Levels of Selected Coplanar PCBs in Fish from the Swedsh Water Environment

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Introduction

There has been an increased interest for the group separation of PCB congeners according to their degree of ortho substitution. This is because the toxic and biological responses attributed to PCB congeners are dependent on the ortho substitution pattern of the biphenyl rings. The levels of the coplanar PCBs (non-ortho substituted congeners - CBs 77, 126 and 169) in fish samples are very low compared to the other PCB congeners but it has been shown that their contribution to the total toxicity of dioxin-like substances is considerable (1-3), probably owing to their spatial and structural similarity to the extremely toxic 2,3,7,8-substituted polychlorodibenzo-p-dioxin(PCDDs) and PCDFs (4-6). Comprehensive analytical procedures are always involved in quantification of these compounds in biological material. To day, a number of countries and international bodies have chosen to monitor PCBs as a set of seven indicator CBs (28, 52, 101, 118, 138, 153 and 180 (7) to avoid the complexity involved in analysing more congeners. No coplanar CB is included in this list mainly because the coplanar CBs occur at concentrations several orders of magnitude lower than the least of the more abundant congeners mentioned above, and are therefore very elaborate and complicated to analyse. This paper examines the levels of some of the coplanar PCBs in fish from the Swedish waters and adds to the dearth of data on levels of these CBs in fish samples.

Method

Fish samples were homogenised and extracted, and the fat extract determined. Prior to extraction three labelled ^{13}C - labelled PCB standards (IUPAC No 77, 126 and 169), were added to the samples. The resulting fat extract was reconstituted in hexane and cleaned with sulphuric acid, followed by elution through a silica gel column (4.5g of 3% water deactivated silica gel) with ca 30 ml hexane. After appropriate reduction in volume the sample was injected into the HPLC system which had earlier been equilibrated or stabilised for about 30 minutes. The system consists of Gilson 305/307 pumps, an autosampler fitted with a 100 µl loop, a fraction collector (FC 205) and a 100 mm x 4.7 mm i.d hypercarb column, packed with 7 µm porous graphitic carbon, PGC (Shandon Scientific Ltd, Cheshire, England). The fractions from the column were monitored with a Gilson 118 uv/vis detector set at 254 nm. The first two fractions 0-4 ml and 4-20 ml collected with hexane/DCM (4:1, V/V) as mobile phase, contained mainly the di-ortho and mono-ortho PCBs respectively. The third fraction was obtained by backflushing the column with DCM (100%). In some cases the silica gel step was skipped and the final result was essentially the same. After each complete run the HPLC column performance was restored by flushing with n-hexane at a flow rate of 1-2 ml/min for at least 30 min, to re-establish equilibrium.

Results and Discussion

A large number of the herring samples analysed here had earlier been analysed for mono- and di-ortho PCB congeners and the results have been submitted for publication elsewhere (8). Tables 1 and 2 show that all the fish species analysed exhibited similar congener profile with respect to CBs 77, 126 and 169. The levels in herring samples ranged, in ng/kg fresh weight, from 55-138, 43-123, 9-36 (east coast) and 48-53, 14-16 and 13-24 (west coast) for CBs 77, 126 and 169 respectively. Other fish types (mackerel, whitefish, eel, salmon and sea trout) and the levels (ranges) of coplanar PCB contamination are shown in Table 1. CB-153 is included for comparison.

Using TEF values proposed by an international expert group(9) for PCBs, calculated TEQ levels for the coplanar congeners are shown in Table 2. CB 126 accounted for more than 80% of the TEQs in all the samples, followed by CB 169 with about 2-8%, while CB 77 gave the lowest contribution, accounting for less than 1% in each of the samples. This shows that the coplanar congener pattern in fish is similar to the pattern observed by Krokos *et al* (10) in milk matrice. Several reports seem to support this pattern in terms of concentrations and TEQ values in Baltic herring and other fish species. It would appear, however, that the level of contribution to the total TEQ value varies between the west and the east coasts. Whereas the contributions of CBs 77, 126 and 169 for samples from the west coast are > 1.5, < 90 and > 10 % respectively, similar contributions for all the fish samples from the east coast (Baltic Sea and the Gulf of Bothnia) are ≤ 1.0, > 90 and < 10 % respectively.

Conclusion

The levels of coplanar CBs in fish from the Swedish water environment are investigated. The final results will improve the dearth of data on the levels of these contiminants in fish samples. Asplund *et al* (12) have indicated that there seemed to be a correlation between CB-153 and the coplanar CBs in Baltic herring. Further work is needed to generate enough analytical data in support of this correlation. In this way a simple routine analytical procedure for environmental monitoring of both the extremely and the less toxic CBs will be preferred to using elaborate, expensive and time-consuming methods.

