorbuscha*) salmon and smoked salmon (*Salmo salar*), kipper (*Clupea harengus*), smoked mackerel, canned sardines, cockles (*Family Cardiidae*), mussels (*Mytilus edulis*), Pacific oysters (*Crassostrea gigas*), native oysters (*Ostrea edulis*) and crabs (*Cancer pagurus*). The samples obtained during 2005-06 were all analysed individually.

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. $^{13}C_{12}$ labelled ortho-substituted PCBs (IUPAC numbers 28, 52, 101, 118, 138, 153, 180 and 194) were added as internal standards. Non-dioxin-like PCBs were analysed using gas-chromatography low-resolution mass spectrometry[5].

Results and discussion

Table 1 shows the results for the full range of 40 non-dioxin-like PCB congeners analysed in the above fish samples. Only those species in which the concentrations were highest (mostly the oily fish species) have been included. Results for dioxins and dioxin-like PCBs in some of the same samples were presented elsewhere[4]. Table 2 shows the results for shellfish. The full results for all the fish and shellfish samples can be found in the contractor's reports[6-8].

Table 1: Concentrations of non-dioxin-like PCBs (µg/kg) in fish and fish products 2003-06

Congener	Concentrations (microgram/kg fresh weight)								
Fish species (No of fish in composite) or [No of individual samples]:	Turbot (Green-land) (60)	Whitebait (60)	Dogfish (60)	Canned herring (2)	Kipper [2]	Herring (Rollmos) (60)	Herring (Rollmops) [3]	Smoked Mackerel [6]	Canned Mackerel (60)
				Range	Range		Range	Range	
PCB28	0.3	0.4	0.3	0.2-0.3	0.1-0.4	0.2	0.2-0.4	0.1-0.2	0.1
PCB52	1.1	2.0	1.0	0.7-0.7	0.5-0.7	0.7	0.4-0.7	0.3-0.7	0.3
PCB66	0.7	1.2	1.0	0.5-1.6	0.2-0.4	0.6	0.3-1.6	0.3-0.6	0.2
PCB99	1.2	3.6	3.1	0.6-0.7	0.4-0.5	0.7	0.5-0.7	0.4-1.2	0.8
PCB101	1.5	5.7	3.8	1.2-1.3	0.7-1	1.3	0.9-1.4	0.6-2	0.2
PCB110	0.8	4.1	1.9	0.5-0.7	0.4-0.6	1.0	0.5-0.9	0.3-1.3	0.7
PCB138	3.2	10	13	2.4-2.5	1-1.7	2.8	1.9-2.5	1.3-5	1.7
PCB149	1.3	7.6	4.1	1.4-2.3	0.7-1.1	1.9	1.1-2.5	0.8-3.1	0.02
PCB151	0.5	2.1	1.0	0.4-0.5	0.2-1.7	0.5	0.3-0.5	0.3-3.3	0.05
PCB153	3.4	12	16	2.2-2.3	1-1.7	2.8	1.7-2.3	1.4-5.4	0.2
PCB170	0.5	1.5	2.5	0.2-0.2	0.1-0.2	0.3	0.2-0.3	0.2-0.6	0.2
PCB180	1.0	2.6	5.3	0.3-0.4	0.3-0.4	0.6	0.3-0.5	0.4-1.2	0.4
PCB183	0.4	1.0	2.0	0.1-0.2	0.1-0.1	0.2	0.1-0.3	0.1-0.4	0.1
PCB187	1.0	3.6	5.5	0.7-1.1	0.4-0.6	1.0	0.6-1.2	0.4-2	0.6
Σ PCBs 28, 52, 101, 138, 153 and 180	**11**	**33**	**39**	**7.0-7.0**	**3.6-5.7**	**8.4**	**5.5-7.7**	**4.1-15**	**3.0**
Σ 40 PCBs	**22**	**68**	**71**	**15-18**	**8.8-15**	**18**	**12.2-20**	**9.8-32**	**7.8**

