PCDD, PCDF, and Dioxin-like PCB in Herring Gull Eggs from the North Sea and Baltic Sea: Levels, Patterns, and Temporal Trends

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Introduction

Seabirds are well studied important bioindicators for the contamination of marine environments. As top predators, they accumulate persistent chemicals, which can be found in high concentrations in their eggs. For this, PCDDs, PCDFs, and dioxin-like PCBs have been monitored in several avian species[1,2,3,4]. However, the recent implementation of new TEF and TEQ concepts with an inclusion of dioxin-like PCBs[5] and an introduction of TEFs not only for humans but also for fish and birds[6] together with a refined and improved analytical methodology raises the need for comparable data especially from former years.

In the framework of the German Environmental Specimen Bank[7] eggs of herring gulls are collected since 1988 from two North Sea islands and since 1993 from one Baltic Sea island. Routinely performed analyses of these samples for a fixed set of substances (including several POPs like DDT, HCH, and HCB) yielded significant differences in contamination between North Sea and Baltic Sea samples[8].

Here, we present data for PCDDs, PCDFs, and dioxin-like PCBs in archived herring gull egg samples in order to critically compare bird and human TEQs and to evaluate the influence of the Elbe flood in 2002 on contamination of North Sea sampling sites.

Materials and Methods

Samples. Eggs of herring gulls (*Larus argentatus*) were collected annually from the islands Trischen (Meldorf Bay) and Mellum (Jadebay) in the German Wadden Sea and from Heuwiese (Kubitzer Bodden) at the German coast of the Baltic Sea[9]. At least 70 eggs were collected annually at each sampling site. Whole egg contents were homogenized and pooled. Collection and processing was performed according to standard operating procedures[10]**.** The material has been stored as a grinded powder in sub-samples of approx. 10 g at max. -140 °C.

Analysis. Sample aliquots of about 10 g fresh weight material (representing approx. 1 g of lipids) were homogenized with sodium sulphate and a column extraction by means of cyclohexane/dicloromethane (v:v, 1:1) was done. Before extraction, a mixture of ^{13}C-labelled internal standards (17 2.3.7.8 substituted PCDDs/PCDFs and 12 dioxin-like PCBs) was added to the sample. All ^{13}C-labelled internal standards were delivered by Cambridge Isotopes Laboratories (USA) or Wellington Laboratories (Canada). After solvent evaporation gravimetric lipid determination was performed. A multicolumn clean-up including silica gel, differently treated silica gel (H_2SO_4-SiO_2, CsOH-SiO_2), activated carbon and alumina followed. $^{13}C_{12}$-1.2.3.4-TCDD and $^{13}C_6$-1.2.3.4.6.7.8- Hepta-CDF were added to the final extract as syringe standards. The measurement was performed by HRGC/HRMS on a HP 5890 II GC coupled with a Micromass AutoSpec mass spectrometer (ionisation mode: Electron impact (EI), resolution: 10,000). A DB 5 column was used for gas chromatographic separation. Quantification was done by means of isotope dilution method using a five-point calibration.

Data handling. Congener concentrations were multiplied either using TEFs for humans or TEFs for birds as recommended by the WHO[6] resulting in corresponding WHO-TEQ_{human}, and WHO-TEQ_{bird}, respectively. For non-detected compounds the whole detection limit was taken into account (upperbound procedure).

Quality control. For internal quality control a laboratory blank and a QC biota pool was run with each batch of ten samples. Control of blank data is an important step in quality control when analyzing PCDDs/PCDFs and PCBs at ultra trace levels. Relative standard deviation for TEQ- data of 14 QC pool samples (analyzed from day-to-day) was found to be 12% for PCDDs, 10% for PCDFs, 18% for non-ortho PCBs and 11% for mono-ortho PCBs. As further quality control measure certified material pools were analyzed.