References

1. Natzeck C., W. Vetter, B. Luckas, G. Moskopp and J. Buijten (1995): Quantitative Determination of Toxic Mono- and Non-ortho PCBs in Cod Liver Oil after selective liquid Chromatographic separation. *Chromatographia* **41,** 585-593
2. Atuma S.S. and Ö. Andersson (1992): Separation of PCB Congeners using Active Coal Columns. *Chemosphere* **27,** 1-8
3. Tuinstra L.G.M.Th., J.A. van Rhijn, A.H. Roos, W.A. Traag, R.J. van Mazijk and P.J.W. Kolkman (1990): Determination of Planar Chlorobiphenyls in animal fat. *J. High Resol. Chrom* **13,** 797-802
4. Pastor M.D., J. Sanchez, D. Barcelo and J. Albaiges (1993): Determination of Coplanar Polychlorobiphenyl Congeners in Biota Samples. *J. Chrom.* **629**, 329-337
5. Wells D.E., I. Echarri and C. Mckenzie (1995): Separation of Planar Organic Contaminants by Pyrenyl-silica High-performance Liquid Chromatography. *J. Chrom A* **718**, 107-118
6. Brφwadt S. and B. Larsen (1992): Rapid screening of Chlorobiphenyl Congeners by GC-ECD on a Carborane-polydimethylsiloxane Copolymer. *J. High Res. Chrom.* **15**, 34-35

Table 1 Levels of planar CBs and CB 153 in some selected fish species caught in the Baltic Sea and the Gulf of Bothnia, expressed in µg/kg fresh weight.
n = number of samples analysed
* = composite samples or homogenates comprising of 10-35 fish species each.
**= Ditto with 2-9 fish species each
Bold figures and the figures in brackets represent the mean values and ranges, respectively.

Fish type	Place of catch	n	Fat content %	CB-77	CB-126	CB-169	CB153
Herring	Baltic Sea	5*	**7.7** (7.3-8.6)	**0.098** (0.062-0.138)	**0.085** (0.047-0.123)	**0.025** (0.010-0.036)	**35** (18-62)
Herring	Gulf of Bothnia	6*	**8.2** (7.3-8.9)	**0.070** (0.055-0.081)	**0.058** (0.043-0.068)	**0.012** (0.009-0.015)	**29** (26-36)
Herring	West Coast	2**	**10** (8.7-11)	**0.050** (0.048-0.053)	**0.015** (0.014-0.016)	**0.018** (0.013-0.024)	**6.7** (4.4-9.0)
Mackerel	West Coast	2**	**24** 23-25	**0.063** (0.045-0.082)	**0.014** (0.013-0.015)	**0.024** (0.022-0.025)	**3.6** (3.2-4.1)
Whitefish	Gulf of Bothnia	4	**2.3** (0.80-4.7)	**0.026** (0.011-0.056)	**0.021** (0.003-0.042)	**0.014** (0.011-0.018)	**9.9** (2.5-19)
Eel	Baltic Sea	4	**20** (14-26)	**0.018** (0.015-0.023)	**0.077** (0.075-0.084)	**0.033** (0.029-0.036)	**59** (43-73)
Salmon	Baltic Sea	2**	**17** 15-19	**0.28** (0.27-0.29)	**0.12** (0.11-0.12)	**0.031** (0.015-0.047)	**58** (56-60)
Sea trout	Gulf of Bothnia	1*	5.3	0.058	0.073	0.042	65

7. de Voogt P., Wells D.E, Reuthergårdh L. and Brinkman U.A.T(1990): Biological activity, determination and occurrence of planar, mono- and di-ortho PCBs. *Int. J. Environ. Anal. Chem.* **40**, 1-46
8. Atuma S.S., Linder C-E., Andersson Ö., Bergh A., Hansson L. and Wicklund-Glynn A. (1996): CB 153 as indicator for congener specific determination of PCBs in diverse fish species from Swedish waters. *Chemosphere* (submitted for publication)

Table 2 The relative composition of the ΣTEQ burden (CBs 77+126+169) in some selected fish species. TEFs values(11): CB 77 - 0.0005; CB 126 - 0.01; CB 169 - 0.01; CB 153 - 0.00001

Fish type	Place of catch	ΣTEQ for CB 77, 126, 169 (ng/kg)	Contribution to ΣTEQ (ng/kg)		
			77	126	169
Herring	Baltic Sea	8.8	0.05	8.5	0.25
Herring	Gulf of Bothnia	6.0	0.04	5.8	0.12
Herring	West coast	1.7	0.03	1.5	0.18
Mackerel	West Coast	1.7	0.03	1.4	0.24
Whitefish	Gulf of Bothnia	2.3	0.01	2.1	0.14
Eel	Baltic Sea	8.0	0.01	7.7	0.33
Salmon	Baltic Sea	12.4	0.14	12	0.31
Sea trout	Gulf of Bothnia	8.0	0.03	7.3	0.65

9. Ahlborg U.G, Brouwer A., Fingerhut M.A., Jacobson S.W., Kennedy S.W., Kettrup A.A.F., Koeman J.H., Poiger H., Rappe C., Safe S.H., Seegal R., Tuomisto J. van den Berg M. Impact of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls on human and environmental health, with special emphasis on application of the toxic equivalent factor concept. *Eur. J. Pharmacol.* 1992; 228: 179-199.
10. Krokos F., Creaser C.S., Wright C. and Statin J.R. (1996): Levels of selected ortho and non-ortho polychlorinated biphenyls in U.K retail milk. *Chemosphere* **32,** 667-673.
11. Ahlborg U.G., Becking G.C., Birnbaum L.S., Brouwer A., Derks H.J.G.M., Feeley M., Golor G., Hanberg A., Larsen J.C., Liem A.K.D., Safe S.H., Schlatter C., Waern F., Younes M., Yrjänheikki E (1994): Toxic Equivalency Factors for Dioxin-like PCBs *Chemosphere* **28,** 1049-1067.
12. Asplund L, Grafström A-k, Haglund P, Jansson B, Järnberg U, Mace D, Strandell M, de Wit C. Analysis of non-ortho polychlorinated biphenyls and polychlorinated naphthalenes in Swedish Dioxin survey samples. *Chemosphere* 1990; 20: 1481-1488.