Organochlorine Compounds in Human Milk and Pilot Whale from Faroe Islands

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1. Introduction

Consumption of food of marine origin considerably contributes to the body burden of humans with polychlorinated dibenzodioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs) and organochlorine pesticides (OCs) such as p,p'-DDT, its metabolite p,p'-DDE, HCH-isomers, HCB and toxaphene[1-8]. Therefore, humans with a high share of seafood in their diet should exhibit higher levels of these compounds compared to humans with a relatively low share. Since levels of these compounds were known to be high in seafood, especially in the whale[6,9], and since mercury levels of the Faroese population[6,10] were found to be elevated[11,12], the association with this kind of food was investigated. Therefore, human milk samples from mothers living on the Faroe Islands were collected and analyzed.

2. Experimental

Samples

Four individual milk samples (A, B, C, D) and 1 pooled sample from 9 mothers living on the Faroe Islands were randomly collected. The mean age of the donors of the individual samples and pooled samples was 29 years each. Individual samples were collected about 2 weeks, samples for the pool in the first week after delivery. Consumption of fish by the mothers (samples A to D) ranged from 1-3 meals per week and that of whale (meat and blubber) from 1-2 meals per week.
The pilot whale blubber was bought in a food store.

Extraction

Fat extraction of milk was performed by using the AOAC method, including partition with hexane and ether[13]. Fat extraction of whale blubber was carried out by grinding the material with sodium sulfate and sea sand followed by column extraction with hexane/acetone (2/1)[14]. Aliquots of the extracts were used for gravimetric fat determinations[14].

Clean-up

The clean-up was performed following the procedure of Smith et al.[15], with some minor modifications[16,17] including columns containing potassium silicate, silica gel, carbon, sulfuric

acid dispersed on silica gel, cesium silicate and alumina. The final extract was concentrated by evaporation to a 30 µl extract for the determination of PCDDs, PCDFs and planar PCBs. The other chlorinated compounds (OCs and non-planar PCBs) were separated together with the remaining fat on the carbon column and were subsequently purified following the procedure of Specht et al.[18] with gel permeation chromatography (GPC) on Bio-Beads S-X3 and a silica filled column. After evaporation the extract was dissolved in 1 ml toluene.

Determination

HRGC-HRMS: The extracts for PCDDs, PCDFs and planar PCBs were separated on a DB-5 column and quantified with a Finnigan MAT 95 instrument (resolution 8 000) on the basis of ^{13}C-labelled internal standards[16,17].

HRGC-ECD: For the determination of OCs (including toxaphene indicator compounds 1, 2, 3; see Table 1) and the PCB indicator compounds PCB-28, -52, -101, -138, -153 and -180[14], the extracts of the combined GPC and silica clean-up were analyzed by GC-ECD on a DB-5 and DB-1301 column[18].

3. Results and Discussion

The concentrations of PCDDs, PCDFs, PCBs and other organochlorine compounds have been listed in Table 1, all on a fat weight basis.

PCDDs and PCDFs

In the human milk samples, the differences in the levels of the individual congeners were found to be very low. The levels of the pooled sample were similar to those of the 4 individual milk samples. Compared to data from west Germany obtained in the same period, the congener levels of the Faroese samples were lower resulting in levels of 6.7 pg I-TEq/g milk fat for the pooled sample and 9.5 pg I-TEq/g milk fat for the mean of the individual samples. The present concentrations ranging between 15-20 pg I-TEq/g milk fat[19,20] in samples from west Germany are about twice as high.

The levels in whale blubber were low and hardly differed from levels in fat of animal origin[21] in the German food. In a harbour porpoise sample from the North Sea a similar level of 2.3 pg I-TEq/g[22] was found. In spite of the fact that pilot whales are carnivores, feeding largely on squid but also on pelagic fish and crustaceans[6], they obviously do not accumulate PCDDs and PCDFs in their body but some other OC compounds.

