Occurrence and Distribution of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/F) in Sediments of the Western Baltic Sea and German Coastal Waters

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1. Introduction

The distribution of PCDD/F in different areas of the world ocean have been reported by several authors [1, 2]. But only very few data are available for PCDD/F in the Baltic Sea [3, 4] and there are a lack of information for many regions of the Baltic Sea.
PCDD/F mainly originate from domestic and industrial wastewater, river run-off and especially atmospheric deposition of combustion products. Major sources are industrial processes contributing to PCDD/F production are the combustion of fossil fuels, metallurgical processes, chlorine bleaching of paper pulp and the production of chlorine compounds (PCBs, Pentachlorophenol).
The athmospheric transport should be a major pathway for the input of PCDD/F into the aquatic environment. In the water column, PCDD/F become frequently associated with particulate matter due to their hydrophobic nature and may accumulate to high concentrations in sediments [5}. Recent investigations have shown that PCDD/F can also bioaccumulate to high concentrations in aquatic organisms via the food chain [6].

2. Sampling area

The investigated sea area covers parts of the Western Baltic Sea and the Baltic Proper. The sampling area includes also a large system of internal coastal waters called Bodden and Haff area along the 340 km long southern part of the Baltic coastline of Mecklenburg-Vorpommern. Boddens are lagoons, connected to the sea by shallow or narrow natural sea channels. This coastline is typical for Mecklenburg-Vorpommern. The hydrography of the innercoastal seas is governed mainly by changing in the intensity of water exchange with the Baltic Sea. Freshwater inflow via the rivers plays an important role. The main rivers in this area are the Warnow, the Uecker, the Peene and the Oder. The inner coastal water have the function of pre-purification areas and are thereby a sink for all types of anthropogenic contaminants.
The investigated surface sediments (0-2 cm) comprise muddy sediments with a high amount of organic carbon. Since sediment structure varies between different sampling sites (grain size effect) a normalization to TOC was performed to correct for this effect. This procedure allows to compare contamination levels between the different areas.

3. Sample preparation and analysis

The surface sediment samples were collected with a Van-Veen grab (0-2 cm). The samples were stored in aluminium boxes by -21 C until analysis. The water content, the carbon content and the fraction < 63 μm was determined. The carbon content (TC) and inorganic carbon content (TIC) were measured using an ELTRA C/S analyzer (METALYT CS 1000 S). PCDD/F analysis is described by [7].

4. Distribution of PCDD/F in surface sediments

The concentrations of 15 PCDD/F congeners and of the sum of the tetra- (TCDD/F), penta- (PNCDD/F), hexa- (HCDD/F) hepta- (HPCDD/F) and octa- (OCDD/F) dibenzo-p-dioxins and dibenzofurans as well as the total concentration also expressed as toxic equivalents are shown in table 1.

The concentrations in the different sediments show wide variations, depending on the investigated region. The total concentration of TCDD/F varied between 6,7 µg/kg and 75,6 µg/kg TOC (Fig.1). The toxic equivalents ranged between 1,1 and 16,3. The 2,3,7,8-TCDD as most toxic congener was found only on 4 stations. The highest concentrations of PCDD were found in the river estuaries of the river Warnow (UW2 to UW4) and of the river Oder (Oderhaff, station KHJ and KHM). The concentration of the sum of the investigated dioxins in sediments of the Warnow river ranged between 23 and 66,2 µg/kg TOC. The concentration of the dibenzofurans varied between 5,6 and 9,3 µg/kg TOC. The values of the sediments of the Oderhaff ranged between 9,9 and 21,1 µg/kg TOC for the sum of the investigated dioxins and 2,4 and 10,4 µg/kg for the sum of dibenzofurans. The high concentrations in the Warnow Estuary may be a result of a high anthropogenic input of PCDD/F in this region. Sources are industrial wastewater especially from the shipyards near Rostock, the traffic around Rostock and coal combustion emissions. Near the shipyard of the city of Wismar (station WB1) also has high PCDD/F concentrations.