Results and Discussion

Sum concentrations of seven 2.3.7.8.-substituted PCDD congeners, ten 2.3.7.8.-substituted PCDF congeners, four non-ortho PCB and eight mono-ortho PCB congeners in eggs of herring gull are given in Table 1. Eggs from the North Sea island Trischen exhibit slightly decreasing concentrations for PCDD/Fs and dioxin-like PCBs since 1994. This trend is interrupted by a yet unexplained increase in concentrations in 2002. In contrast, contamination of eggs from the North Sea island Mellum with PCDD and PCDF decreased continuously between 1988 and 2003 by about 70% and > 80%, respectively. This continuous decrease was also visible for dioxin-like PCBs between 1988 and 2002. However, in 2003 an increase was observed that might be due to an input of PCB loads into the German bight from the Elbe flooding in August 2002. Herring gull eggs from the Baltic Sea island Heuwiese were in general somewhat lower contaminated with PCDD/Fs than eggs from the North Sea islands but showed higher concentrations of dioxin-like PCBs.

Table 1. Sum concentrations of 2.3.7.8-substituted PCDD (ΣPCDDs) and PCDF (ΣPCDFs**)** congeners in pg/g lipid weight, and non-ortho PCB (Σno-PCBs) and mono-ortho PCB congeners (Σmo-PCBs) in ng/g lipid weight.

	Year	**Lipid**	**Σ PCDDs**	**Σ PCDFs**	**Σ PCDD/Fs**	**Σ no-PCBs**	**Σ mo-PCBs**	**Σ PCBs**
		[%]	pg/g lipid weight			ng/g lipid weight		
Trischen - North Sea								
	1988	14.6	126	85	211	7.1	1470	1477
	1990	11.3	103	60	163	5.4	897	902
	1992	13.2	101	59	160	7.4	1430	1437
	1994	11.4	184	137	321	6.4	1906	1912
	1996	8.5	170	90	260	6.3	1140	1146
	1998	8.6	153	100	253	5.1	1270	1275
	2000	10.1	130	104	234	3.5	1060	1063
	2001	9.0	76	67	143	2.6	723	726
	2002	8.5	135	133	268	3.8	1350	1354
	2003	8.7	118	106	224	2.1	868	870
Mellum - North Sea								
	1988	8.8	182	184	366	5.4	2080	2085
	1990	8.7	198	88	286	4.6	1570	1575
	1992	8.4	125	56	181	3.9	1480	1484
	1994	8.8	165	61	226	4.2	1350	1354
	1996	8.7	154	44	198	2.9	1150	1153
	1998	8.7	154	60	214	3.5	1110	1114
	2000	9.2	105	40	145	2.2	885	887
	2001	8.3	89	38	127	1.8	745	747
	2002	8.6	98	38	136	1.9	735	737
	2003	9.9	73	26	99	3.7	928	932
Heuwiese - Baltic Sea								
	1993	8.2	78	42	120	4.6	1970	1975
	1996	8.7	97	44	141	4.6	1650	1655
	1998	8.2	79	34	113	3.6	1610	1614
	2000	9.5	83	31	114	2.9	1200	1203
	2001	8.8	86	36	122	3.4	1320	1323
	2002	8.4	73	31	104	3.5	1340	1344
	2003	8.6	65	36	101	2.7	1220	1223

Compared to recently published worldwide data for several avian species[1], PCDD, PCDF, and dioxin-like PCB concentrations in herring gull eggs from North Sea and Baltic Sea are in the middle to lower range. Herring gull eggs from the contaminated Great Lakes ecosystem investigated in 1998[2] were about two times higher contaminated with PCDDs and PCDFs, and about three times higher contaminated with dioxin-like PCBs than gull eggs from the North Sea islands in the same year.