Fish species (No of fish in composite) or [No of individual samples]:	Red salmon canned [4]	Pink salmon canned [3]	Salmon canned (60)	Salmon smoked [3]	Sprat (60)	Sardine/ Pilchard (60)	Canned sardines (60)	Canned sardines [3]	Canned pilchards (60)
	Range	Range		Range				Range	
PCB28	0.1-0.2	0.02-0.06	0.1	0.2-0.3	0.7	0.5	0.1	0.02-0.08	0.04
PCB52	0.4-0.5	0.05-0.1	0.3	0.5-0.8	1.5	2.2	0.5	0.05-0.1	0.1
PCB66	0.3-1	0.03-0.1	0.2	0.5-0.8	1.2	2.1	0.2	0.04-0.2	0.07
PCB99	0.4-0.5	0.05-0.08	0.5	0.7-0.9	1.8	5.2	0.6	0.07-0.2	0.2
PCB101	0.7-0.9	0.08-0.1	0.2	1.2-1.5	3.6	2.4	0.2	0.08-0.2	0.09
PCB110	0.4-0.5	0.04-0.05	0.4	0.7-0.8	2.3	5.7	1.6	0.06-0.2	0.5
PCB138	0.8-1.1	0.1-0.2	0.5	2.7-2.8	6.7	16	3.3	0.3-1.6	1.6
PCB149	0.6-1.2	0.07-0.2	0.01	1.4-1.6	4.3	9.8	0.05	0.2-2.2	0.02
PCB151	0.2-0.3	0.02-0.03	0.02	0.4-0.5	1.1	2.7	0.09	0.04-0.3	0.05
PCB153	0.8-1.2	0.1-0.2	0.07	2.8-3	7.1	20	0.2	0.4-2.2	0.1
PCB170	0.1-0.1	0.01-0.02	0.06	0.4-0.5	0.7	3.2	0.7	0.1-0.4	0.5
PCB180	0.2-0.3	0.02-0.03	0.1	0.7-0.9	1.3	5.8	1.3	0.1-0.9	0.8
PCB183	0.08-0.2	0.01-0.02	0.06	0.1-0.3	0.5	2.0	0.4	0.02-0.4	0.2
PCB187	0.2-0.5	0.03-0.05	0.2	0.7-1.4	2.7	7.8	1.6	0.1-1	0.7
Σ PCBs 28, 52, 101, 138, 153 and 180	**3-4.1**	**0.4-0.7**	**1.3**	**8.6-9.2**	**21**	**47**	**5.6**	**1.1-5**	**2.8**
Σ 40 PCBs	**7.9-10**	**1.1-1.8**	**4.3**	**20-22**	**44**	**101**	**15**	**2.4-12**	**6.6**