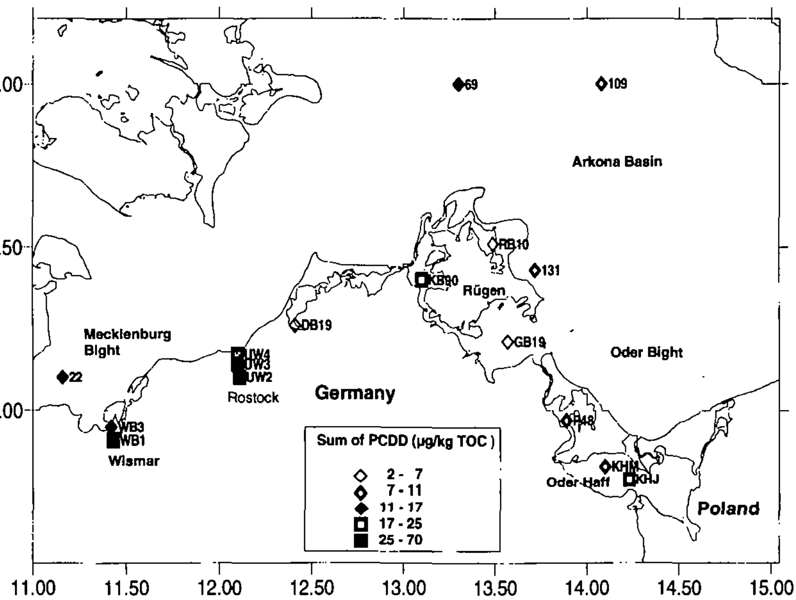

Fig. 1: Distribution of TCDD in the investigated sea area (normalized to TOC)

The PCDD/F content in the muddy sediments of the Oder Haff and the Peenestrom are also relatively high and range between 9,7 and 21,1 µg/kg TOC for the sum of the investigated dioxins and 2,4 and 10,4 µg/kg for the sum of dibenzofurans, suggesting that the Oder river should be the main source of the significantly higher PCDD/F content in these areas.

Surface sediments of three Bodden areas were investigated (Darss-Zingst Bodden-chain, Greiswalder Bodden, Rügener Bodden). The concentration levels of the PCDD/F in the Boddens are rather low compared to the other parts of the investigated areas. The PCDD-concentrations (sum of 15 congeners) ranged between 2,4 µg/kg and 4,5 µg/kg TOC in the sediments of the Bodden area.

The fingerprint profiles of the different congener groups are similar in the whole investigated area. The concentration of the PCDD increased with increasing degree of chlorination (Cl4<Cl5<Cl6<Cl7<Cl8). This trend in conjunction with the presence of Cl_4-Cl_8 PCDF strongly

suggests the influence of combustion sources. These distribution pattern are also reported as typical profiles in air samples [8]. The most abundant congener in the whole investigated area was octachlordibenzo-p-dioxin (OCDD). This compound is thought to be a major component of combustion produced PCDD [9]. The highest concentrations, up to 54 g/g TOC, were analyzed in the Warnow river estuary.

5. Conclusions

The distribution of PCDD/F in surface sediments of the Arkona Sea, Belt Sea and the inner coastal area of Germany was investigated.

In the Baltic Sea sediments a PCDD/F maxima was measured in the sedimentation basins of the Belt Sea (Lübeck Bight). Highest concentrations of PCDD/F were recorded at the rivers and Haff areas with a seaward trend of decreasing PCDD/F concentrations. In this case, a great part of the innercoastal waters has the function of a trap and a pre-purification basin for organic pollutants which are mainly adsorbed on particulate matter.

It is difficult to make an assessment of all potential sources of PCDD/F contamination in the western Baltic Sea. One important source for PCDD/F input to the Oder Haff and the Arkona Basin is the river Oder. Industrial wastewater from the shipyards should be the major source for the elevated PCDD/F concentrations near Wismar and Rostock. According to the distribution pattern of the individual congener groups another major source might be the atmospheric input of combustion derived PCDD/F from central Europe.

7. References

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Table 1: Distribution of PCDD/Fs in the western Baltic Sea and the coastal water of Mecklenburg-Vorpommern (normalisation to TOC [ng/kg TOC])

