Determination of PCDF/PCDD levels in sediments from the Arctic (Barents Sea) including quality assurance and methodological aspects and comparison with concentrations in the North Sea

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Levels of polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD) in seal blubber from the Arctic and from regions much closer to sources such as the North Sea are within the same order of magnitude (10 pg/g 2,3,7,8-tetrachlorodioxin equivalents, 2,3,7,8-TE (Nordic model))[1]. Similar levels are also present in cod liver oil from the North Atlantic[1]. However, in organisms at the lower end of the food chain such as crabs a concentration decrease from the Norwegian coast to the Arctic was found. PCDF/PCDD are mainly transported by the atmosphere and sediments are considered as final sink. According to Wania et al.[2] a decline should be observed from temperate to polar zones for compounds with vapour pressures comparable to PCDF/PCDD. Sediments from the Barents and the North Sea were analysed for PCDF/PCDD and non-ortho substituted polychlorinated biphenyls to obtain information concerning the following aspects:

- Levels in Arctic sediments compared to the North Sea
- Differences between the congener patterns of both regions and information about the most likely sources

Due to the expected low levels in the Arctic the standard analysis method[3] was improved allowing detection limits in the 10-20 fg/g range, and stringent quality assurance measures were included to control contamination and adsorption problems at such low levels.

Experimental

Top layer sediment samples (0-1 cm) were collected with a box corer (0,1 m^2 area) by the Institute of Marine Research at 5 locations in the North Sea/Skagerrak in 1990 and at 11 in the Barents Sea in 1991 (see Figure 1). To control the overall reproducibility of the sampling and analysis methods two independently collected samples were analysed from each site in the North Sea using a substantially modified technique compared to the earlier applied method[3]. The following additional elements were included: Quality control of the activity grade of each batch of prepared adsorbent by azo dyes, additional blank controls, decontamination of glassware by heat, substitution of glass wool by cotton wool and elimination of other

materials susceptible to adsorptive losses or contamination, use of metallic mercury instead of copper powder to remove sulphur and sulphur organic compounds and finally high resolution mass spectrometry at R=10'000.

Results and discussion

Only results were accepted which fulfilled the following criteria: Signal-to-noise ratio >3:1, concentrations >10 times higher than the values of the preceeding blank and recovery rates within 50-120%. Detection limits for tetra- and pentachlorinated compounds were in the order of 0,01-0,02 pg/g dry weight and ≥0,04 pg/g for higher chlorinated congeners.

As can be seen from Table 1, the levels in the Barents Sea were very low and quite homogeneous. Standard deviations were within 20-50% for the calculated average concentrations of single congeners in all samples. When the two samples closest to the Norwegian main land were excluded (somewhat higher levels possibly due to the influence of the Gulf stream) the range was even narrower. The found concentrations are at least 1-2 orders of magnitude lower compared to the North Sea and to any other results reported (mainly from contaminated areas).

The deviations between 4 of the 5 parallel samples from the North Sea were on average 16 ± 5% (range 8-27 %) for all congeners which is comparable with the earlier determined reproducibility of the measuring method (10-15%). This confirms that the sampling method is capable to collect representative samples at homogeneous sites. The parallel samples from the fifth site had a somewhat larger deviation (x=38±17%, range 17-63%; reason not known).

The concentrations in the two samples taken between Norway and Shetland (see North Sea II in Table 1) were comparable to those from the Barents Sea. The most likely reason is the exceptionally low content of clay/silt compared to all other samples (about 10-20 times lower). The total organic carbon content was ca. 1-2% in all samples except no. 2 (0,2-0,3%).

The isomer concentration ratios within groups of the same degree of chlorination were very similar for both sampling areas and matched the general pattern of combustion sources very well. However significant differences were found for the concentration ratios between groups with different degree of chlorination. TCDF and PeCDF were the most dominant congener groups in all samples from the Barents Sea while OCDD and OCDF had the highest levels in the North Sea. An explanation might be different wet and dry deposition rates which alter the congener profile during long range transport. As shown by Koester and Hites[4], the fraction bound to particles is about a factor of 2 lower for TCDF and PeCDF compared to all other PCDF/PCDD congeners. The elevated levels of OCDD/OCDF found in North Sea sediments could be the result of the higher overall scavenging ratios for these compounds which favour deposition not too far away from source areas. Consequently, higher levels of less chlorinated congeners will be found in the Arctic.