Table 2: Concentrations of non-dioxin-like PCBs (µg/kg) in shellfish 2005-06

Congener	Concentrations (microgram/kg fresh weight)							
Species [No of samples]	**Pacific oysters [9]**		**Native oysters [5]**		**Farmed Pacific oysters [4]**		**Crab [4]**	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
PCB28	0.01-0.2	0.05	0.02-0.1	0.04	0.02-0.1	0.05	0.01-0.2	0.1
PCB52	0.03-0.2	0.08	0.05-0.1	0.1	0.02-0.1	0.05	<0.005-0.02	0.01
PCB66	0.05-0.5	0.1	0.06-0.3	0.2	0.02-0.06	0.03	0.02-0.6	0.3
PCB99	0.05-0.2	0.1	0.08-0.4	0.3	0.03-0.3	0.1	0.02-0.9	0.4
PCB101	0.09-0.3	0.2	0.13-0.7	0.4	0.06-0.3	0.1	<0.005-0.5	0.2
PCB110	0.05-0.2	0.1	0.1-0.4	0.3	0.06-0.2	0.1	<0.001-0.6	0.2
PCB128	0.01-0	0.03	0.03-0.1	0.07	0.007-0.04	0.02	0.008-0.8	0.4
PCB138	0.2-0.6	0.4	0.2-1.3	0.8	0.1-0.6	0.3	0.06-5.5	2.8
PCB149	0.1-0.7	0.3	0.1-0.8	0.5	0.2-0.7	0.4	0.06-4.9	2.9
PCB151	0.03-0.2	0.07	0.03-0.2	0.1	0.04-0.1	0.09	0.002-0.08	0.04
PCB153	0.3-0.9	0.5	0.3-1.7	0.9	0.2-1	0.5	0.08-6.4	3.3
PCB170	0.002-0.02	0.007	0.009-0.03	0.02	0.01-<0.02	0.02	0.02-1.1	0.6
PCB180	0.01-0.1	0.04	0.01-0.1	0.04	0.06-0.07	0.06	0.02-1	0.5
PCB183	0.01-0.1	0.04	0.02-0.1	0.07	0.03-0.08	0.05	0.004-0.5	0.2
PCB187	0.1-0.5	0.2	0.1-0.5	0.3	0.18-0.6	0.4	<0.002-1.5	0.6
Σ PCBs 28, 52, 101, 138, 153 and 180	0.6-2.2	1.2	0.7-3.9	2.3	0.5-2.0	1.1	0.2-13	6.9
Σ 40 PCBs	1.2-5	2.7	1.5-7.1	4.6	1.3-3.9	2.6	0.4-25	14
Species [No of samples]	**Cockles [4]**		**Farmed cockles [4]**		**Mussels [7]**		**Farmed mussels [4]**	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
PCB28	0.003-0.03	0.01	0.002-0.1	0.04	0.01-0.1	0.04	0.01-0.2	0.08
PCB52	0.005-0.03	0.02	0.001-0.2	0.05	0.01-0.3	0.1	0.02-0.2	0.1
PCB66	0.006-0.07	0.03	0.004-0.3	0.07	0.03-0.4	0.2	0.008-0.3	0.1
PCB99	0.008-0.06	0.03	0.006-0.5	0.1	0.03-0.6	0.2	0.02-0.4	0.2
PCB101	0.01-0.08	0.04	0.006-0.6	0.2	0.05-1.1	0.4	0.05-0.8	0.4
PCB110	0.009-0.07	0.04	0.003-0.1	0.05	0.03-0.8	0.3	0.04-0.5	0.3
PCB128	0.004-0.02	0.01	0.002-0.1	0.03	0.01-0.3	0.1	0.01-0.2	0.08
PCB138	0.03-0.3	0.1	0.02-1.8	0.5	0.1-2.6	0.9	0.2-2.5	1.3
PCB149	0.02-0.11	0.06	0.02-1	0.3	0.1-1.9	0.6	0.09-1.6	0.8
PCB151	0.003-0.02	0.01	0.02-0.6	0.2	0.02-0.4	0.1	0.03-0.5	0.3
PCB153	0.03-0.25	0.14	0.02-2	0.6	0.2-3.0	1.0	0.2-2.8	1.4
PCB170	0.004-0.04	0.02	0.02-0.2	0.1	0.002-0.03	0.01	<0.001-0.05	0.03
PCB180	0.005-0.08	0.04	0.01-0.3	0.09	0.01-0.3	0.07	0.01-0.2	0.08
PCB183	0.003-0.04	0.02	0.005-0.2	0.06	0.02-0.5	0.15	0.03-0.6	0.3
PCB187	0.007-0.1	0.06	0.02-2.2	0.6	0.07-1.4	0.4	0.1-1.6	0.9
Σ PCBs 28, 52, 101, 138, 153 and 180	0.09-0.7	0.4	0.06-5.1	1.4	0.4-7.4	2.5	0.4-6.6	3.3
Σ 40 PCBs	0.2-1.7	0.9	0.2-12	3.4	0.7-16	5.1	0.9-13	6.8

In the majority of fish species most or all of the congeners analysed were present at concentrations above the limit of determination. However fewer congeners were detected in the shellfish species. The highest concentrations of PCBs were found in the fresh sardines/pilchards composite, followed by dogfish composite. Concentrations were lower in the canned than in the fresh or smoked samples of the same species. In most of both the fish and shellfish samples the most abundant congener was PCB 153, followed usually by PCB 138. However in the case of the canned sardines and canned pilchards samples the concentrations of PCB 153 were relatively low. The six indicator PCBS (PCBs 28, 52, 101, 138, 153 and 180) together accounted for around 50% of the sum of the 40 congeners analysed, but in the canned and smoked fish samples and in cockles and farmed oysters these congeners contributed around 40%. The concentrations are all well within the maximum limit of 40 µg/kg being proposed by the European Commission for these congeners in fish and fishery products.

Of the non-indicator congeners, PCB 149 was usually the most abundant, and in some cockle and oyster samples and one crab sample its concentrations exceeded those of any of the indicator congeners, contributing 32% of the NDL PCBs in the one crab sample. PCBs 99, 110 and 187 (especially in oysters), and sometimes PCB 170 (especially in crab), were also significant. In kippers and canned herring and some shellfish PCB 66 was significant, PCB 151 in farmed Pacific oysters and PCB 170 in crab. In combination, in fish PCBs 99, 110, 149 and 187 constituted 17-28% of the sum of the 40 congeners present. In shellfish the top four congeners was more variable, but in combination contributed 21-45% of the 40 congeners analysed. This suggests that if non-dioxin-like PCBs are to be regulated, account should be taken of these congeners as well as the indicators.

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 metals[9]. No change to the advice was considered to be necessary on the basis of the results of these samples.

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