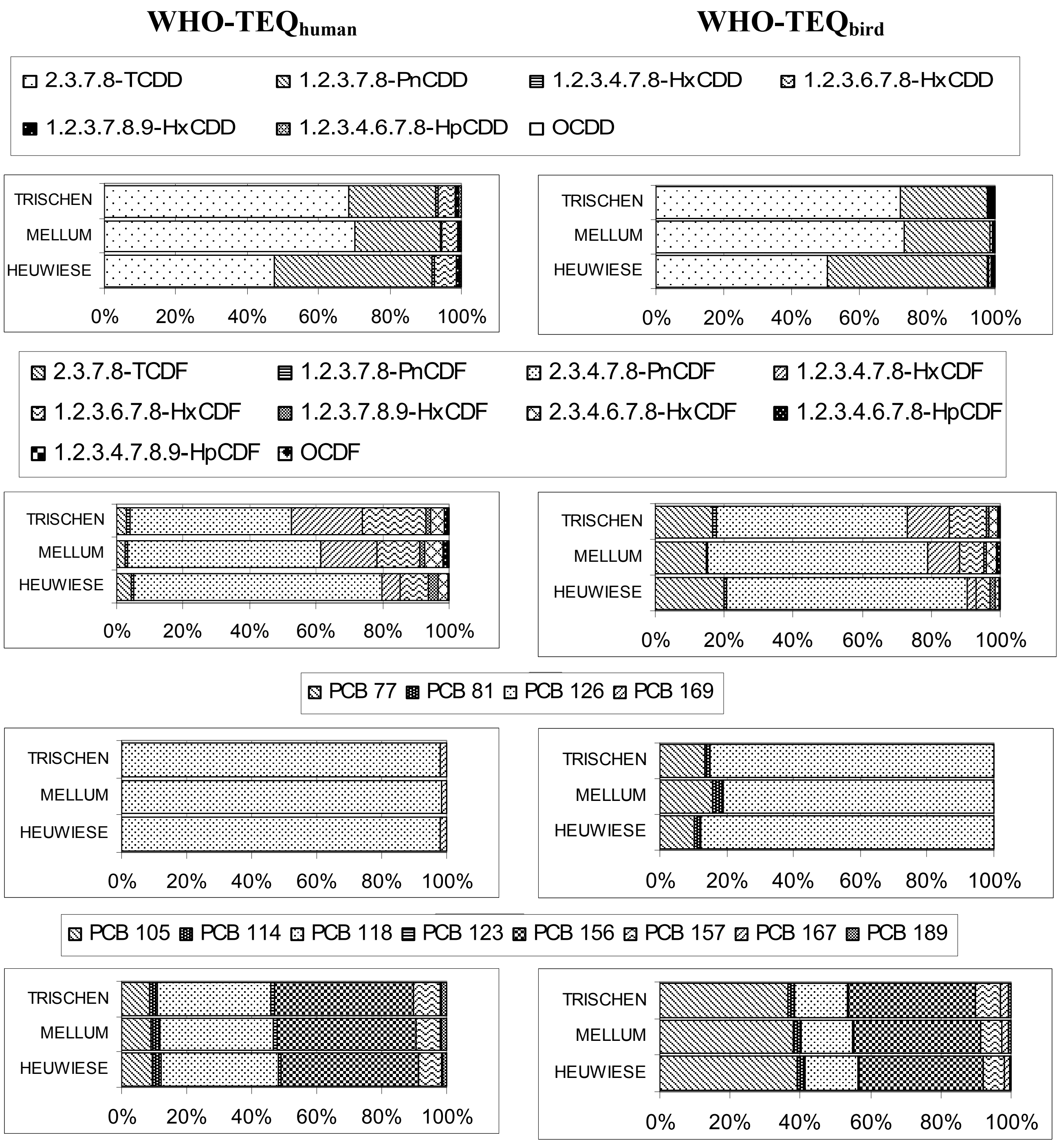

Figure 1. Contribution (%) of PCDD, PCDF, non-ortho PCB, and mono-ortho PCB congeners to the corresponding total TEQs in herring gull eggs from two North Sea sampling sites (Trischen and Mellum) and one Baltic Sea sampling site (Heuwiese) collected in 2003. Left column: calculations performed using WHO-TEFs for human; right column: calculations performed using WHO-TEFs for birds.

In Fig.1 contributions of congener TEQs to total PCDD-TEQ, total PCDF-TEQ, total non-ortho PCB-TEQ, and total mono-ortho PCB-TEQ for two different TEF-concepts are shown. The application of WHO-TEF_{bird} and WHO-TEF_{human} on concentration data yields in differences in the contribution of congeners to the total toxicity. Differences can be seen in case of PCDD with a lower contribution of 1.2.3.6.7.8-HxCDD to WHO-TEQ_{human} compared to WHO-TEQ_{bird}. In case of PCDF