Region	Wismar Bight		Lübeck Bight	Unterwarnow			Darß/Zingster B.	Rügener B.	Kubitzer B.	Greifswalder B.	Peene	Oderhaff		Arkona Basin		
Station	WB1	WB3	22	UW2	UW3	UW4	DB19	RB10	KB90	GB19	P48	KHJ	KHM	69	109	131
TOC (g/g d.w.)	0,0378	0,0252	0,0374	0,104	0,0766	0,0488	0,096	0,1045	0,0235	0,0333	0,1036	0,0461	0,0809	0,0434	0,0471	0,0399
TCDD	5,29	141,27	28,07	0,96	3,39	16,80	2,40	6,79	0,85	8,71	13,22	86,12	28,92	8,29	48,41	16,04
PNCDD	5,03	267,46	77,54	3,27	4,57	29,71	5,94	26,89	7,23	13,51	3,28	32,32	13,60	81,11	84,29	46,62
HCDD	2265,08	772,62	1566,58	1155,00	1505,87	1058,20	247,08	348,13	366,38	584,38	589,38	1419,31	536,59	2130,18	1009,34	1410,03
HPCDD	10961,90	2089,29	2724,33	6758,75	10062,40	4093,65	903,33	527,08	1134,89	1021,32	1729,44	3363,56	1093,33	3161,29	1513,59	2268,67
OCDD	52150,26	7941,67	10029,95	30947,98	54718,02	17831,97	3387,60	1497,03	19575,32	3273,87	7428,47	16162,47	8261,93	10852,53	4813,16	7106,02
Sum of dioxins (PCDDs)	65387,57	11212,30	14426,47	38865,96	66294,26	23030,33	4546,25	2405,84	21084,68	4902,10	9763,90	21063,77	9935,33	16233,18	7468,58	10847,62
2,3,7,8-TCDD	n.n.	1,59	0,53	0,29	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	3,46	n.n.	n.n.
1,2,3,7,8-PNCDD	0,79	12,70	10,16	0,67	n.n.	1,84	0,42	0,67	4,26	1,80	n.n.	3,47	0,99	12,44	2,76	2,51
1,2,3,4,7,8-HCDD	n.n.	26,19	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8-HCDD	225,13	77,78	45,45	98,27	157,31	90,16	6,35	10,24	3,40	9,61	11,87	45,77	7,05	66,36	29,72	39,35
1,2,3,6,7,8,9-HCDD	91,53	38,10	95,72	31,35	49,09	26,02	6,46	10,14	4,68	44,44	18,05	89,80	10,88	242,40	26,33	106,77
1,2,3,4,6,7,8-HPCDD	6424,87	1063,10	1362,83	3876,15	5824,54	2139,75	391,88	271,10	616,17	474,17	895,85	1726,68	451,79	1716,59	706,58	1179,70
TCDF	253,70	1086,11	1487,17	122,60	284,73	312,09	26,04	336,08	77,45	206,01	265,54	794,58	490,98	838,94	926,54	802,01
PNCDF	112,43	940,87	1694,92	78,65	204,70	280,94	24,38	312,15	40,43	180,78	162,93	816,27	428,80	1019,35	744,59	782,96
HCDF	437,83	1305,56	3127,01	353,75	564,36	423,98	55,52	446,99	62,13	192,79	211,49	412,58	823,61	1488,02	1354,99	976,19
HPCDF	1814,02	1159,92	6066,04	1774,23	2571,54	4131,76	120,42	308,33	372,77	417,12	630,60	1495,01	1994,07	1582,95	1733,12	1008,77
OCDF	4750,53	1243,65	32172,73	3275,96	5721,28	2118,65	21,56	493,97	780,43	869,37	1167,86	4314,10	6711,74	n.n.	3887,26	2067,17
Sum of dibenzofurans (PCDFs)	7368,78	5736,51	44547,86	5605,19	9346,61	7267,42	247,92	1897,61	1333,62	1866,07	2438,42	7832,54	10449,20	4929,26	8646,28	5637,09
2,3,7,8-TCDF	149,21	101,19	335,03	78,37	145,95	115,78	7,50	70,72	50,21	88,59	111,97	225,60	111,62	309,68	169,85	239,60
1,2,3,7,8/1,2,3,4,8-PNCDF	16,40	91,67	317,38	3,37	20,63	39,14	3,54	59,43	9,36	42,04	39,58	120,17	94,31	234,79	148,83	164,66
2,3,4,7,8-PNCDF	34,13	85,71	333,42	32,79	80,16	93,24	6,25	68,61	6,81	36,04	28,86	68,11	55,75	263,13	166,24	179,20
1,2,3,4,7,8/1,2,3,4,7,9-HCDF	20,90	142,46	735,83	13,17	34,20	49,80	6,77	73,11	9,36	30,93	33,78	80,91	105,93	286,18	241,40	191,73
1,2,3,6,7,8-HCDF	14,29	112,70	479,14	10,96	16,19	29,51	4,38	59,90	8,51	28,53	22,01	37,74	108,78	235,02	181,95	120,80
1,2,3,7,8,9-HCDF	n.n.	48,81	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
2,3,4,6,7,8-HCDF	21,43	129,37	368,18	15,67	23,89	48,57	8,65	71,00	11,49	47,45	40,35	66,16	103,21	287,56	191,93	148,37
1,2,3,4,6,7,8-HPCDF	962,70	763,10	4401,60	751,44	1060,70	550,00	98,85	271,48	349,79	331,53	430,98	915,18	1179,36	1558,76	1083,44	787,47
1,2,3,4,7,8,9-HPCDF	n.n.	86,90	513,90	14,13	24,80	15,57	n.n.	2,68	n.n.	5,41	3,47	21,69	70,95	n.n.	45,65	14,04
Sum of all	72756,35	16948,81	58974,33	44471,06	75640,86	30297,75	4794,17	4303,44	22418,30	6768,17	12202,32	28896,31	20383,44	21162,44	16114,86	16484,96
TE(according BGA)	10,0	4,0	16,0	16,9	19,8	8,0	2,1	6,1	1,2	1,9	7,1	7,4	9,3	11,7	8,2	7,0
TE (NATO/CCMS)	7,6	3,8	18,7	12,8	16,3	6,5	1,5	7,8	1,1	1,9	6,4	6,6	8,9	14,7	9,6	8,5