RELATIONSHIP BETWEEN DIOXIN-LIKE AND NON-DIOXIN-LIKE ORTHO-POLYCHLORINATED BIPHENYLS IN FISH OIL DIETARY SUPPLEMENTS

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Introduction

There is currently renewed interest in non-dioxin-like polychlorinated biphenyls (NDL-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]. Ortho-substituted polychlorinated biphenyl (*o*-PCBs) are the major subset of NDL-PCBs. Eight mono-ortho- PCBs have been classified as dioxin-like: PCB105, 114, 118, 123, 156, 157, 167 and 189. These *o*-PCBs have been given WHO-TEF values[2].

Pure or blended fish oils, particularly cod liver oil, are a rich source of Vitamins A and D and have therefore long been used as dietary supplements. Recent evidence[3, 4] that long chain polyunsaturated fatty acids that are commonly found in fish oils can reduce mortality from cardiovascular and other diseases have increased the popularity of these products as dietary supplements. Earlier surveys of fish oils in the UK[5] showed relatively high concentrations of dioxins and PCBs, particularly in fish liver oils. This study sets out to examine whether the NDL-*o*-PCBs measured in a large number of laboratories can be used as an indication of the concentrations of dioxin like *o*-PCBs, which are measured by relatively few laboratories but are of potentially greater toxicity and therefore health risk.

Sampling and Analysis

A total of 33 fish oil based dietary supplement products identified by a statistical sampling plan were analysed[6]. The method of analysis has been described elsewhere[7]. $^{13}C_{12}$ labelled ortho-substituted PCBs (IUPAC numbers 28, 52, 101, 118, 138, 153, 180 and 194) were added as internal standards. Ortho- PCBs were analysed using gas-chromatography low-resolution mass spectrometry.

Results and discussion

The summary results for 13 NDL-PCB congeners analysed in the above samples are shown in Table 1 on a whole weight basis. The results are based on upper bound concentrations, i.e. where analyte has not been detected or was below reporting limit the result was set to the reporting limit (0.1 µg kg^{-1}). Table 2 shows the percentage profile for the 13 ortho-PCBs. Figure 1 compares the sum concentration of 6 ICES indicator PCBs (PCB28, 52, 101, 138, 153, 180) with the sum of WHO TEQ (*o*-PCB) for each sample. Results are only included for 32 of the original 33 samples analysed since one of them was of undefined composition.
As shown in Table 1 the main NDL-PCB congeners found were PCB153, 138, 180, and 99. These congeners were detected in all samples. There was a large variation in concentrations for a given congener between samples, especially for those of lower chlorination. This is due to a high number of samples showing PCB levels near or at the reporting limit for these congeners.
The contribution of PCB153 and 138 to the percentage profile (Table 2) was roughly equal. The six indicator PCBs accounted for over 86% of the 13NDL-PCBs, with a low CV indicating that they are a good predictor of total NDL-PCB concentration. However, more data are required from a wider range of NDL-PCB are needed to confirm this.

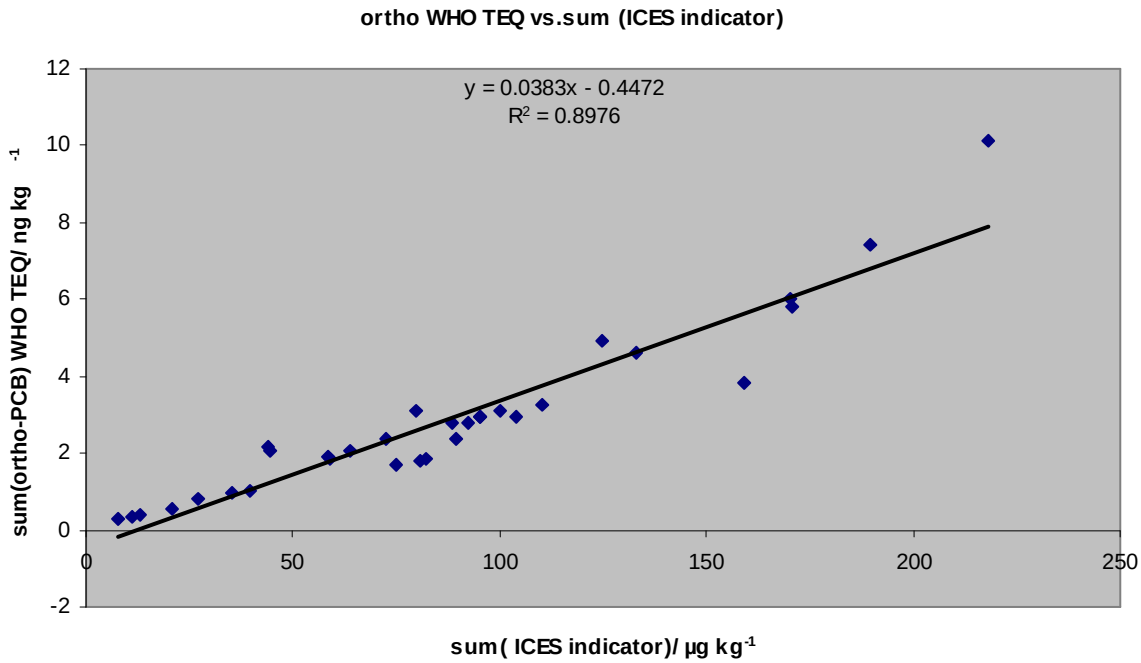
Table 1: Summary of concentration data for NDL-PCBs in fish oils (n=32)