PCBs

For the non-planar congeners PCB-28, -52, -101, -138, -153 and -180 (the last 3 congeners represent 62 % of the total PCBs in human milk[23]), the levels in the milk samples, except sample A, were similar and in the same range as those found in Germany in 1985 and higher by a factor of about 2 than the present levels[20]. Lower chlorinated PCBs, such as PCB-28, -52 and -101 were of minor importance as usually is the case. Levels of PCB-77 were near background contamination in the laboratory and have therefore not been listed. PCB-126 was similar and PCB-169 was up to 4 times higher than in samples from Germany (PCB-126: 83 pg/g, PCB-169: 72 pg/g[24]) but PCB-169 was higher by a factor of 16 in sample A.

In contrast to PCDDs and PCDFs the PCB levels in the whale were very high: For PCB-138 and PCB-153, a 3 000 ng/g level was exceeded in each case . The estimated total PCB amount of 17 000 ng/g is close to the mean reported by Simmonds et al.[6] for more than 50 pilot whales near the Faroe Islands. The sum of the concentrations of co-planar PCBs was

2.7 ng/g corresponding to a share of 0.02 % in total PCBs. Among the co-planar PCBs, congener PCB-77 was the predominant (60 %). Similar levels of PCB-77 had been obtained for harbour porpoise and seal samples from the North Sea and Baltic Sea[22,25].

Other organochlorine compounds

In the Faroese human milk samples, levels of hexachlorobenzene (HCB: <100 ng/g) and ß-hexachlorocyclohexane (ß-HCH: <40 ng/g) were lower in comparison with present levels in Germany (HCB: 218 and ß-HCH: 75 ng/g)[19]. But the levels of p,p'-DDE and p,p'-DDT (see Table 1) were higher compared to those in west Germany (p,p'-DDE: 589; p,p'-DDT: 61 ng/g) and somewhat lower compared to those in east Germany (p,p'-DDE: 1130; p,p'-DDT: 134 ng/g)[19] - except sample A with the highest concentrations by far (p,p'-DDE: 5610; p,p'-DDT: 472 ng/g).

Levels of HCB (400 ng/g) and ß-HCH (19 ng/g) for the pilot whale were comparatively low. The high p,p'-DDE level (16500 ng/g) was in conformity with results obtained by Simmonds et al.[6].

Toxaphene as a mixture of a multitude of polychlorinated bornanes and bornenes has rarely been quantified in the past. Meanwhile, a congener-specific method of quantitation using 3 characteristic bornanes (indicator compounds, see Table 1) which represent the most important toxaphene congeners in fish and human milk was introduced[26] so that comparable and reliable results were obtained for the first time. Although data elaborated with this new method are not available from literature, it seems that the toxaphene levels in human milk from the Faroe Islands are relatively high. This is especially true of sample A with a concentration of 1560 ng/g as the sum of the 3 indicator compounds. Human milk in Germany shows levels of about 5 ng/g (only indicator compound 2, no other congener was found at a detection limit of 2 ng/g[27]). It can be concluded from this study that differences in toxaphene levels between Faroese and German human milk samples are most pronounced.

The pilot whale contained high amounts of toxaphene (6400 ng/g, sum of the 3 indicator compounds) exceeding levels in a combined representative fish fat sample from Germany by a factor of 35[26].

4. Conclusions

Using data on fish and whale consumption on the Faroe Islands (daily consumption 72 g fish, 12 g pilot whale muscle, 7 g blubber[11]) it is obvious that fat consumption from the whale predominates. As the pilot whale contains very high amounts of PCBs, p,p',-DDE, p,p'-DDT and toxaphene, it is likely that these high levels considerably contribute to the high body burden of the inhabitants on the Faroe Islands from these substances[6]. High PCB and toxaphene levels in milk from inuits through the consumption of marine mammals as part of the traditional Inuit diet were also reported by Dewailly et al.[5] and Stern et al.[8]. Levels of HCB, ß-HCH, PCDDs and PCDFs are comparably low both for human milk and whale from the Faroe Islands.

At present, reasons for the particulary high levels in human milk sample A cannot be given.