a higher contribution of 2.3.7.8-TCDF and a lower contribution of HxCDFs to WHO-TEQ$_{human}$ can be observed. In case of non-ortho PCB, congener PCB 77 has a higher contribution to WHO-TEQ$_{human}$ than to WHO-TEQ$_{bird}$, and in case of mono-ortho PCB a strong and reverse difference in contribution of PCB 105 and PCB 118 to WHO-TEQ$_{human}$ can be found.
While North Sea and Baltic Sea samples yielded nearly identical congener patterns for dioxin-like PCB-TEQs, significant differences were observed for PCDD/F-TEQs. Toxicity in gull eggs from the Baltic Sea is made up to nearly identical parts of TCDD and PnCDD while in eggs from the North Sea toxicity of TCDD dominates the pattern. In case of PCDF-TEQs a predominance of 2.3.4.7.8-PnCDF in eggs from the Baltic Sea can be observed while North Sea eggs reveal an additionally significant contribution of HxCDFs.

TEQ congener patterns are relatively constant in the observation period from 1988 to 2003. The lower contribution of tetra and penta chlorinated CDDs and CDFs with time accompanied by an increased share of higher chlorinated PCDDs and PCDFs were not reflected in overall TEQ contributions because of significant higher TEFs for lower chlorinated compounds.

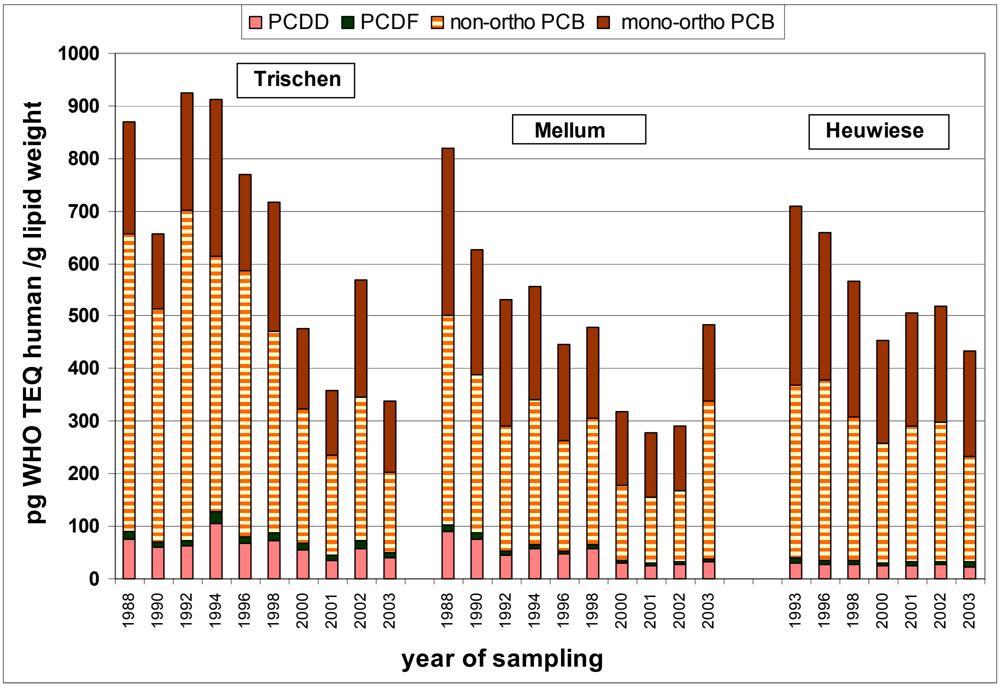

Figure 2. Temporal trend of WHO-TEQ$_{human}$ levels of PCDDs, PCDFs, non-ortho PCBs, and mono-ortho PCBs in herring gull eggs from two North Sea sampling sites (Trischen and Mellum) and a Baltic Sea sampling site (Heuwiese).

In general, total WHO-TEQ$_{human}$ levels in gull eggs from current years are significantly lower than at the end of the 1980s or mid 1990s (Fig. 2). However, eggs from Trischen showed an increase in PCDD/F-TEQs and PCB-TEQs in 2002 unexplained up to now, and eggs from Mellum revealed an increase in PCB-TEQs in 2003 possibly as a result of inputs by the Elbe flood in 2002. In eggs from Heuwiese decreasing tendencies were determined only between 1993 and 2000. Current years showed relatively constant WHO-TEQ$_{human}$ levels in Baltic Sea samples that overweigh the levels in North Sea samples.

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