Analtye	µg kg^{-1}				CV/%
	Mean	Median	Min	Max	
PCB18	0.33	0.10	0.10	1.45	110
PCB28	0.85	0.29	0.10	4.87	125
PCB31	0.55	0.13	0.10	1.96	110
PCB47	1.00	0.42	0.10	4.53	109
PCB49	1.44	0.51	0.12	7.26	118
PCB51	0.11	0.10	0.10	0.25	33
PCB52	3.60	1.14	0.24	19.72	124
PCB99	6.86	4.85	0.29	27.38	86
PCB101	10.69	7.66	0.81	36.88	83
PCB128	3.34	3.21	0.18	8.77	60
PCB138	29.70	29.71	2.11	68.48	59
PCB153	31.11	30.39	2.49	71.08	61
PCB180	10.15	10.60	1.26	20.12	53
Sum (across samples)	**99.74**	**94.40**	**8.62**	**269.44**	**64**
sum (ICES indicator PCBs)	**86.10**	**81.58**	**7.59**	**217.99**	**62**

Table 2: Summary of percentage profile of NDL-PCBs in fish oils (n=32)

Analtye	% Of total NDL- PCBs				CV/%
	Mean	Median	Min	Max	
PCB18	0.4	0.2	0.1	2.7	121
PCB28	0.9	0.6	0.1	4.1	106
PCB31	0.6	0.4	0.1	2.9	104
PCB47	1.1	0.8	0.1	6.7	114
PCB49	1.3	1.0	0.2	4.1	77
PCB51	0.2	0.1	0.0	1.7	148
PCB52	3.2	2.2	0.5	8.2	76
PCB99	6.2	6.1	2.3	10.2	29
PCB101	10.0	9.8	3.6	15.2	30
PCB128	3.3	3.2	2.0	4.4	20
PCB138	30.0	30.5	20.4	34.6	13
PCB153	31.4	31.8	23.8	35.3	10
PCB180	11.2	10.8	6.3	20.0	32
ICES indicator PCBs	**86.8**	**87.2**	**75.2**	**92.3**	**4**

Figure 1: O-PCB TEQ versus sum of ICES indicator PCBs



Data available for the O-PCB TEQ values for each of the samples was plotted against the corresponding Sum (indicator PCBs). A positive linear correlation was observed with r^2 value of 0.90. Such a high r^2 value indicates there are strong relationships between the total concentration of the indicator PCBs, and the *o*-PCB TEQ contribution. It may therefore be possible to predict the ortho-PCB contribution to the total WHO-TEQ in fish oil from Sum (indicator PCBs) value. However, it should be noted that fish oils produced for human consumption undergo processing to remove impurities. These processes could reasonably be expected to modify the profile of PCBs that are found in raw fish oils. More data would need to be collected to verify such an approach and establish the uncertainties involved. Further studies are necessary to see if such a model could be extended to fish and other matrices and if it could be applied to the non- ortho-PCBs.

Acknowledgements

This work was funded by the Food Standards Agency, United Kingdom. The authors also wish to thank all participating staff of Central Science Laboratory

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