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Table 1: Concentrations of PCDDs, PCDFs, co-planar PCBs (pg/g), non-planar PCBs and OCs (ng/g) in human milk and pilot whale on fat weight basis

		HUMAN MILK								PILOT
		4 individual samples							Pool	WHALE
		A	B	C	D	MIN	MAX	MEAN	n=9	
2378-TCDF	*pg/g*	<0.5	1.6	1.0	<3	<0.5	1.6	1.1	0.7	18
2378-TCDD		0.9	1.0	<1	<3	<1	<3		0.8	0.6
12378-PECDF		<0.5	<0.5	<0.5	<3	<0.5	<3		<0.2	1.3
23478-PECDF		7.0	6.2	6.0	5.3	5.3	7.0	6.1	4.2	2.2
12378-PECDD		3.7	4.0	5.2	5.0	3.7	5.2	4.5	2.9	1.0
123478-HxCDF		3.0	5.4	6.0	<3	<3	6.0	4.0	2.5	<2
123678-HxCDF		2.4	3.5	4.5	<3	<3	4.5	3.0	1.9	<2
234678-HxCDF		<0.5	2.2	<0.5	<3	<0.5	2.2		0.9	<1
ΣHxCDFs		5.7	11	11	<9	4.5	11	8.0	5.2	<5
123478-HxCDD		4.5	4.0	3.5	3.2	3.2	4.5	3.8	3.3	0.5
123678-HxCDD		13	17	16	12	12	17	15	11	2.3
123789-HxCDD		1.9	2.1	2.0	<3	<3	2.1	1.9	1.4	<0.5
ΣHxCDDs		19	23	22	17	17	23	20	15	3.0
1234678-HpCDF		2.4	5.3	6.2	9.4	2.4	9.4	5.8	1.6	2.0
1234678-HpCDD		9.8	19	9.3	22	9.3	22	15	9.2	1.1
OCDF		<2	<2	2.8	9.2	<2	9.2		<0.5	<2
OCDD		45	114	75	63	45	114	74	64	<2
I-TEq (PCDDs/PCDFS)		9.0	10.0	9.7	9.4	9.0	10.0	9.5	6.7	4.6
PCB-77	*pg/g*	n.a.	n.a.	n.a.	n.a.				n.a.	1,650
PCB-126		108	38	41	79	38	108	67	107	430
PCB-169		1,160	61	158	205	61	1,160	396	300	610
PCB-28	*ng/g*	12	2	2	3	2	12	5	4	19
PCB-52		96	5	4	6	4	96	28	3	720
PCB-101		273	13	13	18	13	273	79	7	1,430
PCB-138		1,090	136	220	269	136	1,090	428	272	3,280
PCB-153		1,460	194	300	356	194	1,460	576	363	3,670
PCB-180		728	97	130	163	97	728	280	220	1,460
Total PCBs		5,840	715	1,070	1,300	715	5,840	2,230	1,390	17,000
HCB	*ng/g*	90	15	17	17	15	90	35	72	400
ß-HCH		36	13	20	13	13	36	21	34	19
p,p'-DDE		5,610	478	880	1,060	478	5,610	2,010	981	16,500
p,p'-DDT		472	29	62	73	29	472	159	64	2,400
Toxaphene ind. 1		640	25	45	96	25	640	202	77	3,140
Toxaphene ind. 2		750	41	61	124	41	750	244	118	2,670
Toxaphene ind. 3		170	<5	<5	<5	<5	170		<5	590
ΣToxaphene ind.		1,560	69	109	223	69	1,560	490	198	6,400

n.a.: not analyzed; MIN: minimum; MAX: maximum; MEAN and I-TEq calculated using half the detection limits; Total PCBs: Σ(PCB-28,-52,-101,-138,-153,-180)•1,6[23]; ind.: indicator compound;
Toxaphene ind. 1: 2-exo,3-endo,5-exo,6-endo,8b,8c,10a,10b-octachlorobornane;
Toxaphene ind. 2: 2-exo,3-endo,5-exo,6-endo,8b,8c,9c,10a,10b-nonachlorobornane;
Toxaphene ind. 3: 2,2,5,5,8b,8c,9c,10a,10b-nonachlorobornane