Table 1. Average values x, ranges and standard deviations s_d of PCDF/PCDD levels in top layer sediment samples (0-1 cm) from the North Sea and Barents Sea.

Congener	Concentration in pg/g dry weight				
	North Sea I (n=8)		North Sea II	Barents Sea	
	x (range)	s_d	x (range)	x (range)	s_d
2378-TCDD	0,60 (0,31-1,06)	0,25	0,05/0,04	0,06 (0,03-0,13)	0,03
ΣTCDD	17,2 (12,8-27,2)	5,3	1,4/1,0	2,63 (0,63-3,1)	0,83
12378-PeCDD	1,68 (0,86-2,8)	0,61	0,16/0,15	0,11 (0,07-0,15)	0,045
ΣPeCDD	26,5 (14,8-39)	9,2	2,4/2,2	2,41 (1,1,-4,3)	0,95
123478-HxCDD	1,81 (1,4-2,6)	0,49	0,19/0,16	0,10 (0,05-0,19)	0,040
123678-HxCDD	3,1 (1,9-5,0)	1,0	0,40/0,35	0,20 (0,11-0,37)	0,09
123789-HxCDD	3,8 (2,8-5,3)	0,85	0,42/0,41	0,18 (0,09-0,34)	0,07
ΣHxCDD	71 (54-101)	17	7,1/5,8	4,6 (2,1-6,7)	1,5
1234678-HpCDD	25 (11-36)	7,5	2,8/2,6	1,2 (0,54-2,0)	0,45
ΣHpCDD	64 (31-93)	18	6,7/5,9	3,1 (1,5-5,1)	1,1
OCDD	158 (124-215)	26	15/14	9,4 (5,0-16,7)	3,6
2378-TCDF[a]	5,7 (2,8-10,6)	2,6	0,51/0,40	0,85 (0,57-1,4)	0,29
ΣTCDF	54 (30-100)	21	4,8/3,8	14,1 (5,1-26,2)	6,9
12378-PeCDF[b]	6,9 (3,2-14,2)	3,6	0,46/0,48	0,56 (0,28-1,0)	0,20
23478-PeCDF	5,8 (2,90-11,1)	2,7	0,54/0,47	0,31 (0,15-0,67)	0,15
ΣPeCDF	59 (37-114)	28	5,3/5,0	i	
123478-HxCDF[b]	12,7 (6,4-26)	6,4	0,81/0,76	0,51 (0,23-1,0)	0,22
123678-HxCDF	6,7 (3,6-12,3)	2,8	0,42/0,43	0,33 (0,11-0,66)	0,17
123789-HxCDF	0,77 (0,32-1,6)	0,42	0,06/0,03	<0,02-0,04	
234678-HxCDF	5,3 (2,8-8,5)	1,9	0,62/0,59	0,29 (0,12-0,62)	0,15
ΣHxCDF	77 (39-147)	36	6,3/5,9	3,3 (1,3-6,9)	1,7
1234678-HpCDF	29 (12-63)	16	2,2/2,2	0,85 (0,41-1,6)	0,37
1234789-HpCDF	8,2 (3,5-20)	5,5	0,34/0,32	0,14 (0,04-0,24)	0,06
ΣHpCDF	62 (33-134)	35	4,3/4,3	1,3 (0,64-2,4)	0,62
OCDF	155 (67-436)	130	6,2/5,8	1,8 (0,75-3,5)	1,0
2378-TE[c]	9,3 (5,5-17,2)	4,0	0,82/0,74	0,57 (0,31-1,1)	0,22

[a]Partly coelution with 2348-TCDF; [b] Not separated from 12348-PECDF or 123479-HxCDF, respectively; [c] Nordic model; i: Interference at some isomers in some samples

References

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Figure 1. Sampling sites in the North Sea/Skagerrak and the Barents Sea. Levels of PCDF/PCDD and coplanar PCB (no 77, 126, 169) are given as 2,3,7,8-TE (Nordic model) in pg/g dry weight.