6. References

1) Svensson, B.-G., Nilsson, A., Hansson, M., Rappe, C., Akesson, B., and S. Skervfing (1991). N. Engl. J. Med. 324: 8-12
2) Svensson, B.-G., Hallberg, T., Nilsson, A., Schütz, A. and L. Hagmar (1994). Int Arch Occup Environ Health 65: 351-358
3) Ryan, J.J. and E. Dewailly (1992). Organohalogen Compounds 9: 207-209
4) Svensson, B.-G., Nilsson, A., Hansson, M., Rappe, C., Akesson, B., and S. Skervfing (1990). Organohalogen Compounds 1: 505-508
5) Dewailly, E., Nantel, A., Weber, J.-P. and F. Meyer (1989). Bull. Environ. Contam. Toxicol. 43: 641-646
6) Simmonds, M.P., Johnston, P.A., French, M.C., Reeve, R., and J.D. Hutchinson (1994). Sci. Total Environ. 149: 97-111
7) Asplund, L., Svensson, B.-G., Nilsson, A., Eriksson, U., Jansson, B., Jensen, S., Wideqvist, U. and S. Skervfing (1994). Arch Environ Health 49: 477-486
8) Stern, G.A., Muir, D.C.G., Ford, C.A., Grift, N.P., Dewailly, E., Bidleman, T.F. and M.D. Walla (1992). Environ. Sci. Technol. 26: 1838-1840
9) Tanabe, S., Kannan, N., Ono, M. and R. Tatsukawa (1989). Chemosphere 18: 485-490
10) Grandjean, P., Jorgensen, P. J., and P. Weihe (1994). Environmental Health Perspectives 102: 74-77
11) Vestergaard, T., Zachariassen. [Dietary survey 1981-82, in Faroese] Frodskaparrit 33: 5-18
12) Grandjean, P., Weihe, P., Jorgensen, P. J., Clarkson, T., Cernichiari, E. and T. Videro (1992). Archives of Environmental Health 47: 185-195
13) Williams, S. (Ed.) (1984). Official Methods of Analysis of the Association of Official Analytical Chemists, 14th Ed., Washington, 537
14) Beck, H.and W. Mathar (1985). Bundesgesundheitsblatt 28: 1-12
15) Smith, L.M.,Stalling, D.L.andJ.L.Johnson (1984). Anal. Chem. 56: 1830
16) Beck, H., Eckart,K., Kellert, M., Mathar, W., Rühl, Ch.-S. and R. Wittkowski (1987). Chemosphere 16: 1977
17) Beck, H., Eckart, K., Mathar, W. and R. Wittkowski (1988). Biomed. & Environm. Mass Spectrom. 16: 161-165
18) Specht, W. and M. Tillkes (1980). Fresenius Z. Anal. Chem. 301: 300-307
19) Alder, L., Beck, H., Mathar, W. and R. Palavinskas (1994). Organohalogen Compounds 21: 39-44
20) Beck, H. (1995). In: Proceeings: Chlorinated Organic Chemicals - Their Effect on Human Health and the Environment, The Toxicology Forum, 19 - 21 September 1994, Berlin, Germany, 216-247
21) Beck, H., Droß, A., and W. Mathar (1992). Chemosphere 25: 1539-1550
22) Beck, H., Droß, A., Mathar, W. and E. Breuer (1990). Chemosphere 20: 1027-1034
23) Schulte, E. and R. Malisch (1984). Z Anal Chem 319: 54-59
24) Beck, H., Mathar, W. and R. Palavinskas (1994). Data presented at WHO Europe meeting, 23/24 March 1994, Berlin, WHO report in press
25) Falandysz, J., Yamashita, N., Tanabe, S., Tatsukawa, R., Rucinska, L, and K. Skora (1994). Arch. Environ. Contam. Toxicol. 26: 267-272
26) Alder, L. and B. Vieth (1995). Fres' J Anal Chem, in press
27) Alder, L. et al. (1995). Unpublished results